EVALUATION OF THE COMBUSTION PROCESS OF COFFEE HUSK SAMPLES IN A DROP TUBE FURNACE (DTF)

G. Cruz[a,b],

and P. M. Crnkovic[a]

[a]University of São Paulo

Engineering School of São Carlos

Department of Mechanical Engineering

Thermal Engineering and Fluids Laboratory

Bairro Parque Arnold Schimidt

CEP: 13566-590, São Carlos, São Paulo, Brazil

glaubercruz@gmail.com

[b]Ceuma University

Coordination of Civil Engineering

Bairro Renascença II

CEP: 65067-351, São Luís, Maranhão, Brazil

ABSTRACT

Thermal conversion processes that use coffee husk are an alternative to solve the environmental problems of disposal and waste burning in open places and avoid greenhouse gases emissions. The present study evaluates *in natura* coffee husk samples and residues obtained from a combustion process in a Drop Tube Furnace (DTF). Such an evaluation consists in understanding the efficiency of the burning process, therefore the activation energies (E_a) of the combustion process for both samples were determined. The isoconversional kinetic method (Model Free Kinetics) was used for the determination of the E_a values of the samples. The E_a values of the main stages of the combustion process (devolatilization and carbonization) for both samples were compared. Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) data at five heating rates (10, 15, 20, 25 and 30 ºC min^{-1}) were used for the determination of hemicellulose, cellulose and residual lignin. SEM (Scanning Electronic Microscopy) images and EDS (Energy Dispersive Spectroscopy) analysis were applied as complementary techniques in the combustion process. The results show that for both samples the E_a values were higher for the carbonization step than for devolatilization. The E_a values for the stages of devolatilization and carbonization for the residues were 33 and 15% lower than those for the *in natura* coffee husk samples. The lower E_a values in both steps for the residues are indicative of a reduction in the complexity of the reaction mechanism, which can be a parameter for the evaluation of the biomass combustion process. According to the SEM images, the residues showed exploded surfaces caused by the combustion process, whereas in the *in natura* samples a denser and robust structure was observed. The ash formed after the combustion process in the thermobalance was also evaluated by SEM and EDS analyses and showed a more homogenous structure with tiny particles in comparison with the *in natura* coffee husk samples. The EDS analysis confirmed the presence of precursor elements in the samples, such as potassium and other inorganic materials, which were intensified after the combustion process.

NOMENCLATURE

E_a activation energy, kJ mol^{-1}
A   pre-exponential factor, s[-1]
R   universal gas constant, J mol^{-1} K^{-1}
k   constant of reaction rate, s[-1]
T   temperature, K
m   local sample mass, mg
f(α)   reaction model function
t   time, s
Al   aluminum
Ca   calcium
Cl   chlorine

Fe   iron
K   potassium
Mg   magnesium
Na   sodium
P   phosphorus
S   sulphur
Si   silicon

Greek symbols

α conversion degree, %
β heating rate, ºC min^{-1}

Subscripts

a   activation energy
0   initial
α   conversion degree
∞   final

INTRODUCTION

Among several agricultural cultures in Brazil, coffee has been characterized by its large-scale production. Brazil is the largest consumer and producer worldwide and its contribution to the worldwide scenario is approximately 30% (Orsini *et al*., 2011).

The high quality of the Brazilian coffee has added value to the product and increased on average 45% its consumption by the domestic market over the past 10 years. The other 55% of the Brazilian coffee production are commercialized by the international market (http://www.abic.com.br. Acessed: 28.08.15).

55% of the global coffee productions are grains (dried fruits) and the remaining 45% are considered wastes. A good use of the residues generated by coffee crops contributes towards mitigating the negative aspects of the gaseous emissions to the environment and creates new energy sources for the country (Venturim, 2002).

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 soil and water and facilitate the proliferation of diseases (Orsini *et al*., 2011; Teng *et al*., 1997).

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 feedstock in thermal conversion processes, such as biomass combustion for energy production. The Brazilian production of coffee still generates a large amount of residues, which could be utilized for the generation of energy. Although the coffee husks are used by farmers as fertilizers or to heat furnaces for drying beans, two million tons per year still remain and are discarded in rural areas (Orsini, 2012).

Direct combustion is the most common form of thermal biomass conversion for the generation of energy. Other conversion processes, as oxy-fuel combustion, gasification and pyrolysis are promising technologies (Foletto *et al*., 2005). However, the knowledge on the thermal behavior of these conversion processes is limited and there is no sufficient information on the use of oxidative atmospheres, which are essential to the development and optimization of technological processes.

