EFFECTS OF TORREFACTION ON BIOMASS: A THERMAL AND MORPHOLOGICAL EVALUATION

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Abstract. *This study investigates the thermal degradation of biomasses and the effects of the air and nitrogen atmospheres and the particule size. The biomasses studied were pine sawdust and coffee husks in both "in natura" and torrefeid forms. Techniques, such as thermal – Thermogravimetry (TG/ DTG) and Differential Thermogravimetry (DTA) - and morphological analysis (Scanning Electronic Microscopic - SEM) were applied. Experiments were performed under non-isothermal conditions for the combustion (synthetic air) and pyrolysis (nitrogen). The TG/ DTG and DTA curves, identified different steps of thermal degradation and correlated them with hemicellulose, cellulose and lignin content in the biomass in both forms. The morphological structures allowed observing that the torrefaction process and particles size affect the biomass structure, mainly regarding the shape of the porous. Pine sawdust "in natura" presented tubular, piths and lamellas structures, whereas coffee husks presented porous and fragmented structures. After torrefaction, the samples presented an expanded structure with larger pores, depending on the particle size. Concerning the entalpic events, the DTA curves for air condiction showed that the samples in both "in natura" and torrefied forms presented two exotermic peaks related to hemicellulose/ cellulose and liginin. However, these peaks are intense for pine sawdust, but for coffee husks the second peak is almost five times higher than the first one. All biomasses studied showed basic characteristics to be use as biofuels, mainly coffee husks torrefied by having high carbon and low oxygen contents.*

Keywords*: thermal degradation, milling, atmospheres, granulometries.*

1. INTRODUCTION

Many countries have been concerned about the use of renewable sources for energy production. The development of new technologies is important, especially considering the reduction in the environmental impacts, with respect to the CO, CO_2 and NO_x emissions. In this context the use of biomass is a promising alternative (Babu, 2008).

Several biomasses, such as sugar cane bagasse (Nassar *et al*., 1996), rice husks (Zhao *et al*., 2009), pine sawdust (Couhert *et al*., 2009), coffee husks (Wilson *et al*., 2010), olive stones (Šimkovic and Csomorová, 2006), soybean husks, corn straw, sugar-beet, almond shells (Jiménez *et al*., 1991), sunflower stalks and hazelnut husks (Biagini *et al*., 2005), have been studied with the proposed to the used in thermal processes. Some of them have already been tested to replace fossil fuels.

Thermal degradation processes of biomasses include hydrothermal conversion, slow or fast pyrolysis, gasification, torrefaction and their combinations. These techniques are distinguished primarily by the presence or absence of free water, residence time, availability of O_2, heating rate, gaseous atmosphere (presence of nitrogen and water vapor), temperatures and pressures used in the process (Amonette and Joseph, 2009).

The torrefaction process is a thermal pretreatment of biomass, in which the feedstock is heated in an inert or N_2 atmosphere, at low heating rate (< 50 ºC min^{-1}), within a temperature range of 200 ºC to 300 ºC. According to Chen and Kuo (2010); Chen and Kuo (2011) and Amonette and Joseph (2009), the torrefaction process is classified into three categories: soft (≈ 230 ºC), moderate (≈ 260 ºC) and severe (≈ 300 ºC). For the authors, this is an effective way of treating biomass before transportation or thermochemical conversion. It can be used to concentrate the energy contained in the original material or facilitate the process of grinding, which consumes large amounts of energy and overcame obstacles to expand the use of biomass in thermochemical processes (Couhert *et al*., 2009). The process allows the release of moisture and oxygen, removal of volatiles and rearrangement of organic structures, producing a solid hydrophobic with an increased energetic density (Bridgeman *et al*., 2008).

This paper deals with the evaluation of the thermal degradation of two biomasses: pine sawdust and coffee husks (*in natura* and torrefied) in both inert and oxidizing atmospheres. Experiments were performed in a thermogravimetric balance (TG) and in a differential thermal analyzer (DTA). The paper also presents the morphologic properties evaluated by Scanning Electron Microscopy (SEM).

