CISTUS LADANIFER SHRUB- SOME COMBUSTION DATA FROM PELLETIZED SAMPLES: A SMALL CONTRIBUTION TO ENERGY SUSTAINABILITY

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Abstract. *Foreseen energy needs, fossil fuels prices and concerns with climate changes lead society to search for alternatives to conventional energy sources. The Portuguese dependence can be reduced with the use of its biomass potential. On 64% of its mainland, forestry and abandoned lands, there is a large presence of autochthonous species of shrubs and invasive trees. A significant sector of the economy depends on some of the forest products, mainly cork, wood and paper pulp. Thus, a sustainable strategy for the use of the bioenergy is required and using biomass shrubs does not compete with traditional areas.*
In the present work, pellets of Cistus ladanifer *were made and tested under the European standards for solid Biofuels. The obtained quality index does not allow foreseeing domestic use; industrial use, however, can be envisaged to produce heat and power.*
Batches of pellets were burnt in a bubbling fluidized bed between 600 and 800°C at 2-3 U_{mf} with mixtures of air and nitrogen, to assess overall rates of reaction in various experimental conditions. Other batches were subjected to an incomplete pyrolysis process, designated by incipient roasting or torrefaction. The resulting wood 'chars' were burnt in the same above referred conditions. The combustion behavior presented difficulties comparing diffusive and kinetic data due to volatile release. Plots of the Arrhenius law were used to evaluate the chemical reaction rate constants.

Keywords: *bioenergy, pelletizing, fluidized bed, shrub*

1. INTRODUCTION

Concerns about nonrenewable fossil fuels as the primary source of energy has been continuously increasing. This has led researchers, industry officials and government agencies to begin to aggressively investigate the use of alternative and renewable energy resources such as biomass. Energy production through biomass is one of the promising renewable energy options being vigorously pursued in Europe because of its positive environmental implications (EU, 2011). In order to use biomass as an alternative energy source, more research must be done to characterize its physical and chemical properties. Without the knowledge of these properties, optimal design and selection of equipment and facilities to handle, store, and use biomass cannot be achieved. Europe has been taking some serious steps that consolidate bio-energy as a key choice that will allow the greenhouse gas emissions reduction and fossil fuels replacement (EEA, 2009). The use of biomass for energy production may depend on agriculture, forestry and food processing industries. There is a wide variety of local species which energy potential has still to be assessed. Intensive use of land over successive generations gave rise to what some authors call *maquis* and *garrigue* (Ribeiro *et al.*, 1988). Many areas are dominated by heather (*Erica arborea*), broom (*Spartium junceum*) and mostly arbutus (*Arbutus unedo*) and cistus (*Cistus sp.*).

Fluidized bed combustion is a very suitable technology for the energetic use of biomass because of its advantages in terms reduction of pollutants emissions (OAR, 2010) and fuel flexibility (Obernberger, 1998). On the other end it is equally a useful laboratory tool for the determination of kinetic and diffusive data to be lately applied in the design and construction of combustion systems. However, because of the large heterogeneous nature of biomass, the presently available information on biomass combustion is still insufficient. Palchonok *et al.* (1997) refer the need to study the controlling mechanisms of the different phases occurring in the fluidized bed combustion of biomass. Scala and Salatino (2002) said that less attention was given to the study of biomass basic combustion mechanisms than to the study of reliability and performance of fluidized bed combustion in general. Even in the biofuels universe, there is more information about liquid fuels than about solid fuels (Grammelis, 2010). The process of biomass combustion can be divided into different stages: drying, pyrolysis, gasification and combustion. The relative importance of each phase

depends on the combustion technology used, the properties of biomass and combustion conditions (Loo and Koppejan, 2008). The combustion stage can also be divided into combustion of volatiles and coal combustion (char) phases, this last one being the reduced state attained by the biomass after the first three above referred phases. The present work focuses on studying the mechanisms of combustion of pellets made from *Cistus*. More specifically, it aims at determining the kinetic and diffusion burning charcoal (wood char) obtained from samples of that species and, additionally, continues previous work done by Rangel and Pinho (2009, 2011) and Pereira (2012), who studied the behavior of fluidized bed combustion of several wood chars in the temperature range of 600 to 900°C.

2. EXPERIMENTAL

2.1 Pellets preparation

Predetermined size samples were harvested, followed by drying in a solar kiln. The milling process occurred in an Agico wood crusher with constant feed rate. Pelletization took place in a low-cost flat die ZLSP-260 pelletizing machine. After pellets were manufactured, a cooling period was provided before they were characterized by means of a set of standard procedures (Temmerman, *et al.*, 2006; Obernberger and Thek, 2004). This process resulted in high consistency pellets, with 6 mm in diameter and lengths ranging between 10 and 40 mm (Fig. 1); the pellets were then carbonized in nitrogen at 750°C for 60 min through batches of 400 g, Fig. 1.

Figure 1 – *Cistus* shrub (left); *Cistus* pellets, before and after carbonization (center and right).

