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Analysis of the Gaseous Emissions and the Residues Generated under Oxy-fuel Combustion of Biomasses in a Drop Tube Furnace (DTF)

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Authors' contributions

This work was carried out in collaboration between both authors. Author GC designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors GC and PMC managed the analyses of the study. Author GC managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Some environmental problems are caused by pollutants from thermoelectric plants, mainly by burning fossil fuels. Alternatives for reducing such emissions are discussed worldwide and using green fuels is a promising way. Five biomasses (pine sawdust, sugarcane bagasse, coffee and rice husks and *tucumã* seeds) were evaluated for application as feedstock in thermochemical processes. Particular attention is devoted to the residues and emissions (CO, CO_2, SO_2 and NO) produced by biomasses burning in a Drop Tube Furnace (DTF). Oxy-combustion (CO_2/O_2:60/40%)

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experiments were performed and emissions monitored continuously. Thermal analysis, scanning electron microscopy, and energy dispersive spectroscopy were used to characterize *in natura* biomasses and residues after oxy-fuel combustion. CO_2 emissions ranged between 34 and 60 mg Nm^{-3} g^{-1}. Sugarcane bagasse showed the lowest emissions of CO_2 and NO (34 and 21 mg Nm^{-3} g^{-1}, respectively) and highest O_2-consumption (≈ 32%), while *tucumã* seed and pine sawdust samples provided the lowest values of CO and SO_2 (345 and 5 mg Nm^{-3} g^{-1}, respectively). TG/DTG curves of the residues compared to the *in natura* samples aided in diagnosing the performance of the oxy-combustion in a DTF. Organic matter remaining in residues (from 3 to 92%) showed clearly that efficiency of the thermal process varies with biomass-type used. Chemical composition of the residues showed different proportions of inorganic elements (Si, K and Ca) and trace elements (Na, Fe, Cu, S, P, Ma and Cl), demonstrating that individual behavior is an effect of the biomass properties diversity, influencing directly the burning process. The knowledge of some trends is important for the understanding that generalizations of processes cannot be applied when different biomasses are used in thermal processes.

Keywords: Burning; greenhouse gas; metallic parts; thermochemical process; wastes.

1. INTRODUCTION

Some researchers have affirmed that the rapid economic, industrial and world population growth at last decades has been accompanied by the indiscriminate increase in demand for goods and services to improve the quality of life. Such growing by products and services translates into real increase in energy consumption, and is projected to double at 2050 by some projections [1,2].

For Nell and Cooper [3], this increase population together with energetic demand, is a paradoxical condition due to the fact that traditional fossil fuels, which are the great responsible by this production, have its limited reserves [4]. For this reason, bioenergy production or biofuels from biomasses, oilseed fruits or agricultural and animal wastes has gained significant interest also due to rising fossil fuel prices [5,6].

A new and promising combustion process, involving clean energy technologies for bioenergy production is addressed in this study. Such process uses high CO_2 concentrations, mainly produced in fossil fuels thermal power plants and that still cause serious environmental problems. Second Peng et al. [7], these gaseous emissions can be mitigated by several forms, for instance, water absorption at high pressure, combustion in the presence of calcium oxide, electrical absorption, and mainly oxy-fuel combustion. The oxy-fuel combustion process is a new and promising alternative to capture CO_2 and mitigate the gases that cause the greenhouse effects. This technology consists in the combustion or burning of coal, biomass or blends with an oxygen and carbon mixture and recycled fuel gas (*syngas*), principally CO_2 and H_2O vapor ready to be captured and sequestered [8,9,10].

According to Wall et al. [11], the CO_2 capture and storage by the current technically viable options, for instance, pre- and post-combustion capture, and oxy-fuel combustion are imposing from 7 to 10% efficiency penalty on the power generation process. The main contributors for this decrease in efficiency are oxygen production and CO_2 compression.

Gil et al. [12] studied some biomasses types, including olive stones, and its wastes, and evaluated reactivity of these biomasses under oxy-fuel combustion process in a thermo-gravimetric analyzer. The biochar reactivity was obtained by devolatilization under different CO_2 concentrations in an entrained flow reactor (EFR) at high temperature. The devolatilization of the *in natura* biomass was carried out under 100% CO_2 atmosphere, and was observed that olive stones and its wastes samples presented higher apparent volatile yield. Results also pointed that reactivity of olive stones and its residues under CO_2 atmospheres were similar to the mass fraction or mass conversion ratio [12].

Yuzbasi and Selçuk [13] investigated the oxy-fuel combustion (O_2/CO_2: 21/79% and 30/70%) for lignite, olive residues, and its blends (50/50% wt), using TG/DTG curves. The authors stated that replacing N_2 in the combustion ambient by CO_2 caused slight delay (lower maximum rate of weight loss and higher burnout temperature) in combustion of all samples, concluding that burning process is slightly delayed under oxy-fuel combustion atmospheres. However, as oxygen concentration increased, temperatures decreased, weight loss rate also increased and complete combustion was achieved at lower temperatures.

In this study, five lignocellulosic materials (pine sawdust, sugarcane bagasse, coffee and rice husks, and *tucumã* seeds) were evaluated to be applied as potential biofuels in thermochemical processes. Particular attention was devoted to the residues and the gaseous emissions (CO, CO_2, SO_2 and NO) produced by biomasses burning. Oxy-fuel combustion (CO_2/O_2: 60/40%) experiments were carried out in a Drop Tube Furnace (DTF). Thermogravimetry/derivative thermogravimetry (TG/DTG curves), scanning electron microscopy (SEM images) and energy dispersive spectroscopy (EDS analysis) were also used for the physicochemical characterization of both *in natura* biomasses and residues generated after oxy-fuel condition in a DTF.

2. MATERIALS AND METHODS

2.1 Biomasses Origin

The five *in natura* biomass samples used in this study were collected from different regions of Brazil, namely: sugarcane bagasse, pine sawdust, and coffee husk samples (São Paulo State - Southeast region); rice husk (Maranhão State - Northeast region) and *tucumã* seed (Pará State - North region). Each country region exhibits a vegetation and climate clearly well defined and differentiated. Such features facilitate the plantation of several native species, which require very specific natural conditions.