2. EXPERIMENTAL METHODOLOGY

2.1 Biomasses

Two biomasses have been selected for this study: sawdust pine and coffee husks. Both have been received *in natura* and the pre-treatments consisted in washing to remove impurities, grinding to decrease particle size and subsequent sieving for separation. The torrefaction was carried out in a domestic microwave oven at maximum power (≈ 180 V), reaching a maximum temperature of 300 °C, measured with an optical pyrometer (severe torrefaction process) for approximately 30 minutes. The biomasses were received *in natura*, pulverized using a household blender, and sieved. For both *in natura* and torrefied forms, particles of 2.19, 1.55 and 1.02 mm average sizes were selected. For coffee husks *in natura*, only particles of 1.55 and 1.02 mm have been achieved.

2.2 Characterization of the biomasses

Elemental analysis was performed in the *CE Instruments* equipment, EA1110-CHNS-O model. The images of Scanning Electron Microscopy (SEM) were obtained on a *Scanning Electronic Microscope*, LEO440 Model, with amplitude of 1000 times.

The TG/ DTG and DTA experiments carried out in the *Shimadzu* analyzers, TGA-50H and DTA-51 models, respectively. The oxidizing (synthetic air) and inert (nitrogen) atmospheres were promoted by the carrier gas with a flow rate of 100 mL min^{-1}. In these experiments heating rate of 20 °C min^{-1} from room temperature up to 650 °C for pine sawdust and up to 800 °C to coffee husks. Were used samples mass (8.5 ± 0.5) mg and crucible of alumina. The tests were carried out in duplicate and the mean values and standard deviations were considered.

3. RESULTS AND DISCUSSIONS

As presented in Tab. 1 and considering both torrefied samples, carbon and oxygen content are about of 78% and a 76% higher than *in natura* form, respectively.

It can be understood that the torrefaction process releases more moisture, at around 100 °C, and volatiles compounds at around 300 °C, resulting in a concentration of high carbon and low oxygen.

These values are in accordance with the literature (Couhert *et al*., 2009; Wilson *et al*., 2010 and García *et al.*, 2012). These authors also presented a study with pine sawdust and coffee husks showing carbon and oxygen content in a range of 45-60% and 35-45%, respectively.

Table 1. Elemental analysis from biomasses (% dry basis and ash free)

Biomasses	C (%)	H (%)	N (%)	S (%)	O* (%)
pine sawdust *in natura*	46.76	6.33	0.06	n.d.	46.85
pine sawdust torrefied	57.04	5.36	0.07	n.d.	37.53
coffee husks *in natura*	42.89	6.07	0.07	n.d.	50.97
coffee husks torrefied	58.26	5.09	0.07	n.d.	36.58

*by difference (%), n.d. - no detected

Figures 1, 2 and 3 (TG, DTG e DTA curves, respectively) show the thermal decomposition for pine sawdust *in natura* with different particle sizes in two atmospheres: air synthetic and nitrogen. In both atmospheres the first event, related to the moisture content, occurring between 45 °C and 87 °C with mass loss of 7.6% and in the DTA curve an endothermic peak at 63 °C was observed.

The second event is related to the thermal decomposition of hemicellulose and cellulose, which occurs between 200 °C and 350 °C, depending on the particle size, with mass loss of approximately 63% in oxidizing atmosphere. It is difficult to distinguish the hemicelulose and cellulose decompositions due to their overlapping. In the nitrogen atmosphere, this second stage the interval became longer and shifted a higher temperature, i.e. between 250 °C and 400 °C, depending on the particle size.

The DTG curves showed that the compounds would be released faster in air atmosphere than in nitrogen atmosphere. The size and sharpness of the DTG peaks significantly differ between atmospheres. In air, the DTG curves exhibited pronounced and narrow peaks whereas in nitrogen exhibits a much wider temperature range.

The third stage, observed only in air atmosphere, is related to the decomposition of lignin. The TG curves present mass losses 27%, depending on the particle size. This event is characterized by an exothermic peak at around 500 ºC, as observed in the DTA curves (Fig. 3).

The difference in the behavior in both inert and oxidizing atmospheres is clear. The DTA curves for air condition show exothermic peaks at 350 °C, 450 °C and 500 °C, which correspond to the thermal decomposition of hemicellulose, cellulose and lignin, respectively. In nitrogen condition only one endothermic peak was observed around 400 °C.