The combustion process of biomass comprises its burnout in an environment rich in oxygen or air, in which types and properties of biomass fuel, particles size, air flow rate and fuel moisture are considered. Such features directly affect the combustion, as well as the reaction rates, and generation and transfer of heat (Zhao *et al*., 2012; Senneca, 2007). The biomass combustion is a highly exothermic process that involves a series of successive chemical reactions between the biomass fuel and the oxidizing agent for the production of heat and energy. Several biomasses can be used as appropriate fuel feedstock in many thermal conversion systems (Kok and Özgür, 2013).

The knowledge on the kinetic behavior of the biomass thermal degradation steps is an important parameter for the modeling of both combustion processes and reactor design (Poletto *et al*., 2012; Moltó *et al*., 2012). Determining the kinetic parameters of the biomass thermal decomposition is crucial for an accurate prediction of its behavior under different conditions. Several studies have reported different kinetic methods to describe the biomass thermal degradation (Kok and Özgür, 2013; Poletto *et al*., 2012; Wilson *et al*., 2011; Harun and Afzal, 2010; Shen *et al*., 2009; Yao *et al*., 2008; Ramajo-Escalera *et al*., 2006). The determination of the E_a values based on the Arrhenius's equation and using thermogravimetric data has been widely applied for the evaluation of change mechanisms in solid phases.

Based on the scenario presented and using coffee plantation residues, this study investigates the combustion process of coffee husk samples in a Drop Tube Furnace (DTF). Activation energy (E_a) values were obtained by Thermogravimetry (TG) and a mathematical model (Model Free Kinetics) was used as a tool to understand the combustion process. TG experiments were performed under synthetic air atmosphere to simulate conventional combustion. In addition, Scanning Electronic Microscopy (SEM) images and Energy Dispersive Spectroscopy (EDS) analysis were applied for the evaluation of the morphological structure and composition analysis of the coffee husk samples before and after the combustion process.

THEORY

Determination of the activation energies by Model-Free Kinetics

The activation energies for the combustion processes of two samples (*in natura* coffee husk and residues) were obtained using non-isothermal thermogravimetric experiments and Model Free Kinetics.

The Model Free Kinetics method enables the evaluation of the Arrhenius parameters. It is based on isoconversional techniques and calculates the activation energy as a function of conversion (E_a=f(α)) (Vyazovkin *et. al*, 2011; Vyazovkin and Wight, 1999; Vyazovkin and Dollimore, 1996; Vyazovkin, 1997; Vyazovkin and Sbirrazzouli,

1997). The method is supported on the assumption that:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) = A \exp\left(-\frac{E_a}{RT}\right).f(\alpha) \qquad (1)$$

where T is the temperature, t is the time, $f(\alpha)$ is the reaction model, $k(T)$ is the constant of reaction rate, R is the universal gas constant, A is the pre-exponential factor, E_a is the activation energy and (α) is the conversion degree.

Conversion degree is defined as $\alpha=(m_0-m)/(m_0-m_\infty)$, where m is the local sample mass that varies with time, m_0 is the initial sample mass and m_∞ is the final sample mass. For simple reactions, the function of conversion, $f(\alpha)$, can be determined, but for complex reactions it is generally unknown (Vyazovkin et. al, 2011).

There is a temporal dependence on non-isothermal conditions, which can be eliminated dividing $f(\alpha)$ by the heating rate $\beta=dT/dt$. After rearranging Eq. (1) one obtains:

$$\frac{1}{f(\alpha)}d\alpha = \frac{A}{\beta}\exp\left(-\frac{E_a}{RT}\right)dT \qquad (2)$$

Integrating Eq. (2) up to the conversion at the local temperature, one has:

$$\int_0^\alpha \frac{1}{f(\alpha)}d\alpha = g(\alpha) = \frac{A}{\beta}\int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right)dT \qquad (3)$$

Provided that $E_a/2RT \gg 1$, the temperature integral of the right hand side can be approximated by

$$\int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right)dT \approx \frac{R}{E_a}T^2 \exp\left(-\frac{E_a}{RT}\right) \qquad (4)$$

Inserting Eq. (4) in Eq. (3), rearranging Eq. (3) and taking the logarithm of the generated expression one has:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left[\frac{RA}{E_a g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha} \qquad (5)$$

where subscript α represents the values related to a given conversion degree. The activation energies can be obtained graphically by plotting $\ln(\beta/T^2)$ *versus* $1/T$.