2.2 Biomasses Preparation

The samples have been received *in natura* from their respective regions and underwent pretreatments 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 particle sizes of 0.46 mm were selected. The biomass samples used in this research were prepared and established by standard ASTM D2013 [14].

2.3 Characterization of the Biomass Samples

2.3.1 Ultimate and calorimetry analysis

An equipment of elemental analysis of the Instruments brand, and EA1110-CHNS-O model was used. The contents of moisture, and ash were determined by thermogravimetry (TG curves) under oxidizing atmosphere (carbon dioxide: 80% CO_2) and controlled temperature ≈ 700 °C, according to the methodology developed by Torquato et al. [15]. For the High Heating Value (HHV) of the samples was quantified through an adiabatic oxygen bomb calorimeter IKA C200 model, according to the standard ASTM E711 [16], tested and confirmed by García et al. [17] for several biomasses.

Table 1 shows the physical-chemical properties of the *in natura* biomasses, which can be used for the biofuels or bioenergy production. These properties are ultimate analysis, moisture and ash contents, and High Heating Value (HHV).

2.3.2 Thermal analysis (TG/DTG curves)

The TG/DTG curves for the *in natura* samples and the residues generated were performed

Table 1. Percentages of the moisture and ash contents, ultimate analysis and high heating value of the in natura biomasse samples

Samples	Moisture (%)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O* (%)	HHV (MJ kg^{-1})
Sugarcane bagasse	6.4 ± 0.2	4.8 ± 1.9	45.05	5.57	0.25	n.d.	37.93	17.5 ± 0.1
Pine sawdust	7.2 ± 0.1	1.2 ± 0.1	46.60	6.17	0.40	n.d.	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
Tucumã seed	5.3 ± 0.3	5.3 ± 0.1	48.83	6.71	0.88	n.d.	32.98	20.8 ± 0.1

**Difference at 100%; n.d. - not detected or below equipment detection limit* using Shimadzu brand analyzer, TGA-50H model. The oxidizing atmosphere (oxy-fuel combustion) was promoted by 60% CO_2/40% O_2, with a dynamic flow rate of 100 mL min^{-1}, which was kept constant during all the experiments. For these experiments, the constant heating rate utilized was of 10°C min^{-1} from room temperature (≈ 23ºC) 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 for reproducibility of the results by other researchers, where the average values and standard deviations were considered.

2.3.3 Scanning electron microscopy (SEM images)

The morphological and textural analysis of all the biomass samples *in natura* and residues generated were analyzed by means of images produced in a scanning electron microscopy (SEM). The images were obtained with Scanning Electronic Microscope brand equipment, LEO 440 model and with amplitude of 1000 times.

2.3.4 Energy dispersive spectroscopy (EDS analysis)

The *in natura* samples and residues were prepared by powder sintering for the best adherence on the surface of the aluminum support for the EDS analysis, which was also carried out 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.

2.4 Oxy-fuel Combustion in a Drop Tube Furnace (DTF)

A Drop Tube Furnace (DTF) electrically heated (3.5 kVA maximum power) (Fig. 1a and b) was used for the biomass thermal process (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 oxy-fuel combustion reactor (DTF) by means of a feeding system, which has a vibratory mechanical transport and controlled via PWM (Pulse Wide Modulation). The optimal rotational velocities and frequencies were achieved for each lignocellulosic biomass. 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^{-1} with a concentration of 40% oxygen and 60% carbon dioxide (gas inlet) was applied to keep the biomass particles in suspension and facilitate the burning during process in DTF. After burning at ≈ 950°C and under atmospheric pressure (≈ 1 atm), the residues generated in thermochemical process were collected from the furnace bottom (manifold ash) and evaluated by TG/DTG curves, SEM images and EDS analysis.

2.5 Gases Analyzer

Equipment of the SICK brand (GMS 810 model) was used to detect and capture the emitted concentrations by main atmospheric pollutants, during oxy-fuel combustion of biomasses in a DTF, for instance, SO_2, CO, NO and H_2O measured in parts per million (ppm), and CO_2 and O_2 in percentage (%). It was used as a computational program - *SOPAS Engineering Tool* - coupled to the gases analyzer for communication, data capture from gaseous emissions, and equipment calibration.

3. RESULTS AND DISCUSSION

3.1 Thermal Analysis (TG/DTG curves)

Figs. 2 to 6 present the TG/DTG curves for the *in natura* samples and the wastes generated from biomasses evaluated after oxy-fuel combustion (60% CO_2) process in a DTF.

Fig. 2 (a-b) shows TG/DTG curves *in natura* sugarcane bagasse and residues generated after oxy-fuel combustion in a DTF. It was observed by means of thermal profiles (Fig. 2a), a wide consumption from total organic materials (hemicellulose, cellulose, and lignin) approximately 97.25% in relation to *in natura* sample, which was also confirmed by DTG curves (Fig. 2b). This value presented from remaining organic material is a good indicative, that burning process under CO_2 atmosphere was satisfactory.

The thermal degradation for the *in natura* sugarcane bagasse presented a “shoulder” around 310 ºC, which is an indicative of the high hemicellulose content [18,19] and also that hemicellulose and cellulose (holocellulose) are decomposed simultaneously [18,20].