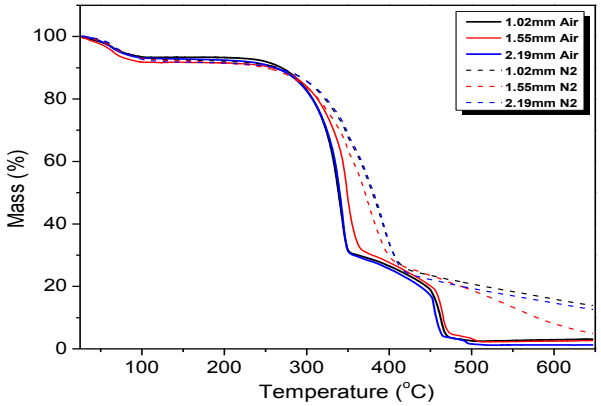


Figure 1. TG curve of pine sawdust *in natura* in different particle sizes and atmospheres

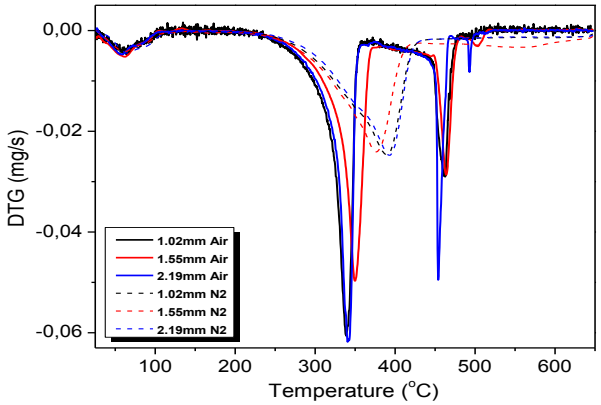


Figure 2. DTG curve of pine sawdust *in natura* in different particle sizes and atmospheres

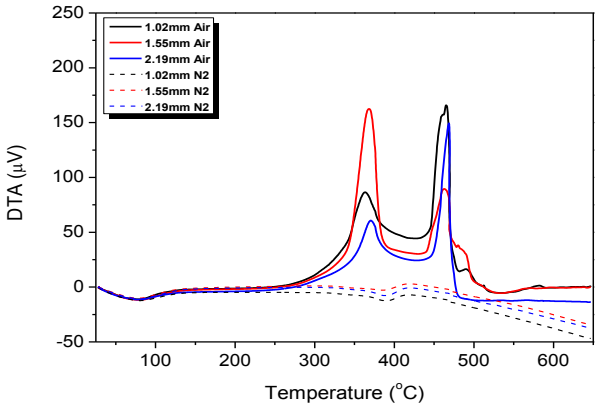
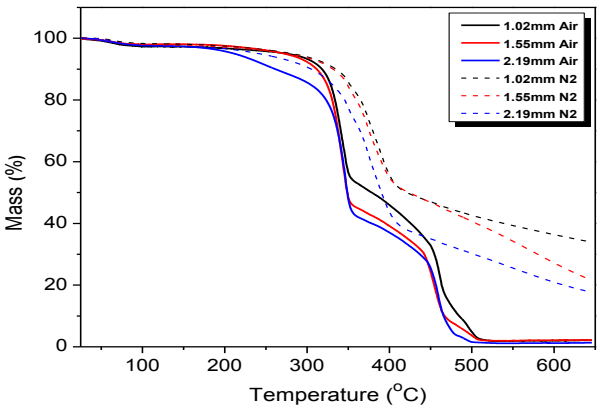


Figure 3. DTA curve of pine sawdust *in natura* in different particle sizes and atmospheres

The TG curves for torrefied pine sawdust in both atmospheres are presented in Fig. 4. They show a 2.5% mass loss related to the moisture content in both air and nitrogen conditions. However, depending on the atmosphere, differences related to several thermal decomposition steps from 200 ºC can be observed. Three events can be more clearly observed through the DTG curves.

It seems that after torrefaction, there is a separation of the hemicellulose and cellulose, i.e., the events at 250-350 ºC, 400-470 ºC and 470-520 ºC are related to the hemicellulose, cellulose and lignin decomposition, respectively.



