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COMBUSTION OF INVASIVE ACACIA DEALBATA CHAR PELLETS – DETERMINATION OF DIFFUSIVE AND KINETIC DATA

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Abstract. *The use of biomass and other renewable energy sources becomes ever more essential due to the necessity to minimize the excessive consumption of fossil fuels and lower emissions of greenhouse gases into the atmosphere. A laboratory scale fixed bed reactor heated up by an electrical resistance was used in order to obtain the diffusive and kinetic parameters that control the combustion of char pellets, using a previously developed mathematical model for the batch combustion of solid biomass particles in packed beds. Thereby, these parameters were obtained both from fluidized and from fixed bed combustion of batches of char particles.* Acacia dealbata *pellets were carbonized in nitrogen, being subsequently cut into smaller and more uniform particles with three average lengths. In fluidized bed, batches of char pellets were burnt at three different temperatures, 700, 800 and 900 °C, using three different average equivalent diameters. Regarding to fixed bed combustion, the char pellets were burnt only at 800 °C using the same equivalent diameters. From the combustions of the* Acacia *char pellets specific diffusive and kinetic data, namely* Sh *and* k_c *values, were obtained.*

Keywords: *invasive species, pellets, combustion, diffusive and kinetic data*

1. INTRODUCTION

Biomass presents a complex physical and chemical composition which often causes substantial problems in combustion processes. The type of biomass and some of its usual properties have important impacts in pollutant emissions and combustion efficiency (Williams *et al*., 2012).

In the combustion of biomass, the slowest phase is the carbonaceous residue combustion, the solid substance that results from the initial pyrolyzing step. Therefore, the present work concentrates on studying and understanding this process, an essential stage for research and design purposes, profiting from previous team expertise on biochar combustion in bubbling fluidized and fixed bed reactors (Ferreira *et al*., 2014; Pereira and Pinho, 2014; Pinho *et al*., 2014; Pereira and Pinho, 2015).

The furnace is a component of upmost importance in a biomass combustion system, being currently the grate burning systems the main technology used in small scale combustion of solid biofuels (Thunman and Leckner, 2001). This system allows burning a wide range of fuels of different moisture content and properties (Yin *et al*., 2008). Grate burning has some flexibility concerning variations of fuel quality, but has slow response to load changes. The fixed bed combustion is one of the different available grate types and is usually adopted for small boiler capacities. Regarding to fluidized beds, this combustion system is more flexible than fixed beds, allowing for a more uniform temperature distribution as well as greater solid-gas contact area, thus ensuring low pollutant levels (Obernberger, 1998; Khan *et al*., 2009). This combustion system has been indicated as one of the most promising ones, mainly due to high efficiency and low environmental impact associated with its use (Scala *et al*., 2013).

The main purpose of this work is to study the combustion of *Acacia dealbata* char pellets in these two different combustion systems, the fluidized and the fixed bed. In both combustion systems, diffusive and kinetic data were determined through the experimentally collected data and using two different mathematical models.

2. MATERIALS AND EXPERIMENTS

2.1 Biochar preparation

The biochars used in the combustion testes were obtained from *Acacia dealbata* pellets manufactured specifically for this work at the lab facilities. *Acacia dealbata* was collected in a local forest and dried in a solar kiln. A hammer mill was used to ground the raw material and thereafter it was characterized by means of moisture content and particle size. Pellets of *Acacia dealbata* with 6 mm diameter were afterward produced in an AGP GK5500 pelletizer press machine. The *Acacia* pellets were then carbonized in nitrogen at 800 °C for 30 min through batches of 300 g. The carbonized pellets were subsequently cut into smaller and more uniform particles with average lengths of 4.5, 7.5 and 11.5 mm. The pellets exact dimensions were determined from digital photographs using the ImageJ software. The equivalent diameter of the pellets defined by the sphericity and the Sauter mean diameter was determined.