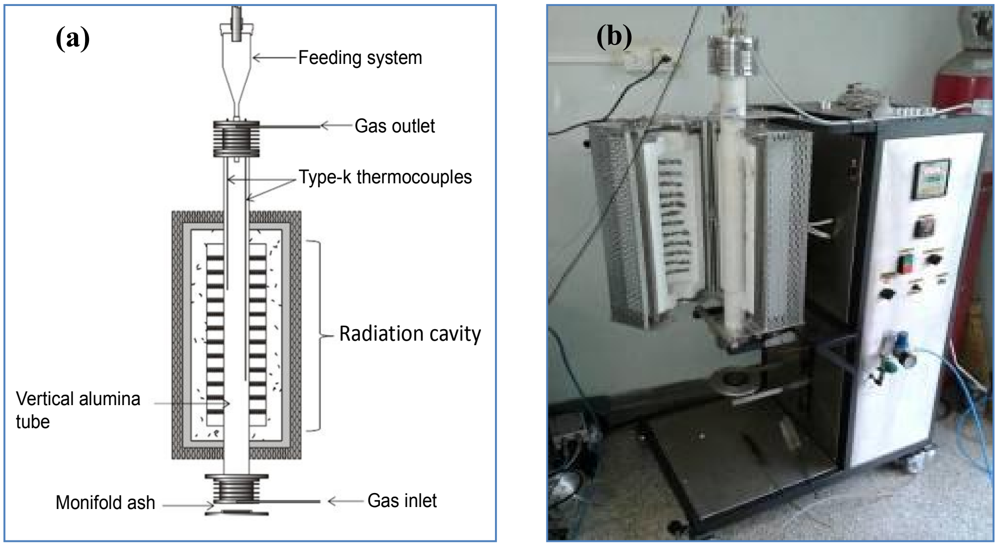

Fig. 1. (a) Schematic representation of the Drop Tube Furnace (DTF) and (b) DTF reactor and feeding system for the oxy-fuel combustion of five biomasses

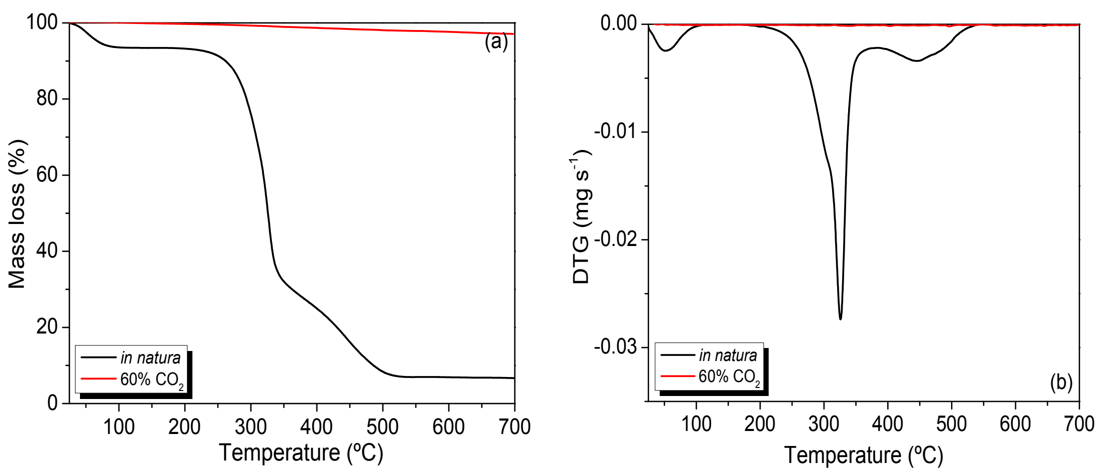

Fig. 2. (a) TG and (b) DTG curves of the *in natura* samples and sugarcane bagasse residues after oxy-fuel combustion (60% CO_2) in a DTF

For the *in natura* samples, other peak was observed at 445ºC, indicating the partial decomposition of residual lignin.

Fig. 3 (a-b) shows TG/DTG curves *in natura* pine sawdust and residues produced after oxy-fuel combustion in a DTF.

DTG curve (Fig. 3b) of the *in natura* sample show peaks well defined at 328 and 460ºC (maximum combustion rate), which can be associated to thermal decomposition of the holocellulose and residual lignin, respectively. According to Polleto et al. [21], the peaks thinner and elongated are a strong characteristic of the crystalline samples [19]. Although, it is known that the most crystalline part of lignocellulosic materials is the cellulose, and lignin the most amorphous region [22,23]. For the residues under oxy-fuel combustion environment, an extensive oxidation of the total organic materials was demonstrated, but it can be noted that there is still some residual material, principally residual lignin, which can be confirmed by the peaks at 340 and 532°C.

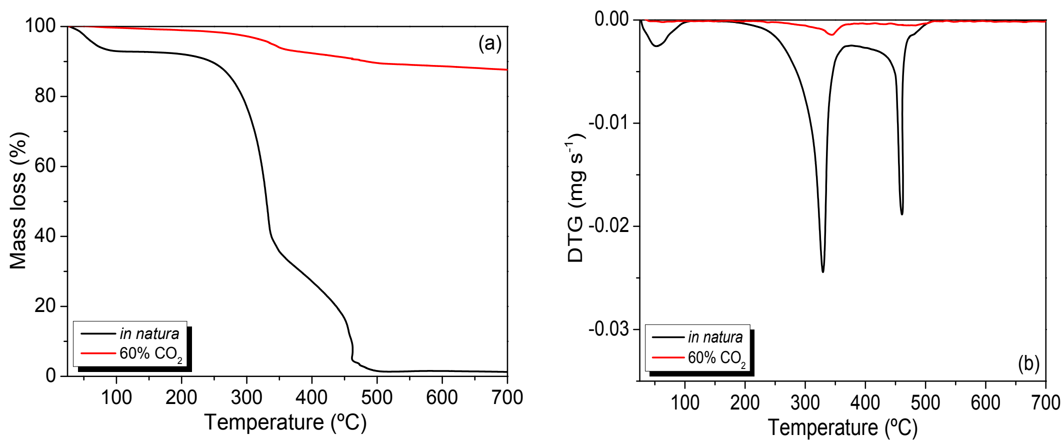

Fig. 3. (a) TG and (b) DTG curves of the *in natura* samples and pine sawdust residues after oxy-fuel combustion (60% CO_2) in a DTF

Fig. 4(a-b) shows TG/DTG curves *in natura* coffee husk and residues generated after oxy-fuel combustion in a DTF.

The high quantity of inorganic compounds present in the coffee husks, primarily, potassium element, makes them most tough to the deformations and, consequently, thermal breakdowns by the oxy-fuel combustion process [24]. Such statement is according to the considerations performed in this work, because the residues assessment demonstrated that inside particles presented a deficit burning process, with only carbonization in outer regions.