EXPERIMENTS

Samples

Two samples were evaluated: *in natura* coffee

husk and the residues formed after the combustion process. The *in natura* coffee husk (*Coffea arabica L.*) originated from São Paulo State - Southeast region was provided by a group of research on Thermal Processes and Environmental Engineering (PTEA) from the Mechanical Engineering Faculty (FEM) at University of Campinas (Unicamp). Physical-chemical characteristics of the *in natura* samples were determined and are presented in other previous studies of our research group (Pécora *et al.*, 2014; Cruz and Crnkovic, 2015).

The *in natura* samples underwent pretreatments that consisted in washing in running water for the removal of impurities, grinding in a laboratory knives mill for reducing the particles size and subsequent sieving for the separation in the required granulometric range. Particles of 0.151 mm average size were used for all the samples.

Combustion in a Drop Tube Furnace (DTF)

A Drop Tube Furnace (DTF) electrically heated (3.5 kVA maximum power) was used for the biomass combustion process. The basic dimensions of the experimental apparatus are 60 mm outer diameter, 400 mm uniform zone and 200 mm heated zone. The particles were introduced into the reactor by a vibratory feeding system controlled by amplitude (8% power at 60 w) and frequency (110 Hz). The sample mass used was 6.0±0.5 g for a 10-minute experiment. An air primary flow rate of 4 L min^{-1} with 20% oxygen concentration was applied so as to keep the particles in suspension during the combustion process in DTF. After burning at 950 ºC, the ash and residue samples were collected for evaluation by TGA, SEM and EDS analyses.

Thermal Analysis (TG/ DTG curves)

TG/DTG non-isothermal experiments were performed in a *Shimadzu* thermogravimetric analyzer, TGA-50H model, for the obtaining of experimental data. The three thermal degradation steps related to hemicellulose, cellulose and residual lignin were evaluated. The conditions used were oxidizing atmosphere (synthetic air) and dynamic flow rate of 100 mL min^{-1}. Five heating rates (10, 15, 20, 25 and 30 °C min^{-1}) from room temperature up to 700 °C were used for the experiments. The samples masses were 10.0 ± 0.5 mg in an alumina crucible. The tests were performed in duplicate and the average values and standard deviations were considered (Table 1).

The activation energies (E_a) *versus* conversion degree (α) curves of the thermal degradation steps for hemicellulose (1st step), cellulose (2nd step) and lignin (3rd step) were obtained by Model Free Kinetics. Each thermal degradation step was based on the peak separation method of the DTG curves (Vyazovkin *et al.*, 2011). Figure 1 show the TG/ DTG curves for the sugarcane bagasse sample in N_2/O_2 atmosphere used
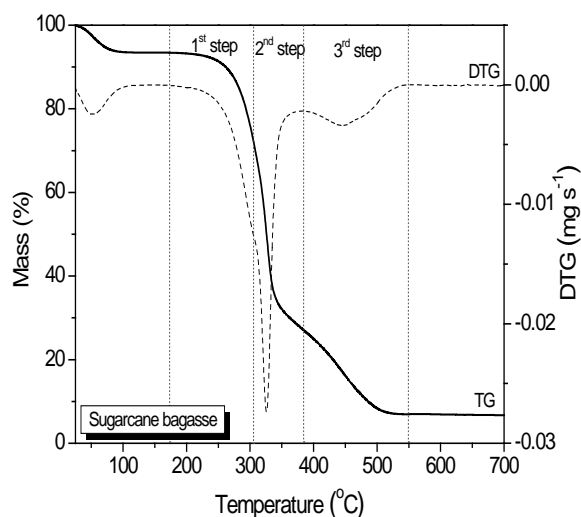
to explain such separation method.

Figure 1. TG/DTG curves for the sugarcane bagasse sample under synthetic air atmosphere at 10 °C min^{-1}, showing the three thermal degradation steps.

Scanning Electronic Microscopy (SEM images)

The morphological analysis of the *in natura*, residues and ash coffee husk samples was conducted under a Scanning Electron Microscope, LEO 440 model of 1,000 times amplitude. Before being placed under the microscope, the samples were deposited on an aluminum support and then metalized in gold bath.

Energy Dispersive Spectroscopy (EDS analysis)

The *in natura* coffee husk samples, residues and ash were prepared by sintering for a 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.