The carbonized pellets were cut into particles with average lengths of 7 to 8 mm and divided into loads of 6 grams. The pellets exact dimensions were determined from digital photographs of the processed batches. The images were shot with a 8.1 megapixels camera and the image processing was performed with ImageJ software (Rasband, 1997). Table 1 presents the proximate analysis of the carbonized pellets as well as density, before and after pelletization.

Table 1. Proximate analysis and particle density of the chars tested.

Cistus ladanifer	Properties
Density before pelletization (kg/m^3)	345.0
Density after pelletization (kg/m^3)	735.0
Apparent density (kg/m^3) [1]	894.8
	Proximate analysis (% wt.)
Moisture [2]	1.6
Ashes [3]	8.2
Volatile matter [4]	14.6
Fixed carbon	77.2

[1] obtained with a mercury intrusion porosimeter, model Poremaster, from Quantachrome; [2] measured at 105°C; [3] EN 14775: 2009; [4] EN 15148:2008

2.2 Experimental setup

The experimental setup consisted of a cylindrical fluidized bed with 80 mm internal diameter 1000 mm long (Fig. 2). The distributor had 101 0.3 mm ID orifices. A convergent nozzle at the gas exit ensured a good mixing of the stack gas and minimized counter flow mixing with atmospheric external air. An external 3.12 kW electrical resistance was heating the bed just above the distributor until the bubbling region, with a surface covering of 250 mm long. Insulation was made with Kaowool ceramic blanket. The bed was formed by silica sand particles in the 300 to 355 μm range with

2600 kg/m^3 density (Pereira, 2012). The mass flow rate of the fluidizing air was measured by an orifice plate flow meter using an Omega Engineering differential pressure transducer model PX143.

A 4 mm internal diameter stainless steel probe sampled the combustion gases leaving the fluidized bed reactor through the converge nozzle. From previous similar experiments it was found that for the used bed operating conditions (Marques and Pinho, 2008; Rangel and Pinho, 2009; Rangel and Pinho, 2011; Ramos *et al.*, 2011; Pereira, 2012; Tomé *et al.*, 2013) it was only necessary to follow the CO_2 concentration in the exhaust gases to get a correct assessment of the evolution of the combustion reaction. This CO_2 concentration was continuously measured with an infra-red ADC 7000 analyzer connected to a Pico ADC-16 data acquisition system, whereas a Pico TC08 system was used for temperature data acquisition.
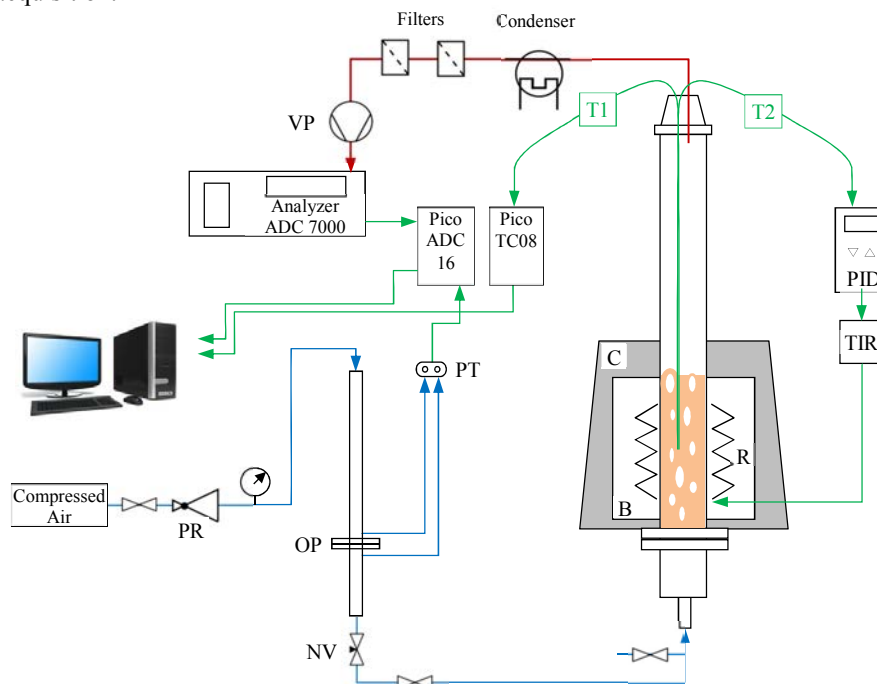

Figure 2 – Experimental set-up. VP - Vacuum pump; T1 and T2 - Thermocouples; PID – Proportional, integral and derivative controller; TIR – Thyristor; C - Kaowool ceramic blanket; B - refractory bricks; R - electrical resistance; PT - Pressure transducer; PR - Pressure reducer; OP - Orifice plate; NV - Needle valve

2.3   Experimental procedure

Batches of 6 g of carbonized pellets of each size were burned at three different bed temperatures, 700, 750 and 800°C. The tests were repeated twice. The fluidization velocity was $2U_{mf}$ in all the experiments and was experimentally determined for each bed testing temperature: 77.3, 76.2 and 75.1 mm/s, respectively. For each burning test the bed temperature, the pressure differential in the fluidizing air orifice plate flow meter and the molar CO_2 concentration in the exhaust combustion gases were continuously measured and recorded. The bed temperature during the combustion experiments had a +/- 5 °C oscillation, depending on the heat release rate during the reaction and on the response of the PID bed temperature controller. The average uncertainty values for the experimental measurements are shown in Tab. 2. The uncertainty analysis was carried out according to the methodology presented in Coleman and Steele (1999).