For the 60% CO_2 atmosphere and by means DTG curves (Fig. 4b), it was possible to observe the presence of thermal event at 184ºC, caused by thermal treatment effect or release of some light volatiles [25]. In 545ºC, other thermal event was observed, which can be associated to the inorganic materials oxidation not burnt at temperatures of approximately 1000°C, for instance, potassium, sulphur, chlorine, among others, which can lead to the formation of corrosive gaseous species and hazardous environmental damage [24,26].

TG/DTG curves (Fig. 5a-b) for the wastes generated from the rice husk after the experiments under carbon dioxide atmosphere (60% CO_2) showed degradation of almost the total of the organic materials (hemicellulose, cellulose, and lignin) present in samples. This statement may be performed and confirmed on the basis of the ash content displayed at the final of the TG curves, which results in approximately 91.0% (average value).

From TG/DTG curves (Fig. 6a-b) for the *in natura* samples and *tucumã* seed residues it was possible to observe three events well defined of mass loss. The first, with peak around 185°C, due to release of lighter volatiles [25] or by the fast thermal decomposition of fatty compounds present in oilseed between 150 and 200°C [27]. It was verified in ≈ 300°C, the maximum combustion rate for the thermal degradation of holocellulose and, at 450°C for the remaining lignin decomposition. On the other hand, DTG curves (Fig. 6b) for the residues under oxy-fuel combustion ambient displayed two events of mass loss between 225 and 550°C, with mass loss maximum in approximately 300°C. *Tucumã* seed samples did not show an adequate yield for the referred thermal process, probably because these biomasses contain a large oiliness amount, which can be prejudicial to the feeding system and, therefore, to the burning process.

3.2 Scanning Electron Microscopy (SEM Images)

Fig. 7. shows the SEM micrographics for the *in natura* samples and the residues produced after thermal process (oxy-fuel combustion).

Fig. 7 (a-b) displays the SEM images for the *in natura* sugarcane bagasse and the residues generated in DTF, after burning under CO_2 condition. The sugarcane bagasse residues exhibited differences in morphological and textural structures, when compared to the *in natura* samples (Fig. 7a.), principally in relation to the fibrous features loss, tubes, marrow and lamellae.

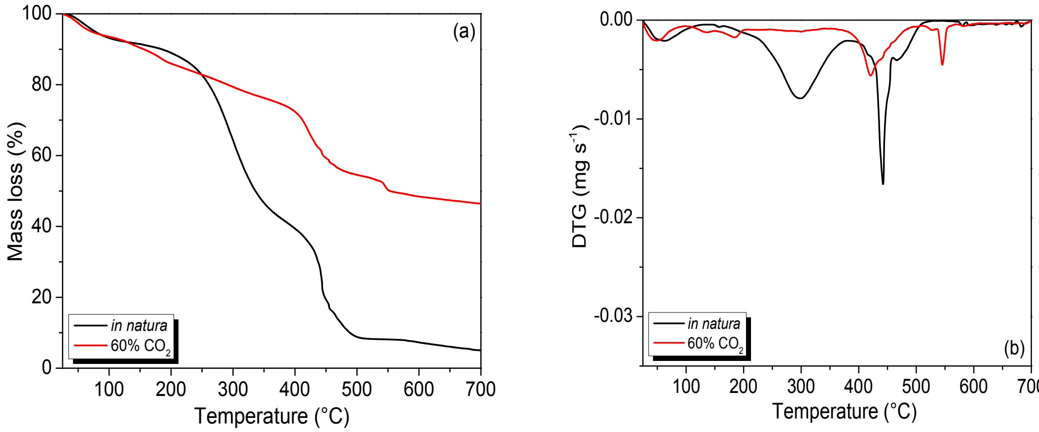

Fig. 4. (a) TG and (b) DTG curves of the *in natura* samples and coffee husk residues after oxy-fuel combustion (60% CO_2) in a DTF

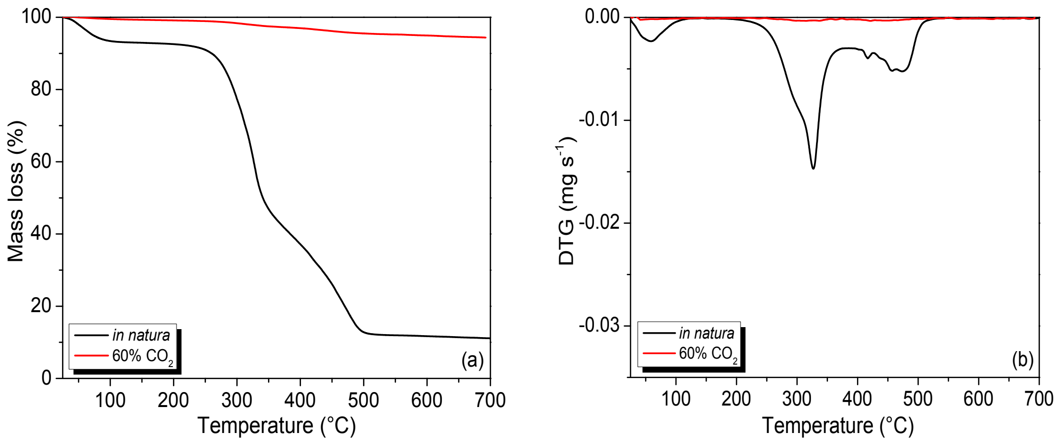

Fig. 5. (a) TG and (b) DTG curves of the *in natura* samples and rice husk residues after oxy-fuel combustion (60% CO_2) in a DTF