RESULTS AND DISCUSSION

Thermal Analysis (TG/ DTG curves)

The TG curves (Figs. 2a and b) show the mass loss events for the *in natura* coffee husk and residue samples, respectively, at 5 heating rates under synthetic air atmosphere. Both samples exhibited a similar behavior. As the heating rate increased, there was a displacement of the TG curves to higher temperatures and lower times (Moltó *et al.*, 2006). This thermal behavior provided information on the reliability of the thermogravimetric data for the application of the kinetic method - Model Free Kinetics.
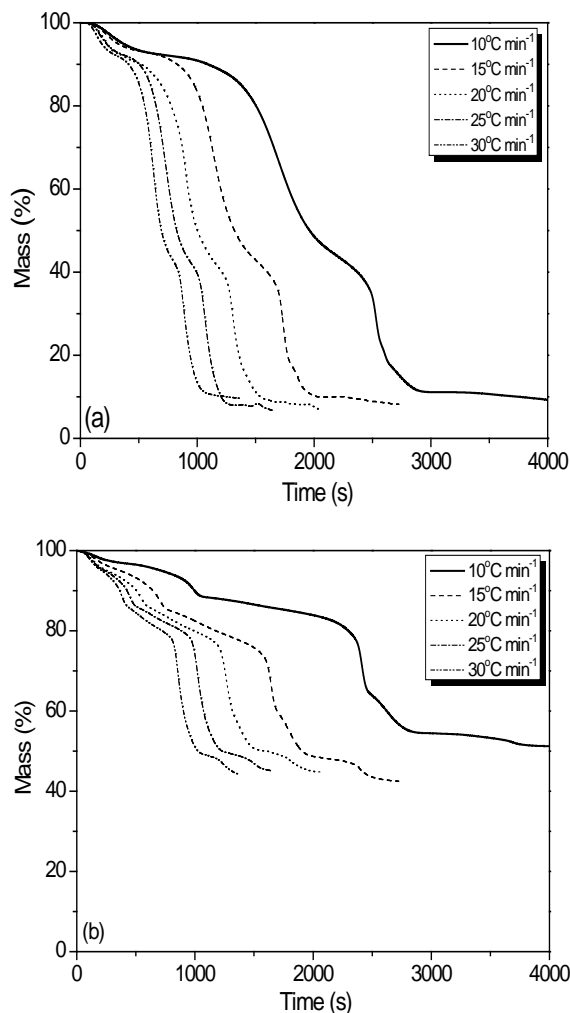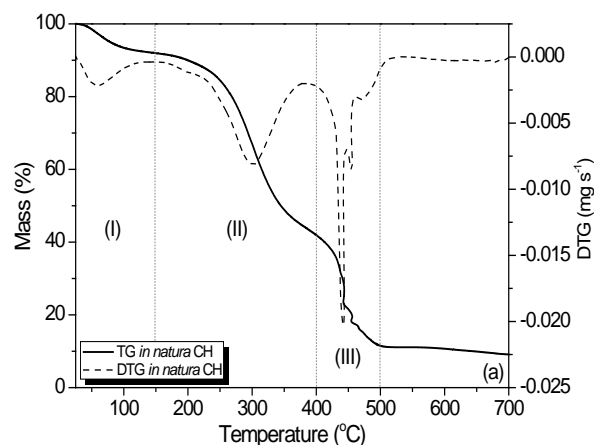

Figure 2. TG curves for the coffee husk samples at five heating rates under synthetic air atmosphere: (a) *in natura* and (b) residues.

The TG/ DTG curves (Figs. 3a and b) for the *in natura* coffee husk and residue samples show the 3 thermal degradation steps under synthetic air atmosphere and related to (I) moisture evaporation, (II) hemicelluloses and cellulose decomposition, and (III) lignin decomposition. The final mass corresponds to the ash content.
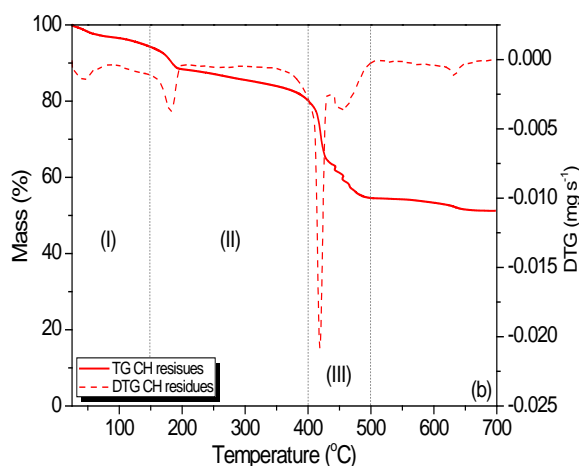
Figure 3. TG/ DTG thermograms for the coffee husk samples at 10ºC min^{-1} under synthetic air atmosphere: (a) *in natura* and (b) residues.