Table 2. Average uncertainty values.

Variable	Uncertainty (%)
CO_2 molar concentration	0.13
Air mass flow rate	1.65
Bed temperature	0.48

3. THE ADOPTED MATHEMATICAL MODEL

3.1   Introduction

There are several mathematical models for the description of the combustion of solid carbon particles in bubbling fluidized bed reactor. The majority of them rely on the basic model proposed by Avedesian and Davidson (1973) which

was itself based on the two phase theory of fluidization (Davidson and Harrison, 1963) and on the assumption that the solid particles are spherical and burn at constant density and reducing size.

Ross and Davidson (1982) derived three evolutions from the original Avedesian and Davidson (1973) model and in the present work the adopted model is the one that considers that the particle carbon burns to CO according to $C+\frac{1}{2}O_2 \rightarrow CO$. Then the CO moves away from the particle and burns to CO_2 in the dense phase of the bed, according to $CO+\frac{1}{2}O_2 \rightarrow CO_2$. The application of this model for all carbon particles burning inside a bubbling fluidized bed reactor was defended by several studies, Guedes de Carvalho *et al.* (1991), Hayhurst (1991), Hayhurst and Parmar (1998), Campos *et al.* (1999), Loeffler and Hofbauer (2002), Fennell *et al.* (2007) and Rangel and Pinho (2011), for example.

So, for this model, the carbon consumption rate R_o can be connected to the oxygen concentration in the dense phase c_p through

$$R_o = 2\pi d^2 K c_p \tag{1}$$

where K is the overall reaction constant defined as (Ross and Davidson, 1982; Ramos *et al.,* 2011; Rangel and Pinho, 2011),

$$\frac{1}{K} = \frac{d}{Sh\, D_G} + \frac{2}{k_c} \tag{2}$$

This equation says that the overall resistance to reaction of a carbon particle is linearly dependent on the particle Sherwood number *Sh* and gas diffusivity D_G and that the intercept depends on the heterogeneous reaction rate constant k_c. Thus diffusive and kinetic data for the fluidized bed combustion of a carbon particle can be easily obtained through the plotting of $1/K$ *versus d*, the particle diameter.

3.2 Experimental calculation of the overall reaction resistance

The combustion of the char particles is supposed to have taken place only in the dense phase of the bed, as suggested by many authors (Ross and Davidson, 1982; Pinho and Guedes de Carvalho, 1984; Guedes de Carvalho *et al.*, 1991; Mota *et al.*, 1994; Mota and Campos, 1995). According to the same authors, it is also assumed that the oxygen concentration in this phase is uniform due the high degree of bed agitation, while the oxygen concentration in the bubble size is obtained in accordance with the two phase theory of fluidization.

For a batch of carbon particles with a mass of m_c, with initial diameter d_i and density ρ_c, burning in a fluidized bed reactor at the temperature T_L, it is possible to connect the overall reaction constant K with a dimensionless reaction velocity k' that is a function of some fluidization characterizing parameters (Davidson and Harrison, 1963),

$$k' = \frac{k H_{mf}}{U} = \frac{12 d^2 K m_c}{\rho_c d_i^3 A_t U} \tag{3}$$

In the above equation H_{mf} is the bed height at incipient fluidization, U is the gas superficial velocity, A_t is the bed cross section area and d is the instantaneous char particles size for the instant under analysis.

It is considered that during the combustion process, bed temperature T_p stays approximately constant and that the char particles burn at constant density under a first order reaction (Ross and Davidson, 1982). Although these assumptions were established in a first instance for coke particles, some previous char studies have shown that these assumptions are still valid for wood chars (Adánez *et al.*, 2001; Rangel and Pinho, 2011; Ramos *et al.*, 2011; Tomé *et al.*, 2013).

The overall reaction resistance can thus be obtained by solving equation (3) to obtain,

$$\frac{1}{K} = \frac{12 d^2 m_c}{\rho_c d_i^3 A_t U k'} \tag{4}$$

The dimensionless reaction velocity k' is determined through the following equation (Davidson and Harrison, 1963)

$$\frac{c_H}{c_o} = \beta e^{-X} + \frac{[1 - \beta e^{-X}]^2}{k' + 1 - \beta e^{-X}} \tag{5}$$

where c_H is the molar concentration of oxygen at bed exit, c_o is the molar concentration of oxygen at the bed entrance, $\beta = 1 - U_{mf}/U$, and X is the bubble sweeping factor which is described in Hovmand *et al.* (1971), Rangel and Pinho (2011) and in Pereira (2012).

