Analysis of Kinetic and Diffusive Data from the Combustion of Char Pellets made with Hybrid Mixtures

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Abstract:

The presence of *Cistus* and *Cytisus spp* in 64% of the Portuguese mainland is a potential source of a autochthonous renewable energy form. Also, Portugal is a main international cork exporter and processor, which leads to a large production of cork powders and residues. Some of these can be incorporated in new fuel products or directly used to produce process heat.

The present work aimed to study the combustion of chars from hybrid pellets in a laboratory scale bubbling fluidized bed reactor. The 6 mm diameter hybrid pellets made from blends of *Cytisus* with cork residues, *Cistus* with *Eucalyptus* and *Cytisus* with *Cistus* were produced in a Tojaltec press machine. They were then carbonized in nitrogen atmosphere at 800 °C, and subsequently cut into smaller and more uniform particles with average lengths of 4.5, 7.5 and 11.5 mm approximately. The mean diameter of the char pellets was determined using the Image J open source image processing program software.

The combustion tests were carried out at three different bed temperatures, 700, 800 and 900 °C. From the analysis of the evolution of the overall combustion resistance of batches of these char pellets, kinetic and diffusive data, namely the heterogeneous phase reaction rate constant of carbon oxidation to carbon monoxide and Sherwood number values, were obtained.

Contrary to the standard expected trend, decrease of the overall combustion resistance with temperature increase, the results show that the overall combustion resistance of for the Cytisus with Cistus char overlap for the 700 and 800 ºC experiments. This is due to the influence of some ash components upon the combustion kinetics and that in some circumstances such influence overrides the standard dependency of the kinetic data with the combustion temperature.

Keywords:

Hybrid pellets, Chars, Fluidized bed, Kinetic and Diffusive data.

1. Introduction

Land availability and the existence of alternatives and associated costs, are examples that large-scale exploitation of bioenergy still faces many socioeconomic, cultural, institutional and technological barriers [1].

The abundant presence of shrubs of *Cistus Ladanifer* and *Cytisus spp* in 64% of the Portuguese continental territory is a renewable source of autochthonous bioenergy still to be explored. Those are native shrub species, lignocellulosic and weeds that thrive, survive climatic variations and incendiary devastation.

On the other hand, Portuguese cork industry technologies are highly energy dependent and some of the cork by-products have high energy content. Pelletizing those by-products allows improvements in combustion processes and technologies, as well as reducing environmental impacts.

Experimental data obtained in the combustion of the biochar pellets were analyzed using a mathematical model for combustion of solid carbon particles in a bubbling fluidized bed reactor [2, 3].

This model was based on the two phase theory of fluidization [4] and it was assumed that the solid particles are spherical and burn at a constant density and reducing size. It was also considered that the particle carbon burns to CO according to $C + \frac{1}{2} O_2 \rightarrow CO$ and that the CO formed burns away from the particle according to $CO + \frac{1}{2} O_2 \rightarrow CO_2$ [5].
For this model, the oxygen consumption rate at the surface of the particle is then half the carbon consumption rate and the heterogeneous phase reaction that takes place at the particle surface is assumed a first order reaction,

$$\dot{N}_{O_2} = \frac{1}{2} R_0 = \pi d \mathrm{Sh} D_G (c_p - c_s) = \frac{1}{2} k_c \pi d^2 c_s \quad (1)$$

where $\dot{N}_{O_2}$ is the molar oxygen flow rate reaching the particle surface, R_0 is the carbon consumption rate, *Sh* is the particle Sherwood number, *d* is the diameter of the burning particle, D_G is the oxygen diffusivity in the air, c_p e c_s are respectively the molar concentrations of oxygen in the bed dense phase and at the surface of the particle, and k_c is the reaction rate constant for the heterogeneous reaction. Manipulating the above equation, it is possible to write that:

$$R_0 = 2\pi K d^2 c_p \quad (2)$$

wherein,

$$\frac{1}{K} = \frac{2}{k_c} + \frac{d}{Sh\, D_G} \quad (3)$$

Looking at the above equation it is apparent that the relationship between the global resistance to the combustion reaction of a single particle $1/K$ and its diameter is linear, where the slope of the straight line depends on the Sherwood number *Sh*, and the oxygen diffusivity D_G, while the intercept depends on the reaction rate constant k_c. Based on the adopted mathematical model and according to equation (3), diffusive and kinetic data for the fluidization bed combustion of a carbon particle were obtained through the plotting of $1/K$ versus *d*, the particle diameter. To obtain the necessary information for the experimental determination of the overall resistance to the combustion reaction of a single particle, it is necessary to analyze the combustion of batches of particles through the evolution of the composition of the exhaust gases, in particular the CO_2 concentration.