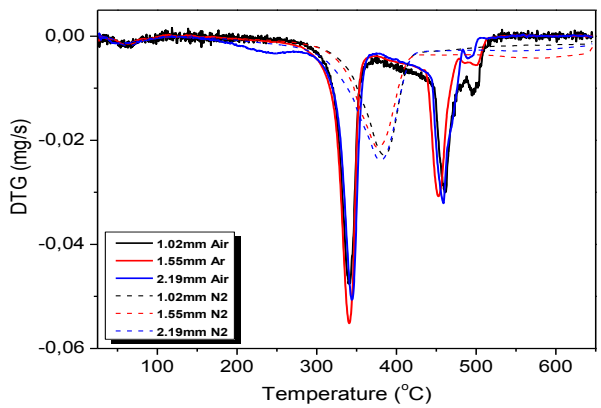


Figure 4. TG curve of torrefied pine sawdust in different particle sizes and atmospheres

Figure 5. DTG curve of torrefied pine sawdust in different particle sizes and atmospheres

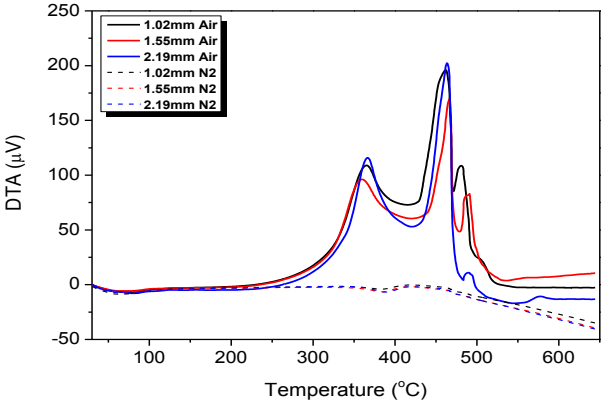


Figure 6. DTA curve of torrefied pine sawdust in different particle sizes and atmospheres

No different decomposition steps could be observed for nitrogen atmosphere, therefore the high reaction rate in air atmosphere is related to the reaction between the released compounds without the oxygen present in the atmosphere.

According to Fig. 5, only the particle size of 2.19 mm exhibited a mass loss event of 18% between 170 and 270 °C. However there is still a lack of information regarding the interpretation of the phenomenon related to particle size.

Figures 7, 8 and 9 present, respectively, TG, DTG and DTA curves for the thermal degradation of coffee husks *in natura* in both air and nitrogen atmospheres.

No considerable changes occurred in the thermal degradation profiles in both environments from room temperature up to 270 ºC. This step is attributed to the hemicellulose and cellulose degradation and presented mass loss of 54%. From this temperature, in air condition, two exothermic events can be detected in hydrogen atmosphere, noting that the peak at 450 ºC is higher than the peak at 330 ºC.

The third event, which corresponds to the lignin thermal degradation, occurs between 430 °C and 470 °C with mass loss of 34%. In air a complete combustion occurs while no enthalpic events in nitrogen atmosphere was observed, characterizing pyrolysis of the volatile material.

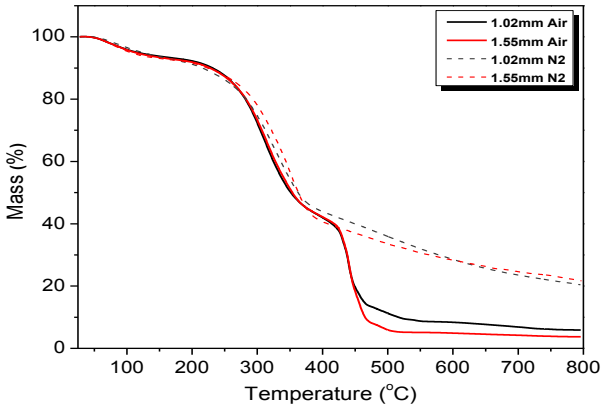


Figure 7. TG curve of coffee husks *in natura* in different particle sizes and atmospheres

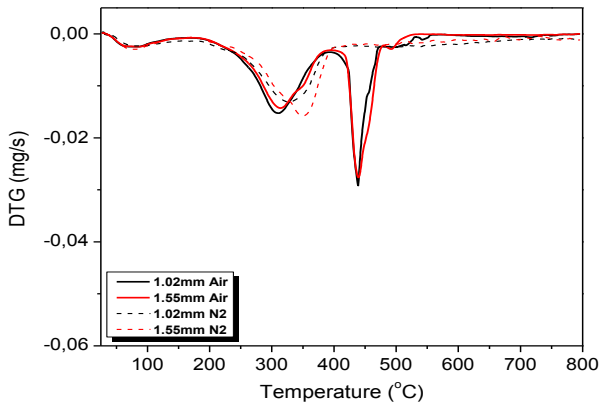


Figure 8. DTG curve of coffee husks *in natura* in different particle sizes and atmospheres