In equation (4) d is the char particles diameter at combustion time t_f. To find this value, it is necessary to know the burned carbon mass up to this instant, and such carbon consumed mass m_{cf} is determined through the integration of the CO_2 concentration curve from the combustion beginning until t_f,

$$m_{cf} = 12\, \dot{V}_{ar}\, \tilde{n} \int_0^{t_f} v_{CO_2}\, dt \qquad (6)$$

In the previous equation, v_{CO_2} is the CO_2 molar fraction in the combustion gases, $\dot{V}_{ar}$ is the volume air flow at the reference pressure and temperature (101,325 kPa and 20 °C) and $\tilde{n}$ is the number of CO_2 moles per unit volume.

If the particles composing a batch have the same initial diameter and all burn at the same speed, then the number of particles composing the batch stays constant during the combustion process, and is equal to N_c. Thus their diameter at time t_f is

$$d = \sqrt[3]{d_i^3 - \frac{6 m_{cf}}{\pi \rho_c N_c}} = d_i (1-f)^{1/3} \qquad (7)$$

where $f = m_{cf}/m_c$ is the burned mass fraction for the time t_f.

For more details about this calculation can be found in Pereira (2012) and Rangel and Pinho (2011).

4. RESULTS AND DISCUSSION

4.1 Particles equivalent diameter and shape

The initial shape of the carbon particles significantly affects the combustion characteristics since, for the same weight, different shapes represent different surface areas. Moreover, the transfer of heat and mass strongly depend on the surface area of the particles. Work from Grammelis (2010) and Lu *et al.* (2010) show that the spherical shape is associated with lower reaction rates.

The used mathematic model considers that the particles are spherical, but pellets have an approximately cylindrical shape. It was necessary to model the shape as spherical, determining the diameter of the sphere that best characterizes the surface area and the volume of a batch of particles. This procedure is commonly adopted by several researchers (Kita *et al.*, 1994; Diego *et al.,* 2002; Sudhakar and Kolar, 2011) and uses an equivalent diameter and an shape factor. Diego *et al.* (2002) stated that the combustion models developed for spherical particles can be applied to different shapes substituting, in the model, the particle size by the equivalent diameter multiplied by the form factor.

In this work, the equivalent diameter (d_{eq}) is the diameter of the sphere with the same volume of the particle and the shape factor used is the sphericity (ϕ), defined by Wadell (1933) as:

$$\phi = \frac{surface\ area\ of\ a\ sphere\ having\ the\ same\ volume\ as\ the\ particle}{surface\ area\ of\ the\ particle} \qquad (8)$$

For each batch load, the corrected particle diameters values, obtained from $d_{corr} = \phi\, d_{eq}$, ranged between 5.2 and 5.5 mm. The volumes and surface areas of each particle load tested were compared to those determined from the corrected diameter. The differences were less than 10% and are related to the fact that the particle shape is not perfectly cylindrical.

4.2 Evolution of the overall combustion resistance

Using the experimental data and through Eq. (4), the overall combustion resistance for each instant was calculated. The evolution of *1/K* with the char particle diameter presents a typical U shaped curved for all tested bed temperatures and initial particle size. Fig. 3 illustrates the evolution for *Cistus ladanifer* char pellets at 700ºC. The plot shows only two sets of data points, one for each length. Other bed temperatures have curves with similar shapes. U type curves are quite common for fluidized bed batch combustion experiments of cokes and chars, as has been referred by many authors (Ross and Davidson, 1982; La Nauze *et al.*, 1984; Pinho, 2006; Marques and Pinho, 2008; Rangel and Pinho, 2011; Pereira, 2012).

The sudden reduction on the overall resistance to combustion at the initial part of the combustion process is generally connected with fragmentation processes that greatly enhance the overall reaction surface and with the

transient heating process of the burning particles. As the combustion launches, when the batch of particles is thrown into the bed, these suffer a sudden thermal shock leading to fragmentation phenomena. The release of particle fragments, or even their full breakage, will increase the total area available for reaction. If such effect is not accounted for in the mathematical treatment of the combustion experimental data, where it is assumed that the number of particles is constant and equal to the initial number, it will appear as a sudden reduction of the overall combustion resistance. The initial particle heating process, where its temperature quickly rises up to burning conditions, will also appear as a sudden reduction of the overall combustion reaction, because for the experimental data treatment it is assumed that the particle heating is instantaneous On the other hand the sudden rise of $1/K$ at the end of the reaction is explained by the decrease on the number of burning particles as the combustion approaches its end. The shape of the particles, not being absolutely regular, and its eventual fragmentation leads to a non-uniform particle size distribution during combustion and, thus, smaller particles disappear earlier. When such events are not considered in the accounting of the number of particles composing the batch, the results reflect these sudden variations on the overall combustion resistance (Pinho, 2006).