2. Materials and experiments

2.1. Experimental procedure

As explained in previous works [6, 7, 8], hybrid pellets from blends of *Cytisus* with cork residues, *Cistus* with *Eucalyptus* and *Cytisus* with *Cistus*, with 6 mm diameter were made in a pelleting press. For 30 minutes, batches of 300 g of these pellets were then carbonized in a fixed bed at 800 °C in a nitrogen atmosphere. The resulting char pellets were cut into smaller and uniform particles with lengths between 4-5, 7-8, and 11-12 mm. Their equivalent diameters, sphericities and Sauter mean diameters, were determined through digital photographs and using the ImageJ software, Fig. 1. More information on the production of carbonized pellet char particles is presented elsewhere [9, 10].

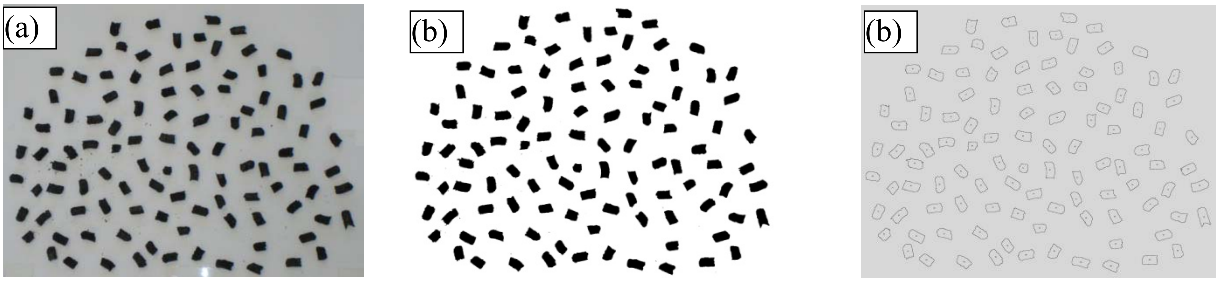

Fig. 1. Digital photograph of 7-8 mm char pellets (a) Image analysis with program ImageJ (b) and (c).

The proximate analysis of the chars was performed at the Polytechnic Institute of Viseu (IPV), School of Technology lab facilities, and their densities were determined by mercury porosimetry technique at the Faculty of Engineering of the University of Oporto (FEUP). Table 1 presents the main properties of the tested char hybrid pellets.

Table 1. Properties of char hybrid pellets

Species 50% (m/m)	*Cytisus and cork residues*	*Cistus and Eucalyptus*	*Cytisus and Cistus*
Apparent density (kg/m^3)	858.3	796.1	813.9
Volatile matter (%)	8.6	5.1	8.2
Fixed carbon (%)	77.0	85.6	77.4
Ashes (%)	14.4	9.3	13.1

The burning tests were carried out at the IPV facilities [6, 7], Fig. 2. Batches of 6 g of char pellets were burned at three different fluidized bed temperatures, 700, 800 and 900 °C, using three average equivalent particle diameters, 4.5, 7.5 and 11.5 mm. The mass flow rate of the air supplied to the combustor was equivalent to $2U_{mf}$ and the CO_2 concentration was continuously measured by an ADC® 7000 infrared gas analyzer.

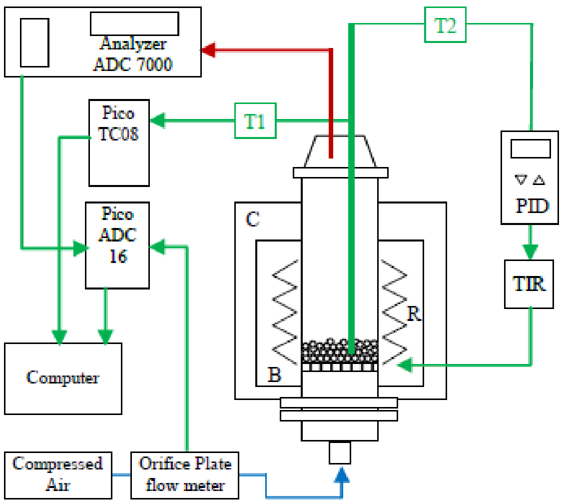

Fig. 2. Experimental set-up: T1 and T2 – Thermocouples; PID – Proportional, integral and derivative controller; TIR – Thyristor; C - Kaowool ceramic blanket; B – refractory bricks; R – electrical resistor.