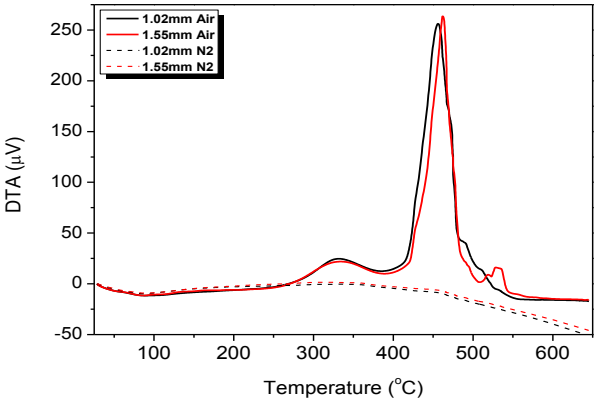


Figure 9. DTA curve of coffee husks *in natura* in different particle sizes and atmospheres

The TG curves of Fig. 10 show that until about 200 °C, there are no substantial changes in the coffee husks torrefied in oxidizing and inert atmospheres, in both environments for this step, the mass loss was about 5.7%.

The DTG curves of Fig. 11 show three events in air and two events in nitrogen.

Thermal decomposition of hemicellulose and cellulose occurring in both oxidizing and inert atmosphere in around 37.2% and 35.0%, respectively, in the temperature range of 250 °C to 400 °C, is noted that peak intensities decreased as the different particles size increased.

The lignin decomposition corresponds to a mass loss of 48.4% in air atmosphere, in a temperature range of 420-450 °C. In nitrogen atmosphere no mass loss to the lignin decomposition could be observed from TG curve.

The DTA curves of Fig. 12 show the occurrence of an endothermic event around 150 °C for both atmospheres, and exothermic events in 350 °C and 450 °C are mass losses of hemicellulose and cellulose, respectively.

Around 550 °C, only for oxidizing atmosphere was presented one exothermic event that is believed to be thermal decomposition from lignin and transformation in tar of the volatiles materials remaining as was related by Yin and Goh (2011).

At the end of the thermal decomposition in synthetic air, is noted that by the TG curves that there are residues of 7.3% for pine sawdust and 7.0% for coffee husks, both *in natura*.

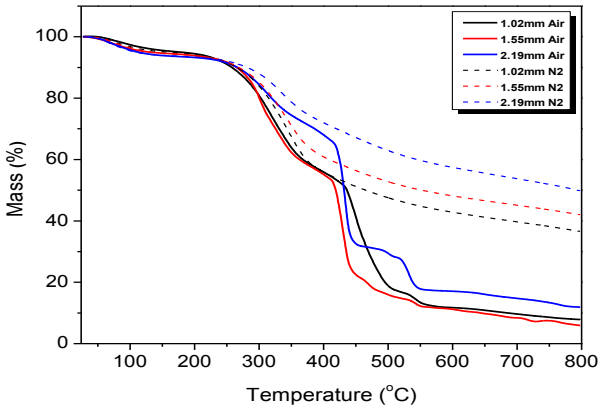


Figure 10. TG curve of coffee husks torrefied in different particle sizes and atmospheres

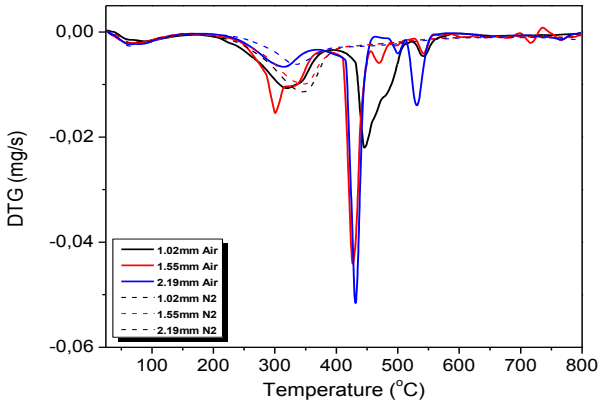


Figure 11. DTG curve of coffee husks torrefied in different particle sizes and atmospheres