In this work, the burning visualization, as well as the kind of noise it produced, suggest that the fragmentation process is of little relevance; further specific fragmentation tests, nonetheless, are needed to understand its influence.
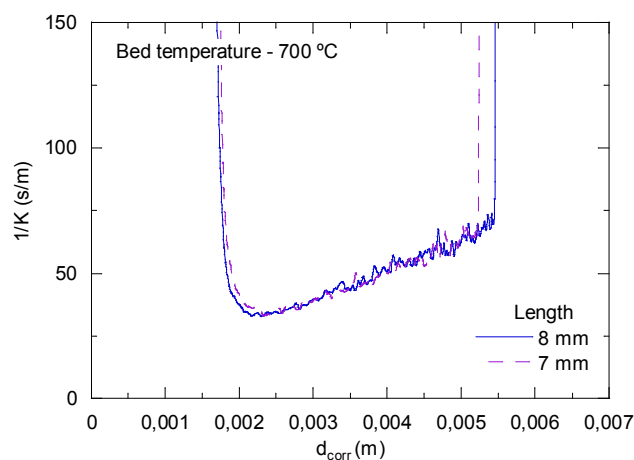

Figure 3 – Evolution of the overall combustion resistance for *Cistus ladanifer* char pellets at 700ºC.

By discarding the transient periods of the batch combustion history, that are patent in Fig. 3, it is quite clear that the $1/K$ *versus d* evolution follows a linear relation, as forecasted in the mathematical model, equation (2). As such and for all the executed experiments, the obtained experimental data points corresponding to burned mass fractions between 5 and 85% where selected. The influence of the transient initial and final phases of the combustion process was in this way minimized. Figure 4 demonstrate such procedure and the linear dependence of $1/K$ with d have a positive slope indicating the importance of the diffusion phenomena on the reaction control. In these figures only 5% of the experimental results are plotted.

The figures show that the overall reaction resistance decreases with the increase of bed temperature, because of the faster reaction kinetics.
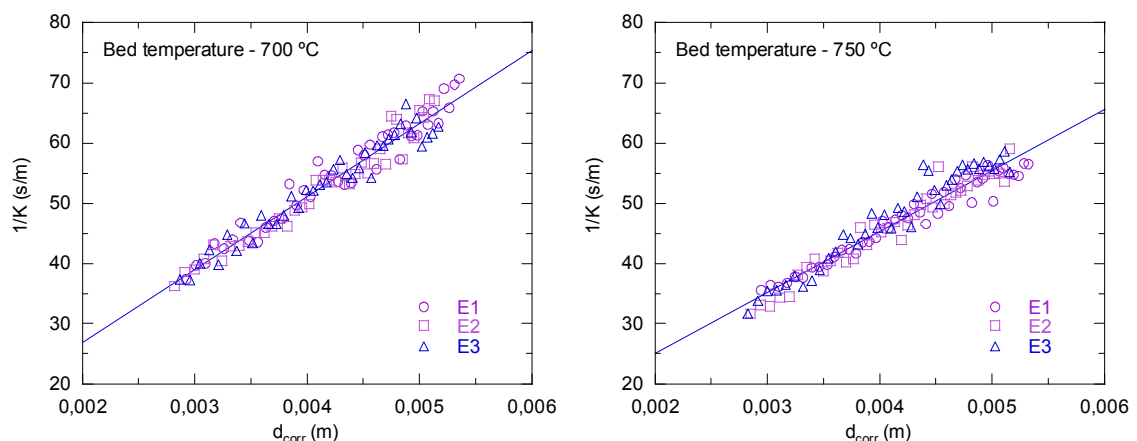

Figure 4 –Overall combustion resistance of *Cistus ladanifer* char pellets obtained at 700, 750 and 800º C (../..).
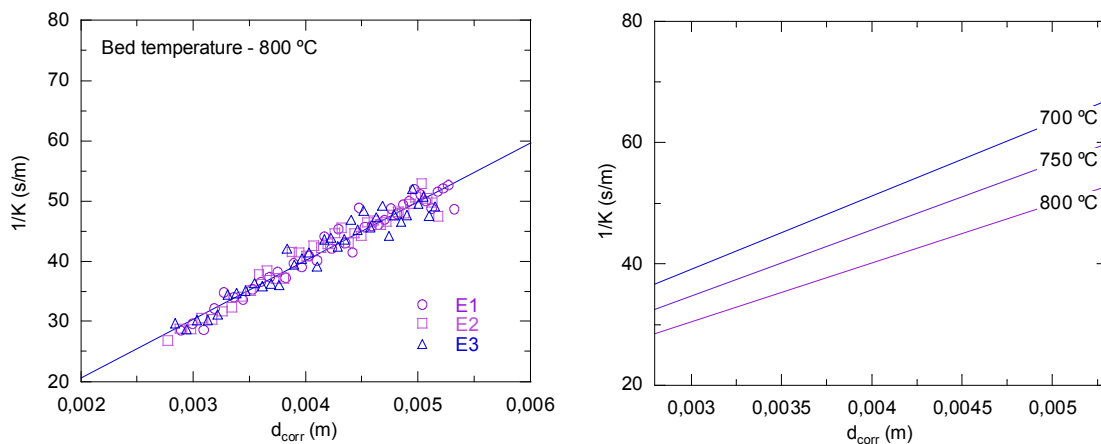
Figure 4 – (cont.) Overall combustion resistance of *Cistus ladanifer* char pellets obtained at 700, 750 and 800ºC and also the overall $1/K$ trendline.