The main properties of the char pellets tested are shown in Tab. 1. The proximate analysis was made by LNEG – National Laboratory of Energy and Geology, in Lisbon, and the apparent density was obtained by mercury porosimetry technique in FEUP – Faculty of Engineering of the University of Oporto.

Table 1. Proximate analysis and particle density of the *Acacia dealbata* char pellets.

	Acacia dealbata
Apparent density (kg/m^3)	660
Volatile matter (%)[(1)]	4.9
Fixed carbon (%)[(1)]	88.8
Ashes (%)[(1)]	6.3

[(1)] dry basis

2.2 Experimental setup and procedure

The experiments were carried out in a refractory steel cylindrical combustion chamber with 80 mm internal diameter and 1000 mm high (Fig. 1). The reactor was heated with an external 3.5 kW electrical resistor and insulated with Kaowool ceramic blanket. This combustor could work both as a fluidized and as a fixed bed reactor. The distributor was made of stainless steel, AISI 316, with 101, 0.3 mm ID, orifices. The bed temperature was measured by a K type thermocouple that was connected to a Picolog Recorder trough a TC-08 datalogger. The mass flow rate of the supplied air to the combustor was measured with an orifice plate flow meter, using both a U-tube water pressure manometer and a differential pressure transducer, connected to the Picolog Recorder trough an ADC 16 datalogger. A stainless steel probe with 4 mm internal diameter sampled the exhaust gases from the reactor and the CO_2 concentration was continuously measured using an infra-red Signal Instruments 7000FM analyzer.

Figure 2. Experimental setup (photo and scheme).

Taking into account previous works and the team expertise on biochar combustion in bubbling fluidized and fixed bed reactors (Pereira and Pinho, 2013; Pereira and Pinho, 2014, Pinho *et al.*, 2014), firstly, combustion tests were performed in the fluidized bed to get information on the kinetic parameters of *Acacia* char pellets. Thereby, batches of 6 g of *Acacia* char pellets were burned at three different bed temperatures, 700, 800 and 900 °C, using three different average equivalent particle diameters. The fluidization velocity was $2U_{mf}$ for all the experiments. The burning time of the batches was registered in intervals of 1 s, using the Picolog Recorder. The combustion tests were, at least, repeated twice.

Regarding to fixed bed combustion, batches of 20 g of *Acacia* char pellets were burnt at 800 °C using the same equivalent diameters. The mass flow rate of the supplied air was 19.2 g/min.

An experimental uncertainty analysis was performed according to Coleman and Steele (2009) and the results are shown in Tab. 2.

Table 2. Average uncertainty values for measured variables.

	Uncertainty
Bed temperature (%)	0.479
CO_2 molar concentration (% CO_2 v/v)	0.204
Air mass flow rate (%)	0.939
Pellets mass (%)	1.213

2.3 Mathematical models

As previously mentioned, the first tests were performed in the fluidized bed mode and the experimental data was analyzed using a mathematical model for combustion of solid carbon particles in a bubbling fluidized bed reactor (Rangel and Pinho, 2011; Pereira and Pinho, 2013). This model was based on the two phase theory of fluidization (Davidson and Harrison, 1963) 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 $C + ½\, O_2 \rightarrow CO$ and the CO formed burns away from the particle according to $CO + ½\, O_2 \rightarrow CO_2$ (Ross and Davidson, 1982).

Based on the adopted mathematical model and according to Eq. (1), 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.

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

The overall resistance to combustion ($1/K$) is a linear function of its diameter d, where the slope of the straight line is dependent on the Sherwood number Sh and on the oxygen diffusivity D_g. The intersection is dependent on the reaction rate constant k_c.