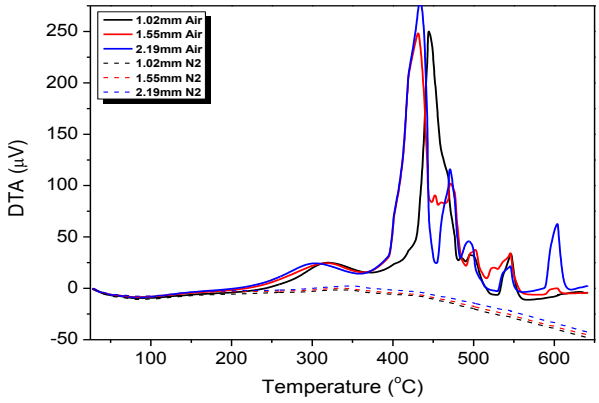


Figure 12. DTA curve of coffee husks torrefied in different particle sizes and atmospheres

Based on the TG/ DTG curves, it was possible to quantify the moisture, hemicellulose, cellulose and lignin present in the samples (see Tab. 2). In addition, the ashes content are also presented.

Table 2. Thermal degradation steps of the biomasses (% dry basis)

Atmospheres	Biomasses	Moisture (%)	Hemicellulose and cellulose (%)	Lignin (%)	Ashes (%)
Air	pine sawdust *in natura*	7.2±0.8	63.1±1.7	27.4±1.0	2.1±1.0
	pine sawdust torrefied	2.3±0.3	52.0±4.4	43.1±5.4	1.8±0.3
	coffee husks *in natura*	6.7±0.3	50.2±0.1	37.4±0.4	4.8±1.0
	coffee husks torrefied	5.5±0.0	37.2±2.2	50.2±3.2	7.2±3.2
Nitrogen	pine sawdust *in natura*	8.0±0.2	69.6±0.8	9.4±0.8	12.7±1.2
	pine sawdust torrefied	2.3±0.1	54.7±8.2	12.5±1.8	31.0±4.1

	coffee husks *in natura*	6.8±0.9	54.6±1.2	18.8±1.7	20.0±0.5
	coffee husks torrefied	5.7±0.5	35.0±8.7	16.2±1.9	42.9±6.2

Experimental conditions: heating rate: 20 ºC min^{-1}; flow rate: 100mL min^{-1}; temperature: 25 ºC to 800 ºC.

Table 2 shows a summary of the mass losses undergone by the biomass of pine sawdust and coffee husks, both *in natura* and torrefied, during the processes of thermal degradation (moisture, hemicellulose, cellulose, lignin and ashes) by mean of thermal analysis: TG/ DTG and DTA in combustion (oxidizing atmosphere) and pyrolysis (inert atmosphere) environment.

Moisture contents of the samples pine sawdust *in natura* in nitrogen, the increase was 90.6% in relation the samples in synthetic air, while that for the samples torrefied in inert atmosphere, this value decreases to 88.9%. For the coffee husks *in natura*, otherwise is noted, that there is increase in oxidizing atmosphere of 95.7% and reduction in inert atmosphere, while that the samples coffee husks torrefied increased 98.3% in inert atmosphere.

Regarding the loss mass by the thermal degradation of hemicellulose and cellulose, the samples of pine sawdust *in natura* in inert atmosphere increased 92.3% in comparison with the samples in oxidative atmosphere. The samples of pine sawdust torrefied in inert atmosphere also showed a 98.2% increase in contrast to the samples in oxidizing atmosphere. The samples coffee husks *in natura* in nitrogen were increased to 98.4% against the samples in synthetic air, while that in the torrefied samples, the opposite was evidenced and these increased 94.4% in oxidizing atmosphere.

In the thermal degradation of lignin, the samples of pine sawdust *in natura* and torrefied showed increases of 43.8% and 54.7%, respectively, in oxidizing atmosphere. The same behavior was observed for samples of coffee husks *in natura* and torrefied in oxidizing atmosphere, an increase in the initial mass loss was approximately 30.0% and 33.3%, respectively.

Concerning the ash content, the samples of pine sawdust *in natura* and torrefied in inert atmosphere showed increases of approximately 18% and 6.2%, respectively, whereas the samples of coffee husks *in natura* and torrefied in inert atmosphere were increased in 25.0% and 20.5%, respectively.