4.3 Diffusive and kinetic data

Table 3 presents the results obtained from the analysis of Fig. 4 plots, based on equation (2) of the followed mathematical model. In general terms it can be said that both the Sherwood number Sh and the heterogeneous phase reaction rate constant k_c increase with bed temperature. It should be emphasized the greater variation of the heterogeneous reaction rate constant which is related to the strong influence of temperature on the reaction kinetics. In this table and in the later mathematical treatment about particle temperature, T_L is the bed temperature.

Table 3 – Obtained Sh and k_c values from $1/K$ *versus* d evolution.

	Cistus ladanifer	
T_L (°C)	Sh (-)	k_c (m/s)
700	0.67	0.75
750	0.74	1.10
800	0.83	1.64

4.4 Activation energy and pre-exponential factor

The above experimental results for the heterogeneous phase reaction rate constant and its dependence with the combustion temperature allow the determination of the activation energy and the pre-exponential factor. To obtain these last two parameters an Arrhenius plotting of k_c as a function of temperature of the particles (Field *et al.*, 1967) must be carried out to achieve the desired result. However before of doing such plot, it is necessary to determine the burning particles temperature.

4.4.1 Temperature of burning particles

The particle temperature measurement or determination for other means is a complex problem for which there is no consensus in the scientific community. The most common experimental technique being used has been the application of a thermocouple inserted in the burning particle (Chakraborty and Howard, 1978; Hayhurst and Parmar, 1998; Dennis *et al.*, 2005; Komatina *et al.*, 2005; Scala and Chirone, 2010). This is however an intrusive technique and by restricting the particles free movement inside the bed it will affect their combustion and heat transfer conditions. Hayhurst and Parmar (1998) have observed that the presence of an inserted thermocouple will influence the reactivity of coke particles and such reactivity is enhanced with the increase of the thermocouple diameter. Photographic techniques have been used (Roscoe *et al.*, 1980; Ross *et al.*, 1981) as well as optical pyrometry (Linjewile *et al.*, 1994; Joutsenoja *et al.*, 1999), but none of these is inconvenient free. These last techniques only manage to register the temperature of the particles appearing on the bed surface where combustion conditions differ from those found deep inside the bed.

It is commonly agreed that the burning particles temperature is superior to the fluidized bed temperature, but the true value of this difference and the best way to find it has no consensus, and it is still necessary more work and study to clarify this point (Oka, 2004). Here the burning particles temperature was calculated by means of a particle superficial energy balance. The methodology already used by Ramos *et al.* (2011), Tomé *et al.* (2012) and Pereira (2012) was adopted. Such particle energy balance considers that heat exchanges between a burning particle and the fluidized bed

are made through conduction and radiation, and that the particle carbon burns to CO at its surface while the CO burns to CO_2 away from the particle. These suppositions are in agreement with the mathematical combustion model previously adopted for the treatment of the experimental data. The energy balance becomes,

$$\dot{m}_C \Delta h' + \dot{Q}_{s-b} + \dot{Q}_{rad} = 0 \qquad (9)$$

In this equation $\dot{m}_C$ is the mass rate of carbon consumption, $\Delta h'$ is the heat of combustion provided to the particle while $\dot{Q}_{s-b}$ and $\dot{Q}_{rad}$ are, respectively, the rate of heat transferred by conduction and radiation from the particle to the surrounding bed. T_p is the temperature of the burning particle.

$$\dot{Q}_{s-b} = -k_{tg} \pi d^2 \frac{dT}{dr}\Big|_{d/2} \qquad (10)$$

$$\dot{Q}_{rad} = \varepsilon_p \pi d^2 \sigma \left(T_p^4 - T_L^4\right) \qquad (11)$$

The properties of the gas involving the burning particle are considered to be identical to the air properties, while ε_p is the particle emissivity. The convection effects were neglected because according to Palchonok (1998), in the fluidized bed combustion of a carbon particle the convective part only weights 0.5–1.7% of the overall heat transfer coefficient and can thus be ignored.