Regarding to the fixed bed, a mathematical model, previously validated using another type of biochar (Pinho *et al.*, 2014) was used. This model is based on the model developed by Kanury (1975) but where the importance of kinetic and diffusion phenomena is simultaneously taken into account. The furnace and the carbon particles in the burning fixed bed are considered at an average uniform temperature T_p, the molar concentration of oxygen, C_∞ , is known and is uniform throughout the furnace, the conditions of the oxygen at the entrance of the furnace are known and the composition of the combustion gases are the same inside and at the furnace outlet, once the furnace is well mixed. Diffusive and kinetic data for the fixed bed combustion of biochar pellets were also obtained through the plotting of $1/K$ versus d, the particle diameter.

From the integration of the CO_2 concentration curve, the consumed mass of carbon m_{cf} could be determined, as well as the total particle carbon combustion rate, $\dot{m}_{tc}$,

$$\dot{m}_{tc} = \frac{m_{cf\,i+1} - m_{cf\,i}}{t_{f\,i+1} - t_{f\,i}} \tag{2}$$

where t_f is the burning time for a given consumed mass fraction f.

Considering that the number of particles N_p, composing a batch of mass m_c, is given by,

$$N_p = \frac{6\, m_c}{\rho_c\, \pi\, di^3} \tag{3}$$

where d_i is the initial diameter of the carbon particles and ρ_c the carbon density of the particles, the single particle carbon combustion rate $\dot{m}_c$ is easily determined using the following equation,

$$\dot{m}_c = \frac{\dot{m}_{tc}}{N_p} \tag{4}$$

This single particle carbon combustion rate is connected to the oxygen molar concentration in the furnace and to the particle diameter *d* through (Pinho *et al.*, 2014):

$$\dot{m}_c = \pi\, d^2\, M_C\, K_{glo}\, C_{O_2} \tag{5}$$

where K_{glo} is the overall combustion resistance for a single particle defined as,

$$\frac{1}{K_{glo}} = \frac{d}{Sh\, D_g} + \frac{1}{k_c} \tag{6}$$

It is thus possible to get the $1/K$ evolution with particle diameter *d*, for the fixed bed combustion of batches of carbon particles.

3. RESULTS AND DISCUSSION

3.1 Fluidized bed – diffusive and kinetic data

Using the experimental data collected in the fluidized bed combustion of *Acacia dealbata* char pellets and the mathematical model mentioned above, the overall combustion resistance was determined at every instant. Figure 2 shows the evolution of the overall combustion resistance for *Acacia* pellets at 700, 800 and 900 °C. The transient combustion periods were discarded and only points in the 25 to 75% mass burned fraction range were plotted. Besides, these figures only show 5% of the experimental data points.