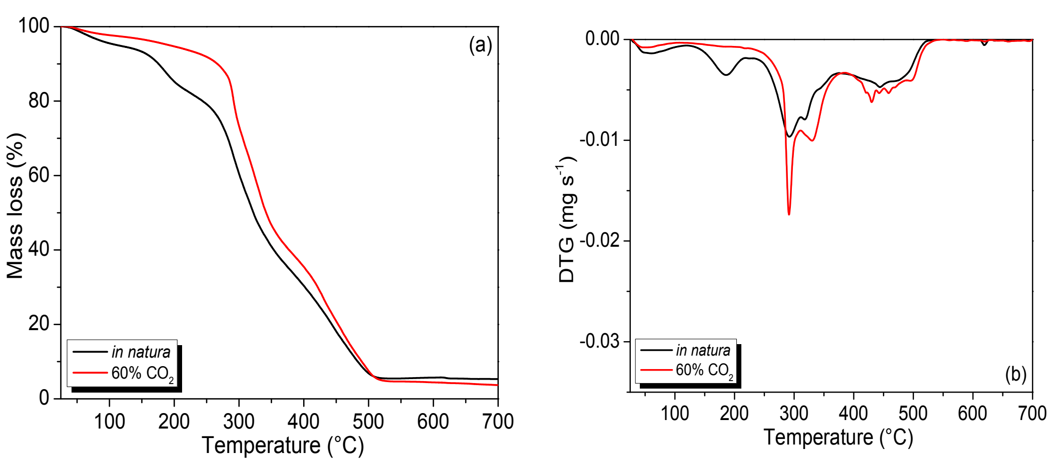

Fig. 6. (a) TG and (b) DTG curves of the *in natura* samples and *tucumã* seed residues after oxy-fuel combustion (60% CO_2) in a DTF

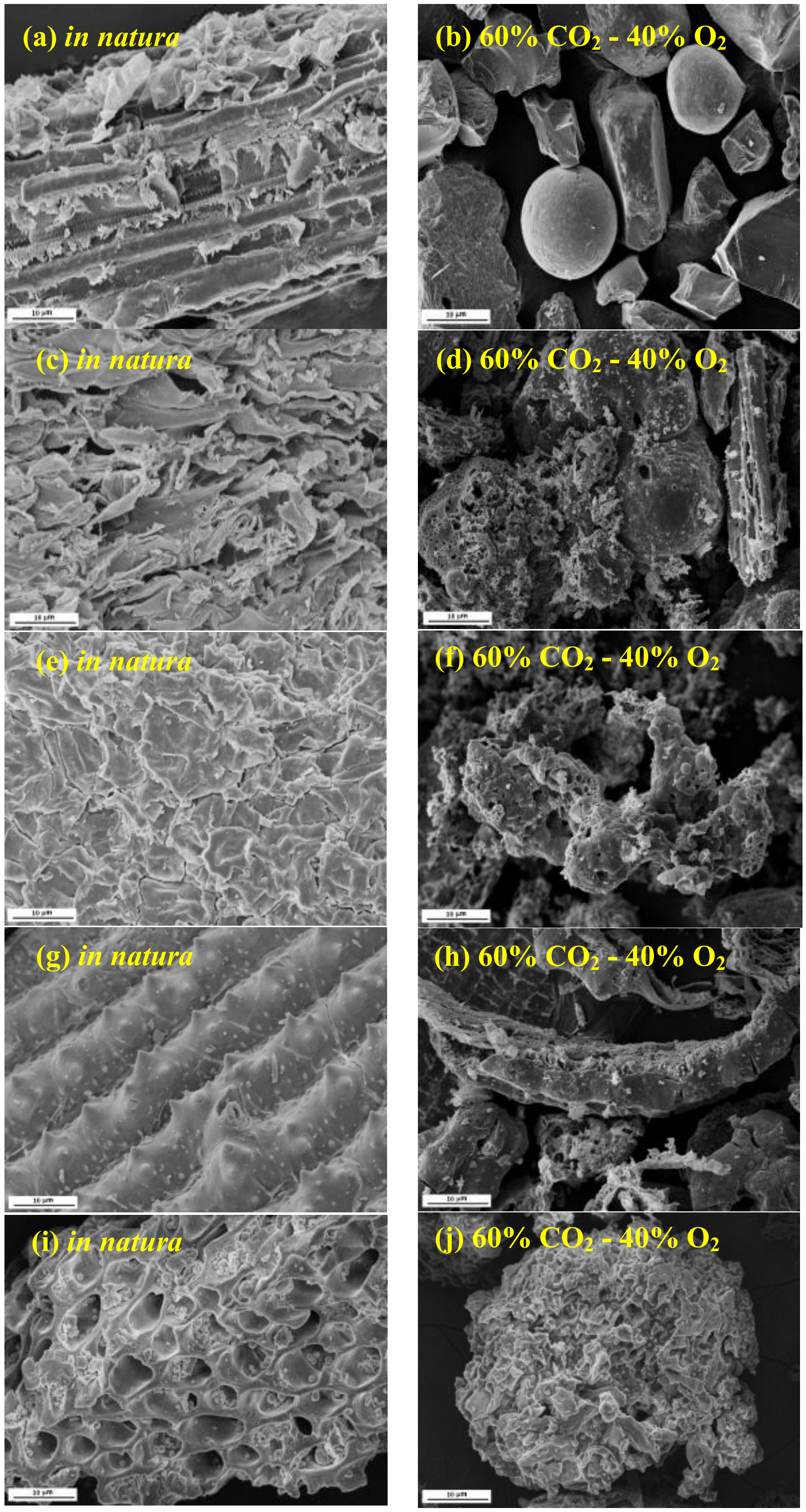

Fig. 7. SEM images of the *in natura* samples: (a) sugarcane bagasse, (c) pine sawdust, (e) coffee husk, (g) rice husk, and (i) *tucumã* seed, and the residues generated under oxy-fuel combustion (60% CO_2) in a DTF: (b) sugarcane bagasse, (d) pine sawdust, (f) coffee husk, (h) rice husk, and (j) *tucumã* seed – all images with magnitude of 1000 x

It was verified that for the samples under 60% CO_2 atmosphere (Fig. 7b), the residues grains demonstrated a format of crystal and, more specifically, in Fig. 7b can be observed a perfect sphere, which is a strong characteristic of the silicon presence or iron oxides [28], and also was confirmed by Fig. 8a (EDS analysis).