It was assumed that a fraction χ of the carbon burns to CO_2 close enough to the particle to influence its temperature, as suggested by Hayhurst and Parmar (1998), Adánez *et al.* (2001) or Dennis *et al.* (2005) and Pereira (2012) when calculating the temperature of the particles. Thus, if Δh_1 (-32797 kJ/kg) is the reaction enthalpy of burning carbon to CO_2 and Δh_2 (-9211 kJ/kg) the reaction enthalpy of burning carbon to CO, the heat of combustion near the particle in these circumstances will be

$$\Delta h' = \Delta h_2 + \chi(\Delta h_1 - \Delta h_2) \qquad (12)$$

The value of the fraction of carbon (χ) that burns to CO_2 near the particle was estimated based on the work of Hayhurst and Parmar (1998). Differences between the fluidization conditions at which data were obtained and the used in this study were taken into account in order to obtain a reliable approximation. The values obtained were 0.24, 0.36 and 0.50 for the bed temperatures 700, 750 and 800ºC respectively.

Figure 5 presents the temperature differential between particles and bed ΔT_{pL}, as a function of the burned mass fraction, for all the bed temperatures. The temperature differential ΔT_{pL} rises along the combustion process and it is also noticed that higher temperature differentials are obtained for smaller bed temperatures.
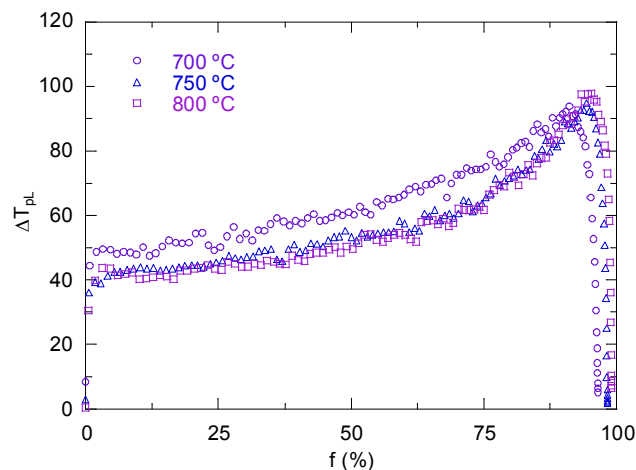

Figure 5 – Particle and bed temperature difference for combustion experiments.

4.4.2 Arrhenius plots

The Arrhenius equation gives the dependence of the reaction rate constant with temperature

$$k_c = A \cdot e^{-E_a/\bar{R}T} \qquad (13)$$

where A is the pre-exponential factor, E_a is the activation energy, $\bar{R}$ is the universal gas constant and T is the reaction temperature and at the present situation is the temperature of the burning particle. It is clear that the plot of $\ln k_c$ as a function of $1/T$ has a linear tendency whose slope determines the activation energy and the intercept the pre-exponential factor.

The above determined particle temperatures have been used to carry out the Arrhenius plot. The adopted procedure was to consider the evolution of the calculated particle temperature along the combustion process and to determine the corresponding average particle temperature, which was then used in the plot. The transient periods have been discarded, so the combustion period considered was in mass fractions range 5 - 85%. There was then correspondence among the average temperatures and the kinetic data for such range of combustion completion.
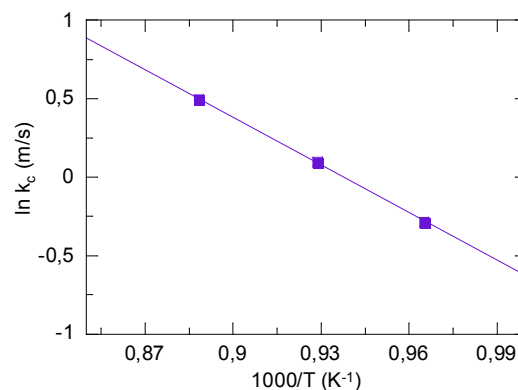

Figure 6 – Arrhenius plot for *Cistus ladanifer* char pellets in the 700 to 800°C temperature range.

Figure 6 presents the Arrhenius plot and in Table 4 are shown the activation energy and the pre-exponential factor that were obtained for *Cistus ladanifer* char pellets. The obtained results are comparable to those obtained by other authors studding wood chars. Janse *et al.* (1998) found in the literature activation energies for different chars going from 84.9 to 160 kJ/mol, depending on the type of wood and testing conditions. Rangel and Pinho (2011) found activation energies from 54 to 117 kJ/mol, for chars made from *Pinus pinea* and *Quercus suber*, although for a fluidized bed temperature range of 600 to 750°C different from the temperature range used in this work. Pereira (2012) studied four chars made from Portuguese woods, namely *Quercus ilex*, *Eucalyptus globulus*, *Pinus pinaster* and *Quercus suber*, and obtained activation energies from 38 to 121 kJ/mol, in the temperature range 750 to 900°C, using also the same fluidized bed technique.

Table 4 – Activation energy and pre-exponential factor for *Cistus ladanifer* char pellets (700−800°C).