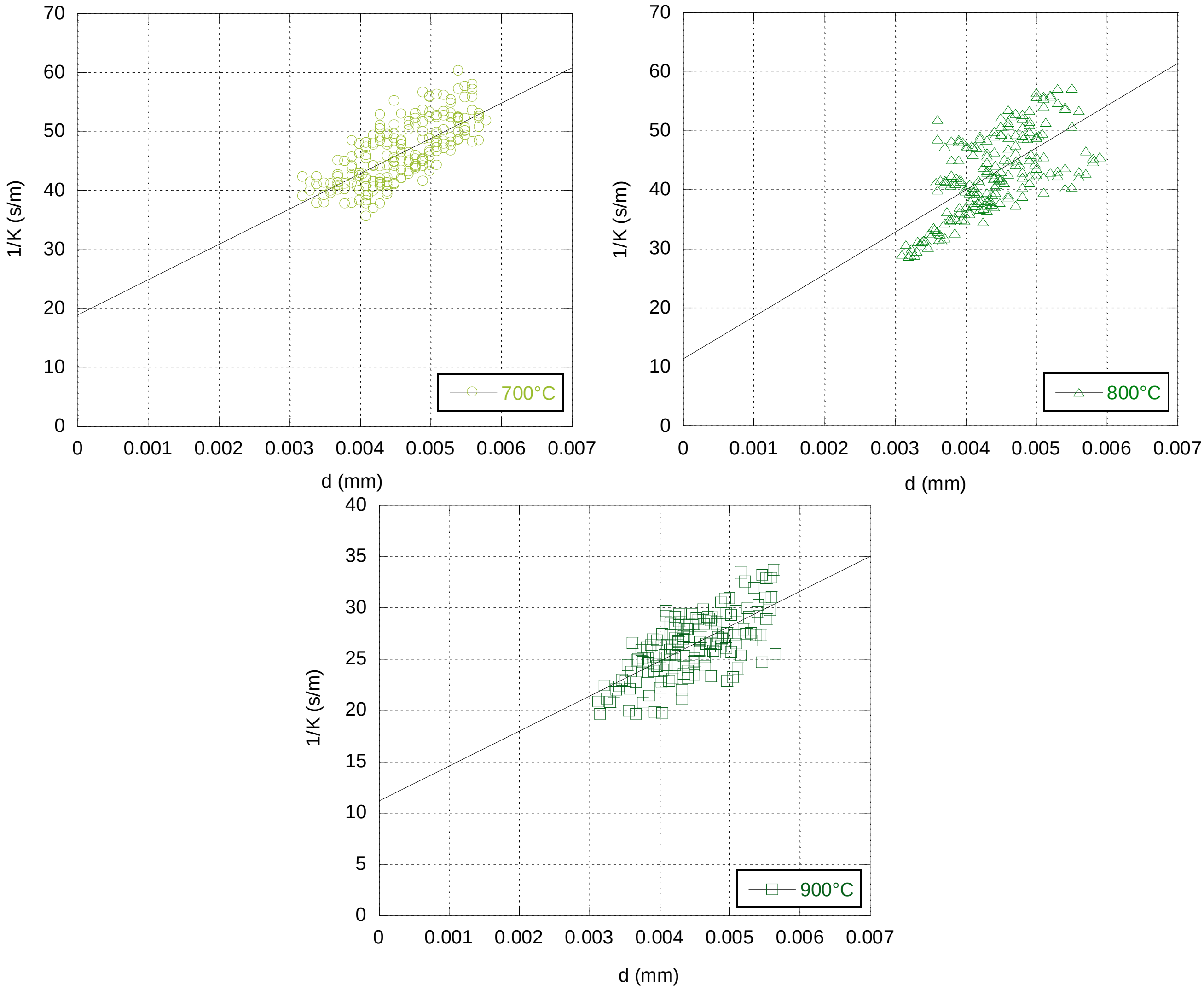

Figure 2. Overall combustion resistance for *Acacia dealbata* char pellets at 700, 800 and 900 °C.

As expected, the overall combustion resistance decreases with the increase of bed temperature, once the reaction kinetics is faster with the increase of the temperature. As can be seen for the trend lines shown in the three plots, the overall combustion resistance is linearly dependent on the instantaneous particle diameter *d*, which allowed obtaining kinetic and diffusive data for *Acacia* char pellets. From the slopes and the intercepts of the trend lines, values of Sherwood number *Sh*, and heterogeneous reaction rate constant k_c were determined for the three temperatures tested and are shown in Tab. 3.

In a general way, the heterogeneous reaction rate constant increases with the increase of the bed temperature, being this increase less pronounced between 800 and 900 °C. Concerning Sherwood numbers, a slight decrease between 700 and 800 °C and a significant increase between 800 and 900 °C was found.

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

T_{bed} (°C)	k_c (m/s)	*Sh* (-)
700	0.106	1.349
800	0.176	0.974
900	0.178	1.796

3.2 Fixed bed – diffusive and kinetic data

After carrying out the tests in fluidized bed, new combustion tests of *Acacia* char pellets were performed in the fixed bed, only at 800 °C, using the same initial particle size. Diffusive and kinetic data were also determined through the experimental data collected, based on the mathematical model previously developed for the batch combustion of solid biomass particles in packed beds (Pinho *et al*., 2014). Figure 3 represents the overall combustion resistance as a function of instantaneous particle diameter for the three biochar sizes tested. Size 1 represents the tests with shorter pellets (average length of 5.5 mm), size 2 represents the tests performed with intermediate length (average length of 7.5 mm) and size 3 represents the tests carried out with longer pellets (average length of 11.5 mm).