The average uncertainty values for the experimental measurements were determined in a previous work [11] and are shown in Table 2. These values refer to the total uncertainty obtained by quantifying the fixed and random errors, associated with the measurements, data acquisition, and conversion processes.

Table 2. Average uncertainty values for CO_2, fluidizing air mass flow rate, and temperature measurements

Measured variable	*uncertainty*
CO_2 molar concentration (% CO_2 *v/v*)	0.13
Air mass flow rate (%)	1.65
Bed temperature (%)	0.48

3. Results and discussion

Using the experimental data collected in the fluidized bed combustion of char pellets and the mathematical model mentioned above, the overall combustion resistance was determined at every instant. Figure 3 shows the evolution of the overall combustion resistance for char hybrid pellets made of *Cytisus* and cork residues, with an initial mean equivalent diameter value of 5.66 mm, at 700, 800 and 900 °C.

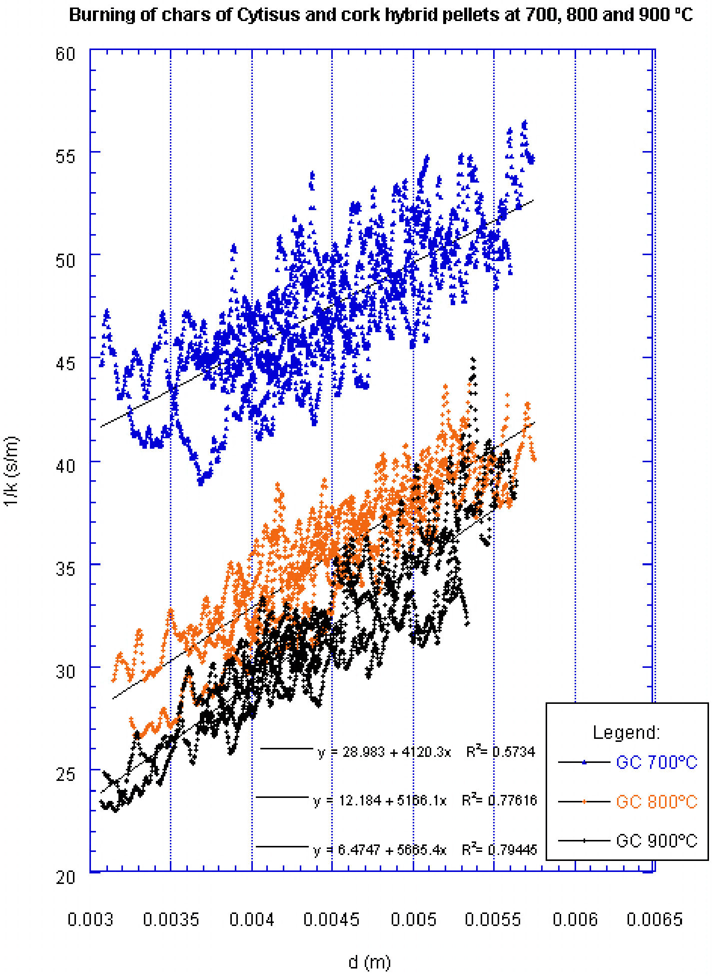

Fig. 3. Overall combustion resistance of char hybrid pellets of Cytisus and cork, as a function of particle diameter at 700, 800 and 900 °C.

In Figure 3, a decrease in the overall resistance of the reaction with the increase of temperature was verified. There appears, however, to be an overlapping of the burning results at 800 with those at 900 ° C.

Table 3 summarizes the kinetic and diffusive data obtained during the combustion of char hybrid pellets of *Cytisus* and cork, at the three bed temperatures under study.

Table 3. Diffusive and kinetic data of char hybrid pellets of Cytisus and cork

	$\bar{d}_{eq}$ (mm)	*Sh (-)*	k_c *(m/s)*
700 °C	5.65	1.958	0.069
800 °C	5.70	1.349	0.164
900 °C	5.62	1.076	0.309

Figure 4, below, shows the evolution of the overall combustion resistance for char hybrid pellets made of *Cistus* and *Eucalyptus*, with an initial mean equivalent diameter value of 5.81 mm, at 700, 800 and 900 °C. This figure also shows a decrease in the overall combustion resistance with increasing temperature. However, a closeness of the burning results at 700 with those at 800 °C seems to be taking place.