	Cistus ladanifer
A (m/s)	13503
E_a (kJ/mol)	84.3

4.5   Combustion of the torrefied pellets

Wood torrefaction is a biomass pretreatment whose goal is to increase the energy density. During this process, the lighter volatiles and the moisture evaporate and the hydroxyl (-OH) groups responsible for the absorption of moisture are removed. The torrefied product is a fuel with higher heating value, improved processing properties and hydrophobic. If pelletized, the resulting material will have a higher density compared to standard pellets (Rosendahl, 2013).

This work aimed at studying the burning of pellets obtained from torrefied *Cistus ladanifer*. The product was subjected to the above referred process in an inert atmosphere at 250°C for 30 minutes. The torrefied biomass was then pelletized. Hemicellulosis and lignin decomposition made the pellet manufacturing difficult to achieve, as the brittle behavior was significantly increased (Rosendahl, 2013). Nonetheless, the obtained pellets were cut to an approximate lenght of 8 mm (Fig. 7).
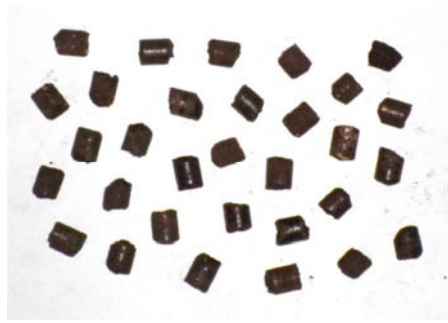
Figure 7 – Image of the torrefied pellets used.

Burning tests were conducted in the fluidized bed with 6 grams loads. The procedure was identical to that used for the former combustion process. During the burning there was an initial release of volatile compounds, followed by heavy smoke combustion. This period was clearly detected in the experimental data collected.

Figure 8 illustrates the typical shape of the curve of the recovered carbon mass, which was obtained from the CO_2 concentration in the stack gases. The period of release and combustion of volatiles is responsible for the peak that occurs in the early stages. Once this phase is over, there is a linear evolution identical to that observed when burning the pellets. This linear evolution actually reflects the char combustion taking place after the volatiles release.
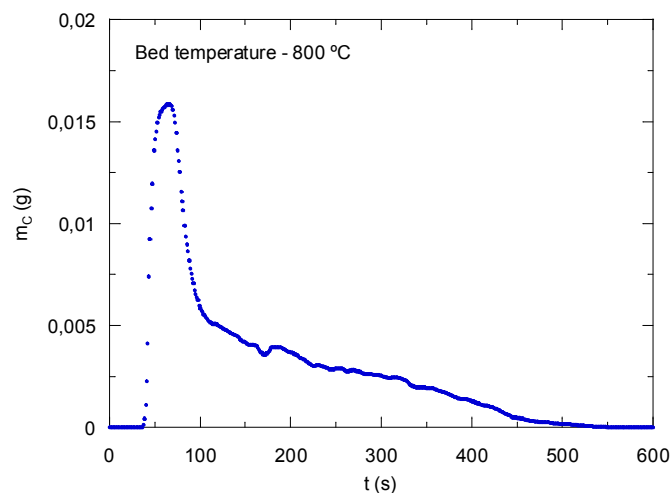

Figure 8 – Carbon mass evolution during torrefied pellets combustion at 800°C.

The curve configuration of Fig. 8 prevents naturally the application of the mathematical model adopted in this study because. It was a model designed for coal particles combustion. The product resulting from roasting still contains a considerable amount of volatiles and the results evidence that a proper treatment requires the modification of the model to incorporate the combustion of these compounds released from the particles. It will be the object of further studies.

5. CONCLUSIONS

Cistus ladanifer pellets were manufactured with the purpose of testing its combustion behavior. The quality of the pellets was acceptable, with interesting durability values. Those pellets were then carbonized in nitrogen and the resulting char was used to obtain kinetic and diffusive data using the bubbling fluidized bed combustion technique, in the 700 to 800°C bed temperature range. The calculation procedure was based on the two phase theory of fluidization and on a mathematical model of combustion originally developed for the combustion of coke particles, which was afterwards applied with success to the study of wood char particle combustion. The cylindrical shape of the pellets was modeled as spherical, using the equivalent diameter and the sphericity. The results showed that the Sherwood number of the particles slightly increases with bed temperature and highlighted the strong dependence of reaction kinetics with temperature.

The temperatures of the burning char particles were determined through an energy balance and the maximum temperature differential found between the bubbling fluidized bed and the char particles was approximately 100°C.

The activation energy and pre-exponential factor obtained from the Arrhenius plot of the kinetic data were of the same order of magnitude of those found by other authors for wood chars.

Experimental essays performed with torrefied pellets made from *Cistus ladanifer* highlighted the need for further development of the mathematical model and subsequent experimental work.The use of the fluidized bed combustion technique at laboratory scale for the determination of diffusive and kinetic is a fruitful and reliable methodology to achieve a collection of results of real and industrial interest.

6. ACKNOWLEDGEMENTS

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