It was observed that morphological configuration of the pine sawdust residues after 60% CO_2 atmosphere (Fig. 7d.), when compared to *in natura* sample (Fig. 7c.) showed an agglomerate of particles, structures that seem cenospheres [29] and particles shrinkage [30]. For the 60% CO_2 atmosphere, the occurrence of some perforations at several points of the samples was noted, probably, due to the solid matrix consumption, totally burnt structures and other partially, materials left on the surfaces, particle agglomerates and some particles with shape of irregular spheres (Fig. 7d).

From coffee husk residues generated under 60% CO_2 - 40% O_2 atmosphere, it was possible to note an amalgam type structure (Fig. 7f), probably, because of the agglomeration phenomenon due to the alkaline compounds melting, mainly potassium element, whose content for some biomasses is of the order 40.0% [31], and for the *in natura* coffee husk samples of this study was ≈ 4.0% (Fig. 7e). Probably, for this atmosphere was reached the higher temperatures, which may have been caused by the higher oxygen concentration, *i.e.*, 40% O_2 [32].

For the rice husk samples, it was noted that the residual wastes from thermal process under carbon dioxide atmosphere (60% CO_2) demonstrated changes in relation to the *in natura* sample (Fig. 7g). These residues (Fig. 7h) demonstrated greatly porous structures (mesopores and macropores) and, evidently, without either possibility of identification between them, beside common structures with breakage of the primary condition, but also some conservation of the original lignocellulosic matrix. For Luan et al. [30], some very thin particles deposited on the rice husk samples surfaces after thermal process under oxidizing atmosphere, may be principally, compounds of aluminum-alkali silicates and/or alkali metal chloride.

It was observed that structure of the *in natura tucumã* seed is compound by an axial and radial microchannels set, that seem to traverse its whole structure (Fig. 7i), while for other *in natura* biomasses, there is the predominance of a most fibrous structure. Even after being submitted to the thermochemical process, *tucumã* seed residues (Fig. 7j) kept their same physical features, presenting the microchannels and, apparently, without ruptures in regard to the *in natura* sample, also differing of other biomasses, and can be a large effect of their physical characteristics, *i.e.*, rigidity or hardness [18].

It is interesting to highlight that some SEM images presented in this research for the different biomasses under the oxy-fuel combustion atmosphere were not found in the consulted literature, *i.e.*, are firstly shown in this study.

3.3 Energy Disperse Spectroscopy (EDS Analysis)

Fig. 8 displays the energy dispersive spectroscopy analysis (mass percentage terms or concentrations) for the *in natura* samples and the wastes produced after the thermochemical process of oxy-fuel combustion. Such procedure was utilized to evaluate the elemental composition of the biomasses and estimate their compositional evolution during the oxy-fuel combustion, for prediction the potential changes occurred in the biomasses samples, and the possible environmental effects that can be occasioned by using of these biofuels in the metallic parts of the direct combustion apparatus.

Chemical elements, *e.g.*, sodium (Na), potassium (K), magnesium (Mg), phosphorus (P), and calcium (Ca) among others are present in lignocellulosic materials, and form oxides, hydroxides, and carbonated forms of alkaline metals and alkaline earth, which are problematic constituents in the direct combustion system, because they prevent the good functioning of the thermal power plants [31].

Biomasses are considered a biofuels special class, due to present few or none aluminum (Al), iron (Fe), and titanium (Ti) and most silicon (Si), potassium (K), and occasionally more calcium (Ca), when compared to the coal. The contents of nitrogen, chlorine (Cl), and some metals, also vary considerably amongst biomasses [33]. According to Rizvi et al. [34], such components are precisely associated to the NO emissions, corrosion, slag, and ash deposition in thermal power plants, also presenting a large difference in the elemental composition of the biomasses.

It was found that sugarcane bagasse residues generated under 60% CO_2 atmosphere (Fig. 8a) did not exhibit carbon content, a strong clue that all organic material from sample was consumed in this process, which can be confirmed by SEM images for this atmosphere (Fig. 7b).

For the *in natura* samples, rice husk (Fig. 8d) presented on average 8.1% Si and sugarcane bagasse, 0.4%. After burning under 60% CO_2 atmospheres the sugarcane bagasse residues presented average values of 44.5% Si. And for the rice husk sample, after the burning (60% CO_2) the residues presented levels 36.7%. The high Si presence in sugarcane bagasse residues is not due to the biomass natural composition, but its contamination by impurities incorporated in the sugarcane harvest process or itself storage in plant sheds after juice extraction, mixing it with soil or sand [35].