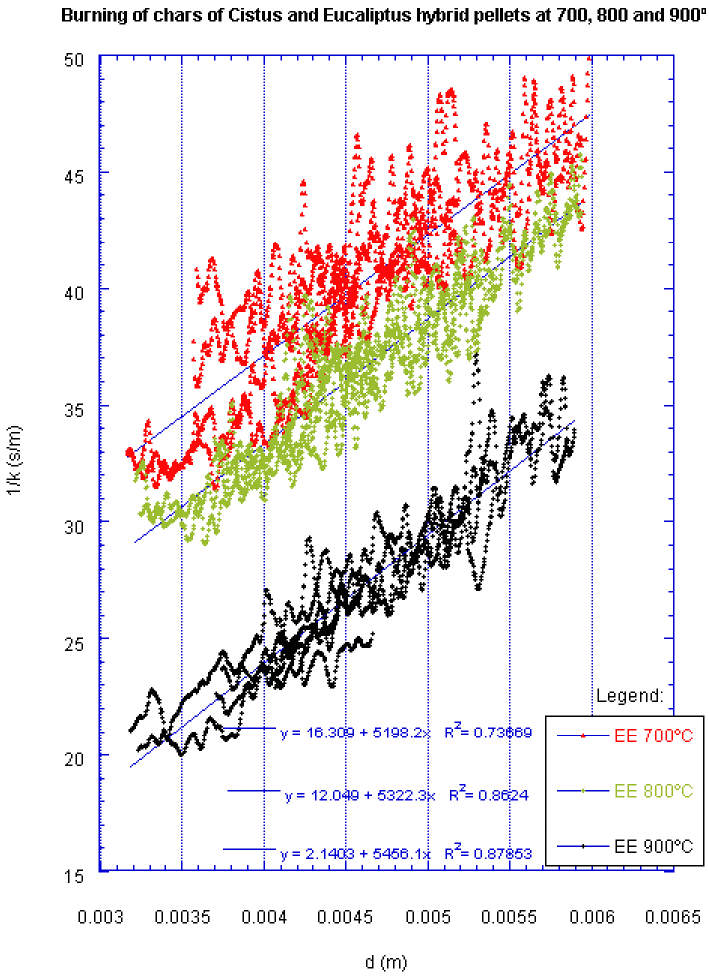

Fig. 4. Overall combustion resistance of char hybrid pellets of Cistus and Eucalyptus, as function of particle diameter at 700, 800 and 900 °C.

Table 4 summarizes the kinetic and diffusive data obtained from the burning of *Cistus* and *Eucalyptus* char hybrid pellets at the three tested bed temperatures.

Tables 3 and 4 show an increase in the heterogeneous reaction rate constant with temperature, for both types of char hybrid pellets.

Table 4. Diffusive and kinetic data of char hybrid pellets of Cistus and Eucalyptus

	$\bar{d}_{eq}$ (mm)	*Sh (-)*	k_c *(m/s)*
700 °C	5.76	1.552	0.123
800 °C	5.84	1.309	0.166
900 °C	5.83	1.117	0.934

Figure 5 shows the evolution of the overall combustion resistance for char hybrid pellets made of *Cytisus* and *Cistus* with an initial mean equivalent diameter value of 5.54 mm, at 700, 800 and 900 °C.

Although a reduction of the global reaction resistance with the increase of combustion temperature was expected, an overlapping of the burning results at 700 with those at 800 °C is possible to observe in Fig. 5. As far as the results at 900 °C are concerned, the trend line shows that the reaction is purely controlled by the diffusion process.