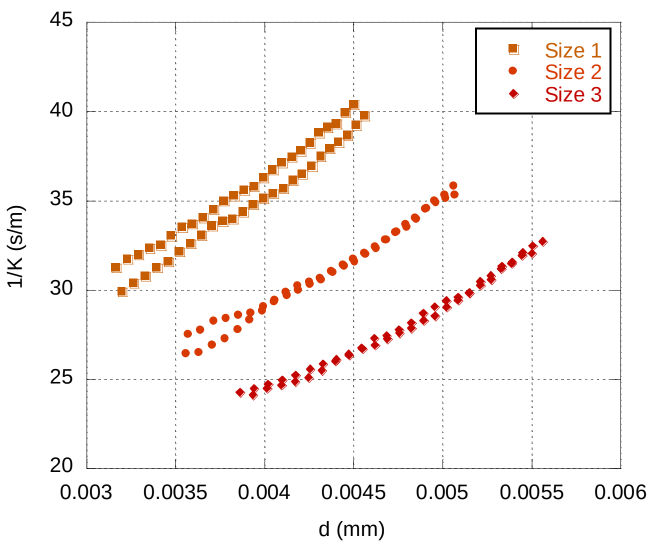

Figure 3. Overall combustion resistance of *Acacia dealbata* char pellets at 800 °C.

As expected, the overall combustion resistance decreases with the decrease of the carbon particle diameter for the three sets of tests. For the same instantaneous particle diameter, the overall combustion resistance was higher for the biochar pellets with initial lower average length. Analyzing the linear tendency of the three set of tests, the slope is almost the same, but the intersection is substantially different. It was observed, during the biochar preparation, that the particles with smaller length were denser, while the particles with greater length presented more vulnerable areas and were more porous. In fact the most homogeneous and compacted particles are less porous and therefore less reactive, thus their overall combustion resistance will be greater.

Table 4 presents the Sherwood numbers and the heterogeneous reaction rate constants obtained from the analysis of Fig. 3. A slight increase in Sherwood number with the increase of equivalent diameter was verified, namely with the increase of the length of the pellets. Concerning the heterogeneous reaction rate constant, the opposite was observed and there seems to be a tendency for a small decrease in k_c with the increase of the pellets equivalent diameter.

Table 4. *Sh* and k_c values for fixed bed combustion.

Test	*Sh* (-)	k_c (m/s)
Test 1 – size 1	1.014	0.129
Test 2 – size 1	0.993	0.133
Test 1 – size 2	1.139	0.122
Test 2 – size 2	1.142	0.121
Test 1 – size 3	1.259	0.120
Test 2 – size 3	1.274	0.111

Because the amount of experimental data obtained, for the fixed bed batch combustion of pellet chars, is still rather limited, no general trend lines were determined. Further tests will be carried out for the other bed temperatures of 700 and 900 ºC before more general conclusions can be drawn.

3.3 Activation energy and pre-exponential factor

The dependence of the heterogeneous reaction rate constant with temperature was analyzed both for fluidized and fixed bed, through the Arrhenius plot:

$$k_c = A.\, e^{-E_a/\bar{R}T} \tag{7}$$

where A is the pre-exponential constant, E_a is the activation energy, $\bar{R}$ is the universal gas constant and T is the reaction temperature that was considered, in this analysis, to be the bed temperature (Rangel and Pinho, 2011; Pereira and Pinho, 2013).