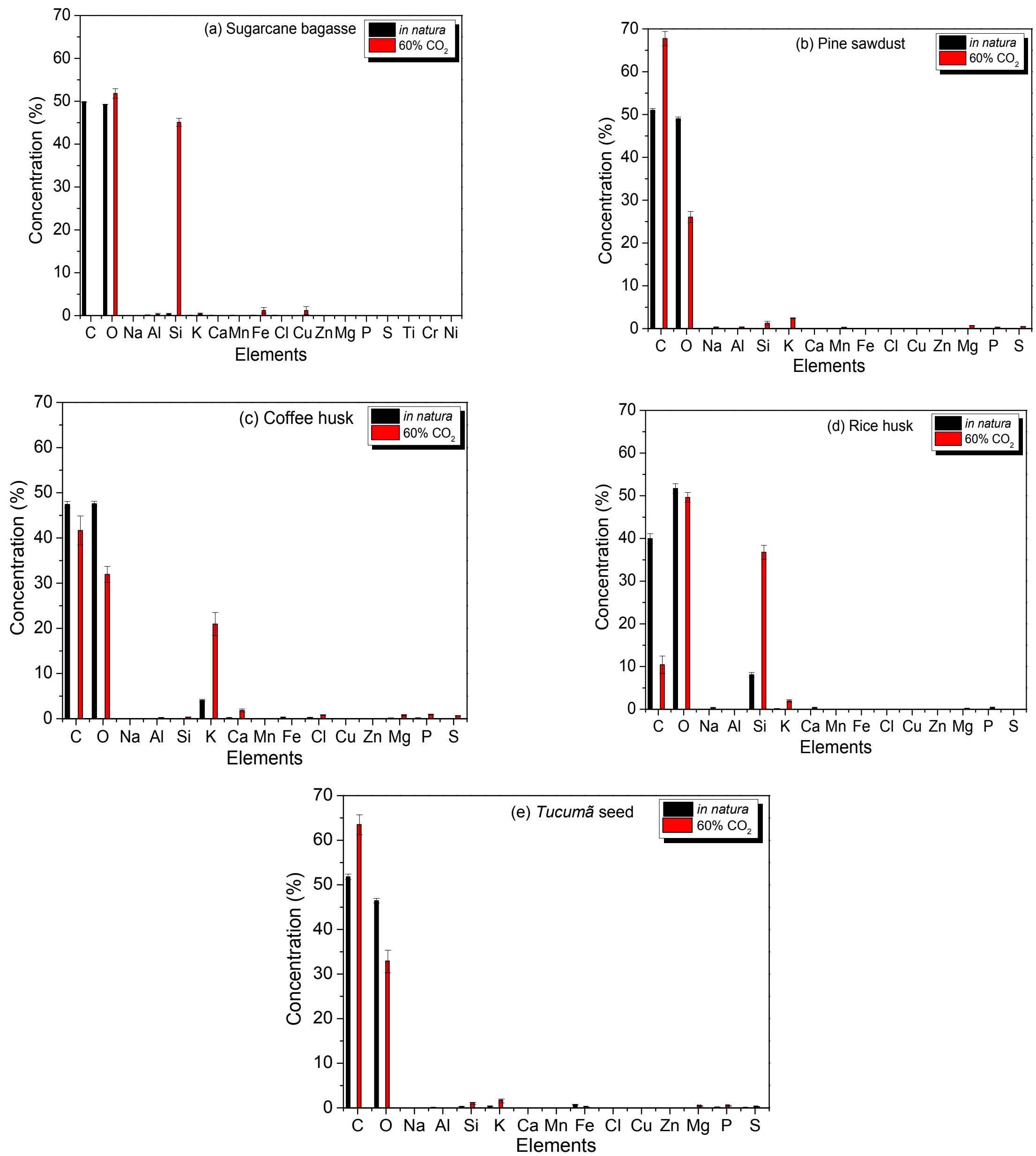

Fig. 8. Elemental composition obtained by EDS analysis of the *in natura* biomasses and the residues generated under oxy-fuel combustion (60% CO_2) condition: (a) sugarcane bagasse, (b) pine sawdust, (c) coffee husk, (d) rice husk and (e) *tucumã* seed

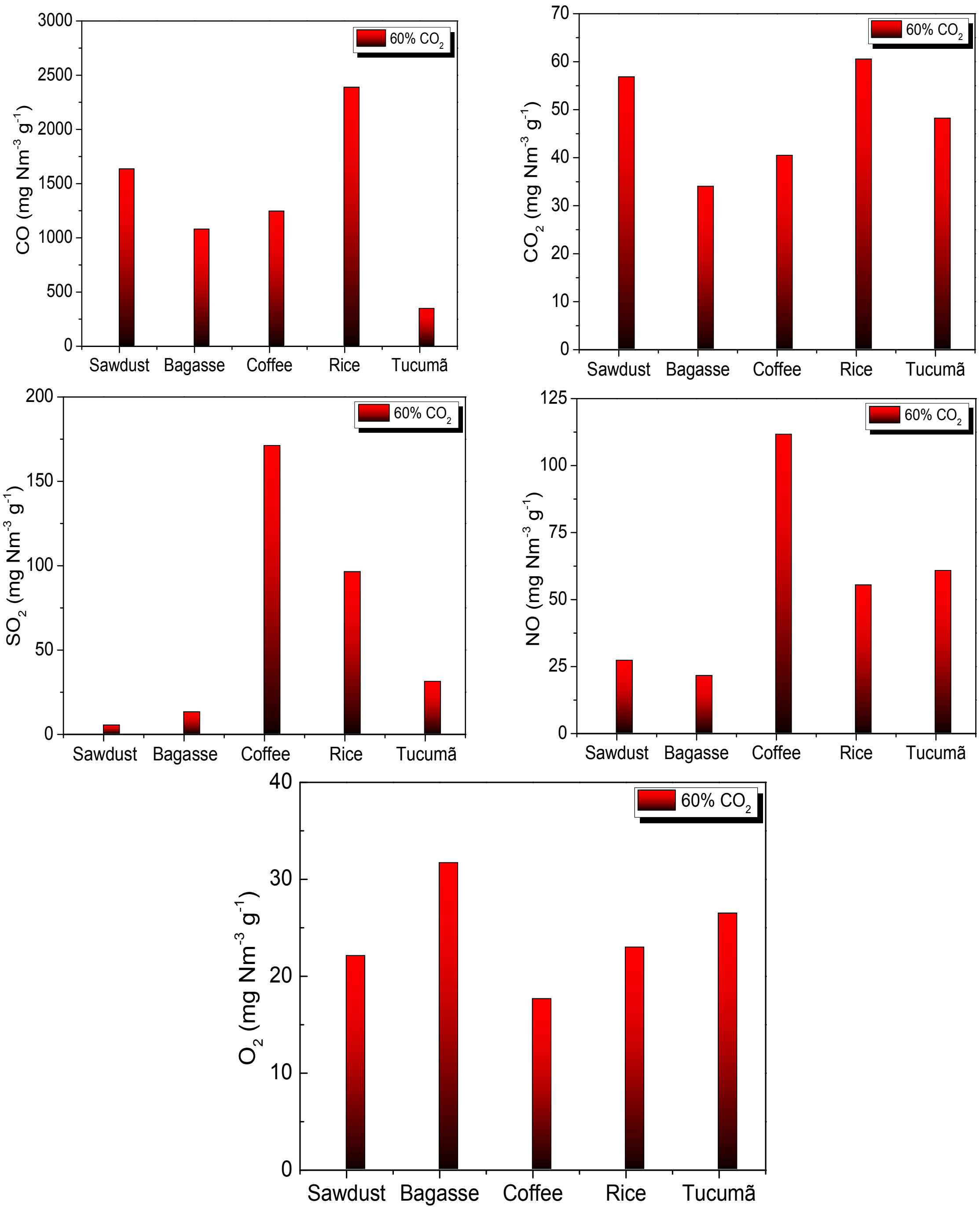

Fig. 9. Major atmospheric pollutants produced by different biomasses under oxy-fuel combustion condition (60% CO_2) in a DTF. Experimental conditions: furnace temperature: 1000ºC, primary airflow rate: 1.5 L min^{-1} and mass flow rate: 0.3 g min^{-1}