The decomposition of each component for two samples showed well-defined temperature ranges. In the moisture release step (I region) in the residue samples, there was a lower mass loss of 62% in comparison with the *in natura* coffee husk samples, because the residues underwent a thermal pretreatment in DTF and part of their moisture was eliminated in the combustion process.

According to the DTG curves, in the II region of the *in natura* samples under combustion atmosphere, hemicellulose and cellulose exhibited a decomposition temperature peak at ≈ 300 ºC. However, for the residues this temperature was achieved at approximately 180 ºC. This displacement to lower temperatures for the coffee husk residues can be explained by the breakdown of the lignocellulosic matrix and volatiles release, which caused a progress in the reaction rate (Jenkins *et al*., 1998).

For both *in natura* coffee husk and residue samples a maximum combustion rate (≈ 0.020 mg s^{-1}) with maximum temperature peaks at 442 and 419 ºC, respectively, was also observed, which indicates that in the III region between 400 and 500 ºC there occurred the onset of the char particles combustion and first clues of the ash formation are provided. This same behavior was observed by Haykiri-Açma (2003) for cone pine and sunflower shell samples.

The oxygen present in the atmosphere strongly influences the volatile release and the combustion stage and benefits ignition (Kumar *et al*., 2009). For both samples the residual lignin decomposition achieved its maximum degradation temperature under combustion atmosphere at approximately 460 ºC.

The temperatures for the maximum combustion rates to take place are significantly affected by the higher alkaline metal content present in the biofuels (Williams *et al*., 2012). Significant differences were also observed in the ignition temperatures for both samples. For the *in natura* samples, the ignition temperature ranged between 130 and 150 ºC, whereas

for coffee husk residues it varied from 90 to 98 ºC. This difference may be related to the high consumption of lignocellulosic material (large mass loss) by its transformation into gases (mainly CO_2 and H_2O vapour) and solid wastes after a combustion process (Fernández *et al*., 2012), in this case in a DTF.

In the IV region, the final carbonization process occurs and the residual mass corresponds to the ash content. For the coffee husk samples, in particular, this ash formed is composed of inorganic materials, predominantly potassium and its oxides. In this study, for all samples, the K content ranged from 4 to 36%. The inorganic materials are precursors of several problems during thermal processes, such as agglomeration, slagging, fouling in feeding systems, damage to the heat transfer and energy generation in many real thermal processes.

Table 1 shows the percentages of mass loss (contents of moisture, hemicellulose, cellulose, lignin and ash) for the *in natura* coffee husk and residue samples along their thermal degradation processes. The values were obtained by thermal analysis under synthetic air atmosphere.

Table 1. Mass loss percentages (%) under synthetic air atmosphere for the thermal degradation steps.

Coffee husk samples	*in natura*	residues
moisture	8.2 ± 0.3	3.1 ± 0.3
hemicellulose	50.2 ± 2.0	9.0 ± 0.0
cellulose	23.3 ± 1.6	24.4 ± 0.4
residual lignin	10.0 ± 1.1	12.2 ± 0.2
ash	8.3 ± 2.5	51.3 ± 0.2

Regarding the moisture release, the mass loss for the residues showed a decrease of ≈ 62% in comparison to the *in natura* samples. The moisture content associated with biomass fibers is very difficult to be removed due to the hydrophilic nature of lignocellulosic materials (Sasmal *et al*., 2012).

The amount of hemicelluloses for the residues showed a decrease of ≈ 82%. Variations of 5 and 18% were detected for the thermal degradation of cellulose and residual lignin, respectively. These compounds exhibit deeper layers on the cell wall and a higher thermal stability (Yang *et al*., 2007).

In general, the biomasses show higher volatile materials, of the order of 70 to 80%. For the *in natura* samples, the volatile material content was approximately 74% (García *et al*., 2012; Saenger *et al*., 2001). The coffee husk residues showed approximately 33% of volatiles released, probably due to the partial release of these compounds by the combustion process.

The residues exhibited a high ash amount, which corresponds to thermal decomposition of organic and inorganic materials in DTF.