The SEM images presented in Figs. 13 (a - f) show changes in the morphology of the samples of pine sawdust *in natura* and torrefied. As the average particle sizes *in natura* decreased, there was loss in the structure with tubular format, presence of lamellar and pith structures and pores with average diameter of about 10 μm; while that for the torrefied samples (Figs. 13d - f) the lamellar structural characteristics are maintained. Average pore diameter underwent expansion, giving a range of 10 to 30 μm, i.e. characterized by thermal expansion of the materials, probably favored by rise of the temperature torrefaction process (≈ 300 °C). For samples *in natura* with medium particles smaller than 2.19 mm, the loss of the tubular structure and possible turbostraticity, i.e., twisted tapes that are rearranged randomly in space (Gonçalves *et al*., 2009 and Downie *et al*., 2009), that characterizes them as pith structure, as confirmed by Driemeier *et al*. (2011) and Gonçalves *et al*. (2009) and can be seen in Fig. 13b.

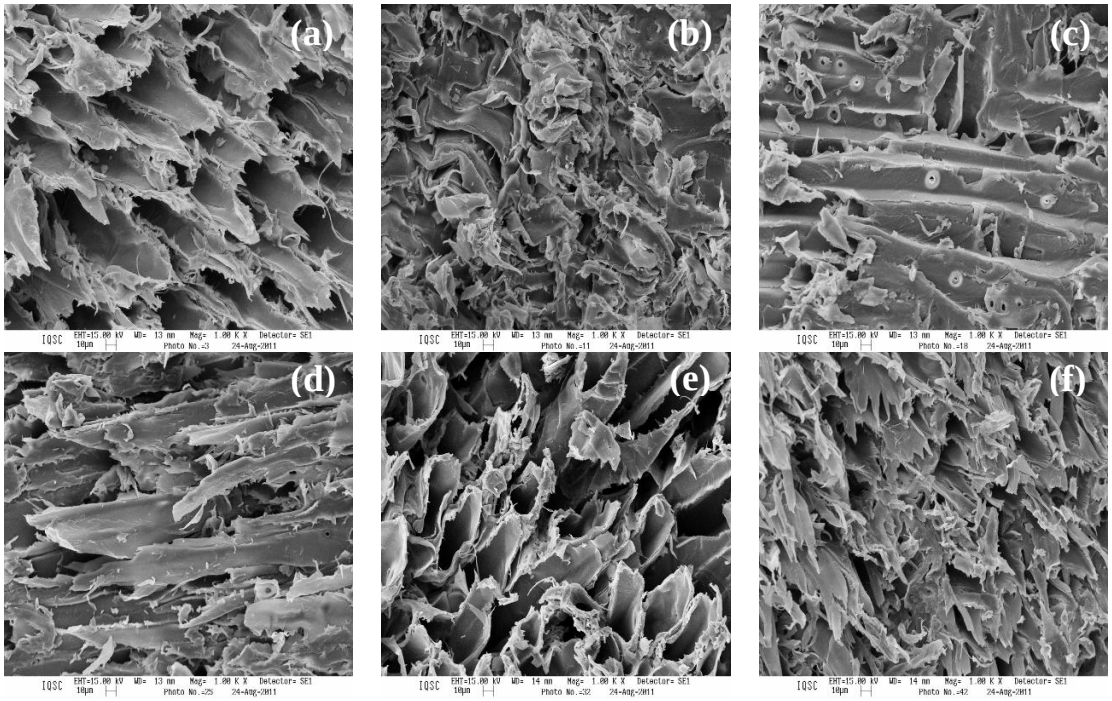


Figure 13. Images SEM pine sawdust *in natura*: (a) 2.19 mm; (b) 1.55 mm; (c) 1.02 mm and torrefied: (d) 2.19 mm; (e) 1.55 mm; (f) 1.02 mm

Figures 14a - e (SEM images) show significant differences in both samples of coffee husks (*in natura* and torrefied). The samples *in natura* (Figs. 14a and b) showed a ticker morphological structure more, homogeneous, slight elevation, roughness and cracks surface (Fig. 14a), larger grains of about 50 μm and rearranged cell, grain boundaries with better definitions, according to increase in particle size range, whereas the samples torrefied coffee husks had a melting substances in the surface (Fig. 14d), possibly being hemicellulose, cellulose and/or lignin by torrefaction process, or other volatile materials released during hard torrefaction (≈ 300 °C), demonstrating crystalline non-uniformity, excessive fragmentation, pores or holes expanded along of the structure caused by increase temperature (Figs. 14c - e).