Figure 4 represents the Arrhenius plot for the fluidized bed combustion in the 700 to 900 °C temperature range. The fixed bed condition for the 800 ºC combustion was also placed in this picture; it corresponds to the mathematical average of the heterogeneous reaction rate constants presented in Tab. 3. From the observation of Arrhenius plot, the theoretically expected linear trend of the logarithm of heterogeneous reaction rate constant with the inverse of bed temperature was verified. Relatively to the fixed bed, the point corresponding to the experimental k_c at 800 °C was found close to the fluidized bed trend line.

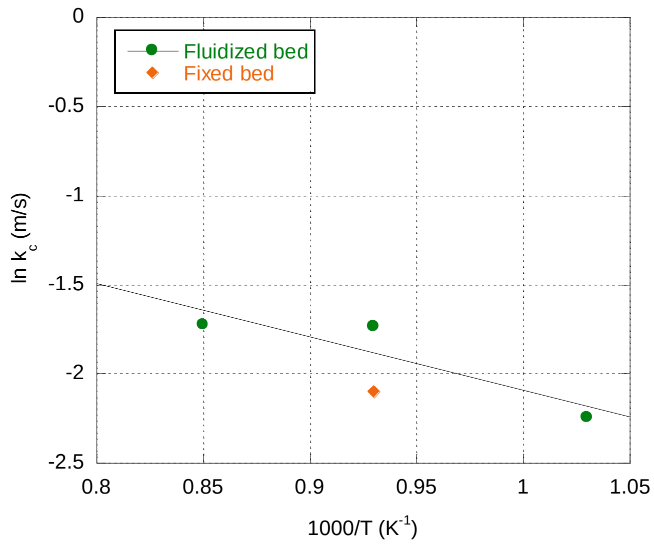

Figure 4. Arrhenius plot for *Acacia dealbata* char pellets for fluidized and fixed bed.

Through the knowledge of experimental heterogeneous reaction rate constant and using the Arrhenius plot, it is possible to get the activation energy and the pre-exponential factor through the slope and the intercept of the corresponding tendency line, respectively. For *Acacia dealbata* char pellets the results are shown in Tab. 5. Compared with other studies (Rangel and Pinho, 2011; Pereira and Pinho, 2013), the activation energy needed for the combustion of *Acacia* char pellets in a fluidized bed was lower, nevertheless it was of the same order of magnitude as in the results obtained by the mentioned authors. This can be explained by the fact that *Acacia* chars were obtained from pellets, which are more porous and thereby more reactive, therefore requiring a lower activation energy.

Table 5. Activation energy and pre-exponential factor for *Acacia dealbata* char pellets.

	Acacia dealbata
A (m/s)	2.618
E_a (kJ/mol)	25

4. CONCLUSION

Diffusive and kinetic data that control the combustion of *Acacia dealbata* char pellets were obtained using two different combustion systems, a fluidized and a fixed bed. As such, two different types of combustion models were used. For the fluidized bed the combustion tests were carried out at 700, 800 and 900 °C. However, in the case of the fixed bed, preliminary tests were only performed at 800 ºC.

In the fluidized bed, the results show that the overall resistance decrease with increasing bed temperature, which clearly shows the significant importance of the kinetics in the combustion reaction. Concerning the Sherwood number, a significant variation, and therefore non-linear values, was observed as the temperature of the bed increases.

The mathematical model tested in this work, and previously developed for the batch combustion of solid biomass particles in packed beds, showed sustainable and easy application. Diffusive and kinetic data obtained in the fixed bed were similar to those obtained in the fluidized bed using the same *Acacia* char pellets.

Based on the Arrhenius plot, a correlation for predicting the heterogeneous reaction rate constant as a function of bed temperature was obtained, considering that carbon particles were at bed temperature.

This is a work in progress and further experiments are still required. It will be necessary to carry out more combustion tests, specifically in fixed bed at other temperatures (700 and 900 °C) and also using different pellet sizes.

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