Kinetic Study (Model Free Kinetics)

A kinetic model for the thermal decomposition of a solid biofuel was adopted for the description of the conversion process of *in natura* coffee husk and residue samples in the volatiles release and char formation (Shuangning *et al*., 2006). Isoconversional methods, as Model Free Kinetics estimate the E_a values as a function of the conversion degree (α), without the need for choosing a model or a reaction order. A basic assumption of this method is that the reaction rate for a constant extension of the conversion degree (α) depends only on the temperature (Ramajo-Escalera *et al*., 2006). The authors divided the conversion degree (α) into four regions to better explain the E_a behavior: (I) evaporation, (II) devolatilization, (III) carbonization and (IV) ash formation, with determined temperature ranges.

The E_a *versus* (α) curves for the thermal degradation of hemicelluloses and cellulose (1st step) for the *in natura* coffee husk samples (Fig. 4a) showed a heterogeneous behavior, *i. e*. they ranged from 2 to 175 kJ mol^{-1}. Such a behavior can be explained by changes in the mechanism during the thermal decomposition and the complexity of the samples. However, a more stable behavior was observed for the residues (Fig. 4b). In this step devolatilization (II), which covers 15 to 60% of the conversion process, is the dominant mechanism of mass loss. The biomasses release a large amount of volatiles at temperatures below 400 °C. The devolatilization occurs faster than the carbonization, as the former requires a higher E_a (García *et al*., 2012; Shen *et al*., 2009; Nassar *et al*., 1996).

In the 2st step, both samples (*in natura* coffee husk and residues) showed a similar behavior and the E_a ranged from 91 to 196 kJ mol^{-1} and from 83 to 172 kJ mol^{-1}, respectively, which can be associated with the thermal decomposition of cellulosic compounds of high thermal stability (Carrier *et al*., 2011; Yang *et al*., 2007).

In the III region, known as carbonization step, which corresponds to 60 to 70% of the conversion process, between 400 and 500 °C, there occurs the onset of the combustion of the char particles (Saenger *et al*., 2001). In the 3rd step, no significant variation in E_a was observed.

In the IV region, 70 to 95% of the combustion process was concluded. This region is characterized by the burnout of remaining materials in the samples and full formation of ash.
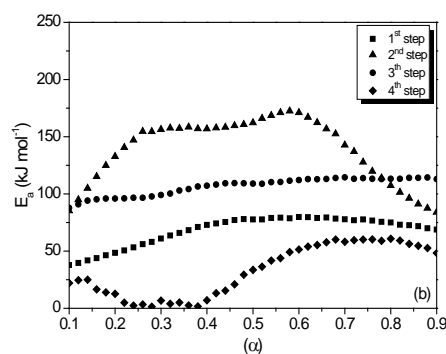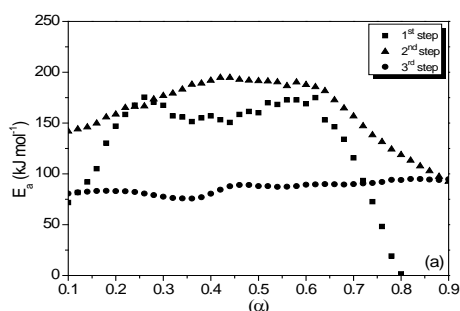

Figure 4. Activation energies (E_a) *versus* conversion degree (α) under synthetic air atmosphere for the coffee husk samples: (a) *in natura* and (b) residues.

Table 2 shows the E_a values for both *in natura* coffee husk and residue samples.

Table 2. Activation energy (E_a) values (kJ mol^{-1}) for the thermal degradation steps of both coffee husk samples under synthetic air atmosphere.

Coffee husk samples	1st step	2nd step	3rd step	4th step
in natura	98 ± 77	153 ± 36	87 ± 7	-
residues	66 ± 16	130 ± 35	101 ± 10	32 ± 21

The E_a values in the 1st and 2nd steps for the residue samples showed decreases of 33 and 15%, respectively, in comparison with *in natura* samples. Such lower values are possibly associated with the decrease in the complexity of the thermal degradation reactions of hemicellulose and cellulose, which may have been affected by an increase in the temperature during the combustion process in a DTF and, consequently, the disruption of the lignocellulosic structure (Teng *et al*., 1997).

In the 3rd step a 16% increase in the E_a value for the residue samples was observed. This increase can be indicative of the variation in the mechanism of the chemical reactions in thermal processes (Saddawi *et al*., 2010; Ledakowicz and Stolarek, 2002).