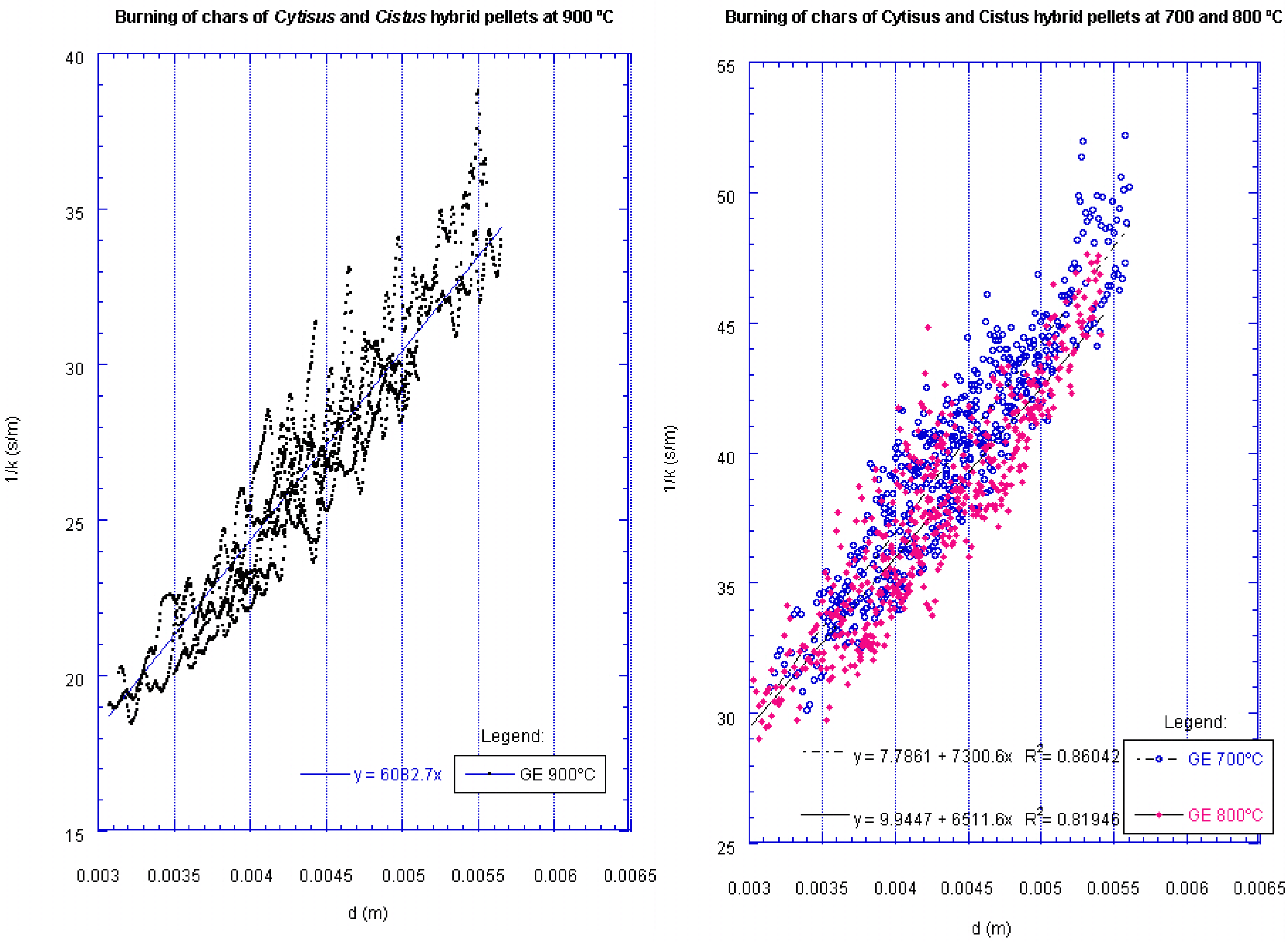

Fig. 5. Overall combustion resistance of char hybrid pellets of Cytisus and Cistus, as function of particle diameter at: 900 °C on left; 700 and 800 °C, on right.

Table 5 resumes the kinetic and diffusive data obtained from the burning of char hybrid pellets of *Cytisus* and *Cistus* at 700, 800 and 900 °C.

Table 5. Diffusive and kinetic data of char hybrid pellets of Cytisus and Cistus

	$\bar{d}_{eq}$ (mm)	*Sh (-)*	k_c *(m/s)*
700 °C	5.65	1.105	0.257
800 °C	5.70	1.070	0.201
900 °C	5.62	1.002	∞

Contrary to what was observed in Tables 3 and 4, Table 5 shows that the heterogeneous reaction rate constant k_c decreases with the increase in bed temperature. Although waiting for further studies concerning the behaviour of the ashes of this last type of biochar, this situation seems to be similar to that found by Pereira and Pinho [12] when studying the combustion of chars made from *Quercus ilex*. Some alkaline earth metals might be acting as combustion catalysts and after their release a reduction of the combustion reaction rate is detected, this phenomenon probably overriding the normal trend of reaction rate increase with the increase of the combustion temperature. In fact, the major inherent ash forming elements in biomass include Si, Al, Ti, Fe, Ca, Mg, Na, K, S and P, and the material that is inherently volatile at combustion temperatures includes derivatives of some of the alkali and alkaline earth metals [13]. However, studies about the influence of ash components on solid fuel consumption are mainly concerned with the technological and environmental problems [13,14] and not necessarily with its impact upon the reaction kinetics, which is the present case. Consequently, further studies are still going on to clarify such situation for this *Cytisus* and *Cistus* hybrid char.