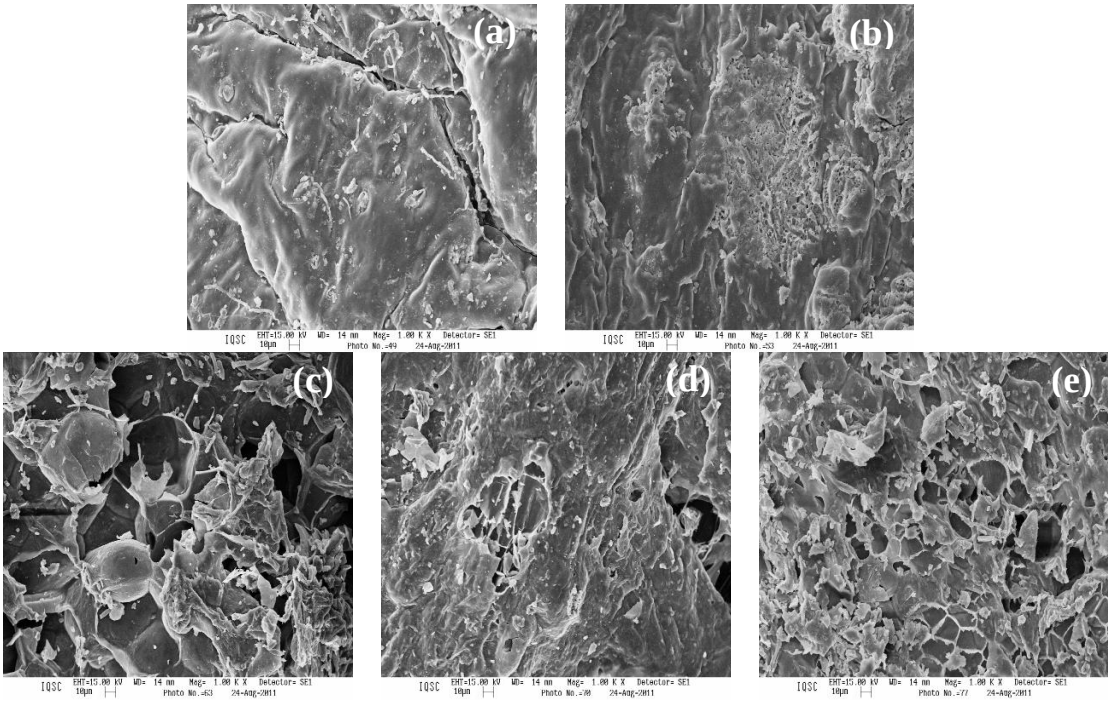


Figure 14. Images SEM coffee husks *in natura*: (a) 1.55 mm; (b) 1.02 mm and torrefied: (c) 2.19 mm; (d) 1.55 mm; (e) 1.02 mm

4. CONCLUSIONS

Based on non-isothermal thermograms was observed that the biomasses *in natura*, both pine sawdust and coffee husks showed homogeneous behavior for the different particles size for both atmospheres, therefore this parameter did not influenced these results.

Thermally treated samples (severe torrefaction) showed significant differences with related to particles size in the TG/ DTG curves, through which was possible to evaluate the steps of thermal degradation occurred during processes. The DTA curves provided identification and evaluation of the presence of endothermic and exothermic events in the steps of thermal decomposition from biomasses. Peaks with same intensity were observed in the samples of pine sawdust *in natura* and torrefied in oxidizing atmosphere around 350 °C, was found that in this temperature the thermal degradation from cellulose is intensified. Only in the combustion of pine sawdust torrefied with particle of 2.19mm a peak endothermic was found between 250 °C and 270 °C showing the presence of the torrefaction process.

The SEM images showed differences in the morphology of both samples, taking into account the different particles size. The presence of tubular structures with diameters in the range 10 to 30 μm for the samples of pine sawdust torrefied, while the samples *in natura* showed tubes with a diameter about 10 μm, pith and lamella structures. The samples of coffee husks *in natura* showed well defined grain boundaries and melting of volatile materials on the surfaces, whereas the samples torrefied showed expansion and exploded pores like honeycomb, cracks surface and excessive fragmentation.

All biomasses evaluated presented basic characteristics be used as biofuels, mainly coffee husks torrefied by have high carbon and low oxygen contents. When biomasses are employed to be utilized like biofuels, in some situations, pretreatment of torrefaction are essentials procedures to reach high efficiencies in the production and consume of the fuel.

5. ACKNOWLEDGEMENTS

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