In addition, it is agreed that a more in-full study is required to obtain detailed information on the probable applications of biomass and/or wastes, containing these inorganic elements that degrade the environment. A promising application to resolve these troubles would be the employee of the ashes produced by several thermal processes by the factories of concrete, cement, bricks, tiles, asphalt, composites, among others [18,31,36].

3.4 Emissions Gaseous (Atmospheric Pollutants)

Fig. 9 presents the mean values of the major atmospheric pollutants (CO, CO_2, SO_2 and NO) produced under oxy-fuel combustion (60% CO_2) atmospheres in a DTF for the *in natura* samples. In this study, like a criterion of validation of the gradual progress from respective thermochemical process was utilized the O_2 concentration.

For some species of pollutants, such as carbon monoxide (CO), its reactions of formation and destruction are closely linked, and for the understanding of these reactions are necessary to know of the complex chemistry of the combustion process [37]. In high partial pressures and high temperatures, CO_2 can be dissociated into CO and O_2, by means of strongly endothermic reactions [38]. In the flame zone or heated zone of the reactor under typical oxy-fuel combustion process both above conditions were verified in anterior study developed by our research group [32]. Under oxy-combustion environment (60% CO_2), the highest and lowest CO emissions were observed, respectively, for rice husk (2,385 mg Nm^{-3} g^{-1}), and *tucumã* seed (341 mg Nm^{-3} g^{-1}). This increase in CO emission can be due to the Boudouard reaction as demonstrated in other studies [39,40,41].

Rice husks showed the highest CO_2 emissions under oxy-combustion process with 60% CO_2 (61 mg Nm^{-3} g^{-1}), while sugarcane bagasse, the lowest (34 mg Nm^{-3} g^{-1}). For Aghamohammadi et al. [42], these variations in the formation rates of the flue synthesis gases, for instance, CO_2 are because of the main constituents of biomasses (hemicellulose, cellulose and lignin). The excess of oxygen and a better blend between the lignocellulosic materials can be helpful in the gaseous emissions control in this combustion step. The unburned biomass is naturally decomposed to release CO_2.

Coffee husks presented the highest elemental nitrogen content (1.55%), and the sugarcane bagasse, the lowest (0.25%) (Table 1). The first sample showed the highest NO emissions under oxy-fuel combustion (112 mg Nm^{-3} g^{-1}), probably due to the total oxidation of its nitrogen content in this atmosphere. The second biomass showed the lowest limits of NO (21 mg Nm^{-3} g^{-1}) under the same condition. It is important to note that samples of rice husk and *tucumã* seed exhibited under 60% CO_2 atmosphere, a gradual increase in its NO emissions, whereas pine sawdust and sugarcane bagasse, a decrease.

Coffee husks also presented the highest elemental sulfur content (0.67%), and consequently, during burning under 60% CO_2 conditions, the highest values for the SO_2 emissions (171 mg Nm^{-3} g^{-1}). Although, pine sawdust showed no detectable limits of sulfur in its elemental composition, this still exhibited the lowest values (5 mg Nm^{-3} g^{-1}) for these emissions under oxy-fuel combustion. Higher SO_2 emissions in thermal systems are indicative of complete combustion or partially completed, because this gas effectively participates of the overall reaction of combustion and is released completely in volatiles form during char combustion [43,44]. For the lowest SO_2 emissions under oxy-combustion atmosphere, Toftegaard et al. [38] and Normann et al. [41] related that this reduction is an expected common feature in this thermal conversion process type.

By means O_2 concentrations, it was possible to verify the performance from thermochemical process inside DTF. The following trend on O_2 consumption was observed for the 60% CO_2 ambient and, consequently, a better burning process. For this oxidizing atmosphere, sugarcane bagasse presented the highest O_2 consumption (32 mg Nm^{-3} g^{-1}) and coffee husk, the lowest (18 mg Nm^{-3} g^{-1}).

4. CONCLUSIONS

This study evaluated the physicochemical properties and thermal behavior from different biomasses under oxy-fuel combustion atmosphere (CO_2/O_2: 60/40%) in a Drop Tube Furnace (DTF).

Thermal analysis (TG/DTG curves) indicated that the highest conversion degree was obtained for the sugarcane bagasse and rice husks samples under 60% CO_2 atmosphere and also showed that these residues presented lower remaining total organic matter contents in relation to the *in natura* biomasses and, consequently, a good efficiency and performance of the thermal process of oxy-fuel combustion.

Considering the gaseous emissions (CO, CO_2, NO, SO_2 and O_2), it was observed that for all the air pollutants there was an extensive range of emission levels, since these, besides the biomasses physicochemical composition, are also intrinsically related to the experimental conditions employed.

Morphological characterization (SEM images) for the *in natura* biomasses allowed observes its main original structures. However, for the residues under oxy-fuel combustion, some degraded lignocellulosic structures were observed. For some samples the original structures losses were clear and for the others, the conservation of its structures could be observed. By means of the morphologies for the different residues under CO_2 atmosphere, it was understood that thermal process affected each biomass in a well specific ways.

Chemical composition determined (EDS analysis) for the *in natura* biomasses and residues, is also an important information in studies about thermal processes. Elements as chlorine, sulfur, trace elements among others, deserves special attention, due to the damage caused to the metal parts of burners and boilers and also to the environment when these are released directly into atmosphere.

Finally, it was noted that other parameters, such as social and economic aspects, should also be taken into account, when it is intended to use different biomasses in specific processes of bioenergy generation.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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