The coffee husk residues showed a 4th degradation step with a lower E_a value ($\approx$ 32 kJ mol^{-1}), possibly attributed to the oxidation of inorganic materials not burned at temperatures below 700 °C, which may lead to the formation of corrosive gaseous species, such as potassium, sulphur and chlorine (Saidur *et al*., 2011; Saenger *et al*., 2001).

Scanning Electronic Microscopy (SEM images)

Figures 5a to 5c show the SEM micrographies for the *in natura*, residues and ash coffee husk samples, respectively. The biomass samples used showed quite different morphological characteristics.

For the *in natura* samples (Fig. 5a), the surface structure is denser and robust and contains large elongated grains, non-homogeneous surfaces, well-

defined grain contours, a thicker morphological structure with a slight elevation, roughness, and cracks surfaces. The residues (Fig. 5b) exhibited a non-uniform structure, several cracks emerging on the surface and holes, possibly due to the volatile materials released during the combustion process. Such features are also typical of severe torrefaction processes ≈ 300 °C (Biagini *et al.*, 2005). In general, the studied samples seem to exhibit some macroporosity. Cetin *et al.* (2004) reported that at low heating rates (20 ℃ s⁻¹), the porosity of biomasses enables high volatile releases with no major morphological changes.
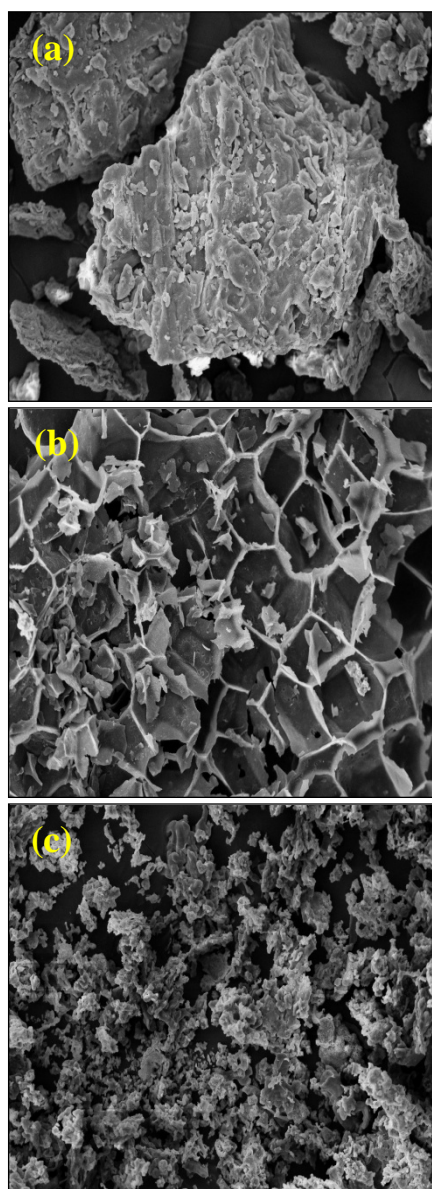

Figure 5. SEM micrographies of the coffee husk samples with magnitude of 1,000 times: (a) *in natura*, (b) residues and (c) ash.

The ash samples obtained by thermogravimetry (Fig. 5c) confirmed that the combustion process was concluded satisfactorily. A more homogeneous

structure (amalgam-type) with tiny particles, probably because of the agglomeration phenomena due to the melting of alkali compounds was observed (Fernández *et al.*, 2012). The inorganic materials contained in the ash, mainly potassium and its oxides, contribute to the agglomerate, slagging, fouling and corrosion in many real thermal processes (Saenger *et al.*, 2001).

Energy Dispersive Spectroscopy (EDS analysis)

Figure 6 shows the EDS analysis in terms of mass percentage for the *in natura*, residues and ash coffee husk samples. This technique determined the elemental composition and compared its compositional evolution. The results were obtained from three different points of the samples. The average values and standard deviations are showed in the Fig. below.
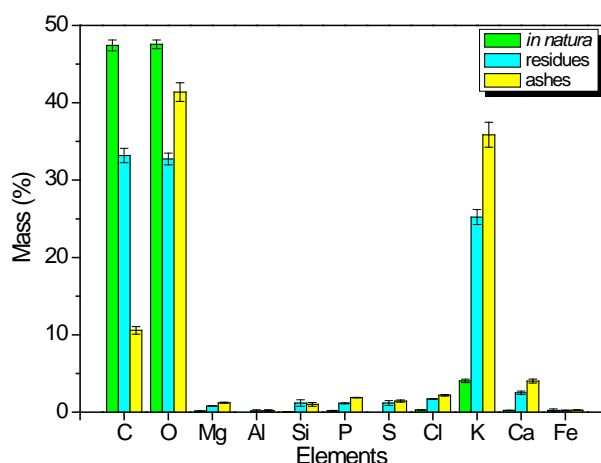

Figure 6. EDS analysis of the *in natura*, residues and ash coffee husk samples.