4. Conclusions

The combustion of three types of char hybrid pellets made of *Cytisus* with cork residues, *Cistus* with *Eucalyptus* and *Cytisus* with *Cistus*, was studied in a bubling fluidized bed. Diffusive and kinetic data were obtained at three different temperatures, 700, 800 and 900 °C for three different equivalent diameters.

Though further studies still waiting to be accomplished, based on previous work carried out in the same laboratory [12], some alkali and alkaline earth ash components may be responsible for overlapping reaction results. The overall resistance of the reaction seems to remain constant or slightly increase for *Cytisus* with cork residues and *Cistus* with *Eucalyptus* chars at certain temperatures, while for chars made from *Cytisus* with *Cistus* there are no differences at 700 and 800 ºC. For the *Cytisus* with *Cistus* chars there is even a decrease in the heterogeneous reaction rate constant k_c with the increase in bed temperature, and for combustion at 900 °C the reaction control is purely physical.

References

[1] Rosillo-Calle, F., Groot, P., Hemstock, S., Woods, J., The Biomass Assessment Handbook. Bioenergy for a Sustainable Environment", Earthscan publishes in association with the International Institute for Environment and Development; 2007.

[2] Rangel, N., Pinho, C., Fragmentation Effect on Batches of Pine Wood Char Burning in a Fluidized Bed. Energy Fuels 2010;24: 318-323.

[3] Pereira, C.C., Pinho, C., Influence of particle fragmentation and non-sphericity on the determination of diffusive and kinetic fluidized bed biochar combustion data. Fuel 2014; 131:77-88.

[4] Davidson, J.F., Harrison, D., Fluidized particles. Cambridge, UK: Cambridge University Press; 1963.

[5] Ross, I.B., Davidson, J.F., The combustion of carbon particles in a fluidized bed". Trans. IChemE 1982; 60:108-114.

[6] Marques, E., Paiva, J.M., Pinho, C., The New Portuguese Energy Challenge? Pellets from Shrubs. COBEM 2011: In Proceedings of the 21st International Congress of Mechanical Engineering; 2011; Natal, RN, Brazil.

[7] Almeida, D., Ferreira, T., Marques, E., Paiva, J. M., Solar Drying Acacia – Influence in Pellets Quality: Experimental Results. COBEM 2013: In Proceedings of the 22nd International Congress of Mechanical Engineering; 2013; Ribeirão Preto, SP, Brazil.

[8] Almeida, D., Ferreira, T., Marques, E., Pereira, C., Paiva, J.M., Pinho, C., Cistus Ladanifer Solar Drying, Milling and Pelletizing. ENCIT 2014: In Proceedings of 15th Brazilian Congress of Thermal Sciences and Engineering; 2014; Belém, PA, Brazil.

[9] Pereira, C., Marques E., Paiva, J.M., Pinho, C., Cistus Ladanifer shrub – Some combustion data from pelletized samples: A small contribution to energy sustainability. COBEM 2013: In Proceedings of the 22nd International Congress of Mechanical Engineering; 2013; Ribeirão Preto, SP, Brazil.

[10] Pinho, C., Ferreira T., Marques E., Almeida D., Pereira C., Paiva J.M., Obtaining diffusive and kinetic data from batch combustion of invasive species char pellets. ENCIT 2014: In Proceedings of 15th Brazilian Congress of Thermal Sciences and Engineering; 2014; Belém, PA, Brazil.

[11] Pereira, C. C., Pinho, C., Determination of Fluidized Bed Combustion Kinetic and Diffusive Data of Four Wood Chars from the Central Region of Portugal. Energy & Fuels 2013, 27, 7521−7530.

[12] Pereira, C. C., Pinho, C., Analysis of the fluidized bed combustion behavior of Quercus ilex char. Applied Thermal Engineering, 2015; 81: 346-352.

[13] Khan, A. A., de Jong, W., Jansens, P. J., Spliethoff, H., Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology, 2009; 90: 21-50.

[14] Vassilev, S. V., Vassileva, C. G., Song, Y-C., Li, W-Y, Feng, J., Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. Fuel, 2017; 208: 377-409.