The *in natura* samples are formed basically by carbon content (≈ 47%) and oxygen (≈ 48%). The combination of these two elements confers the biomass a high heating value. Both elements suffered a decrease in the residues of the order of 30% and 31%, respectively, probably due to the partial combustion and volatile releases.

Regarding the ash samples in comparison with the residues, the carbon content suffered a ≈ 68% decrease due to the complete combustion and the oxygen content increased ≈ 26%. Such an increase may be due to either the release of the oxygen contained in the sample or the incorporation of oxygen of the oxidizing atmosphere by the different oxides formation.

Other elements, such as Mg, Si, P, Cl, Ca and Fe were also found in smaller amounts in the *in natura* samples. Chlorine traces that appear in the *in natura* samples may be due to the use of fertilizers during the growth of the crop. Such an element may cause corrosion problems in the combustion chamber and environmentally unfriendly emissions during the

combustion process (Fernández *et al.*, 2012).

After the combustion in the DTF, the residue samples showed changes in their composition whereas some trace elements, such as Mg, Si, P, Cl, Ca and Fe had a slight increase. Al and S appear only in the residue samples and ash composition. The presence of some elements, as P, Ca, Al and Si, and their respective oxides in the solid wastes still generates large environmental problems. A deeper study is necessary for the obtaining of information on possible applications of these elements, as for example, their use in industries of concretes or composites (Foletto *et al.*, 2005).

The *in natura* samples showed a 4% composition of potassium (K), which is their major constituent among the inorganic materials. It appeared as the main precursor in the ash formation, slagging, agglomeration and fouling in feeding systems (Sanger *et al.*, 2001). After the combustion in DTF, the K composition increased considerably (530% and 800% for residues and ash samples, respectively), probably due to its exposure or intensification at high temperatures (≈ 700 ºC).

The EDS analysis was used to identify possible alkalis elements in the ash, such as Na, K, Mg and Ca (oxides, hydroxides and carbonates of alkaline metals and alkaline earth), which generate slagging. A combustion process that uses residues with a high amount of those elements is environmentally undesirable (Fernández *et al.*, 2012).

CONCLUSIONS

In this study *in natura* coffee husk and residue samples were used for an investigation into the efficiency of the combustion process in a Drop Tube Furnace (DTF). The residues of the combustion were also evaluated by TGA, SEM and EDS analyses.

The efficiency of the burning process in the DTF was evaluated by means of TG/ DTG curves. The *in natura* coffee husk samples were partially carbonized, possibly due to the short residence time or particles agglomeration. DTF can be used in thermal conversion processes and fast pretreatments of biomasses to enhance their intrinsic characteristics.

Regarding the Model Free Kinetics, for the 1st and 2nd steps, the residues showed E_a values ≈ 33 and 15% lower than those of *in natura* samples. However, for the 3rd step a ≈ 16% increase was observed. On average, the E_a values were lower in residues than in *in natura* samples, due to the disruption of the lignocellulosic structure after the burning process. The residues showed a 4th step with low E_a values. In the devolatilization stage, the E_a values were lower than those in the carbonization stage. Such characteristics may be indicative of the efficiency of the biomass combustion process in a DTF.

The SEM images of the *in natura* samples showed a denser and robust structure, elongated grains, roughness, and crack surfaces, whereas the residues exhibited a non-uniform structure and several cracks emerging on the surface by the release of volatiles. The combustion process occurred only on the sample surfaces, which may be indicative of the severe torrefaction process. The ash generated after TG analysis showed a more homogenous structure with tiny particles, probably due to the agglomeration and melting of alkaline compounds.

The EDS analysis identified possible alkaline elements, such as K, Mg and Ca, which are main precursors in the ash formation, agglomeration, slagging, and fouling in thermal systems.

ACKNOWLEDGEMENTS

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