Abstract. The use of alternative energy sources, like biomass, becomes ever more important due to the necessity to minimize the large energy consumption of fossil fuels and fight climate changes. The laboratory scale determination of kinetic and diffusive combustion data is necessary for research and design purposes. A mathematical model for batch combustion of biochar particles was developed and tested with a laboratory scale fixed bed reactor where batches of wood chars, produced from invasive species at the lab facilities, were burned at bed temperatures of 800°C, using four different average equivalent diameters (4.79, 4.82, 5.62 and 5.69 mm). Continuous measurements of CO₂ and O₂ concentrations were carried out during the running tests. The main purpose of this work was to apply a developed mathematical model to test carbonized pellets combustion made of invasive species in a fixed or packed bed combustor, to obtain specific diffusive and kinetic data (Sh and k_c).

Keywords: combustion; diffusive and kinetic data; pellets; invasive species

1. INTRODUCTION

Energy and fuels needs have always been present throughout the history of mankind, in close relation with every achievement and ambition, therefore influencing life standards and technological progress (Klass, 1998). The development of societies, industrialization and population growth seen in recent times, has triggered a sharp rise in worldwide energy consumption (Lee et al., 2007). About 80% of total primary energy consumption comes from fossil fuels (IEA, 2009) and for countries with no fossil fuel reserves, it causes high external energy dependence. Biomass represents approximately 14% of the world’s energy supply. In developing countries biomass contributes to 35% of primary energy consumption; in industrialized countries the situation is completely different, estimations being made that only 3% of the energy used derives from this particular source (Demirbas, 2005). The ability of biomass to be converted into electricity, heat and fuel makes it very flexible and allows a direct competition with fossil fuels (Greenpro, 2004). Furthermore, the combustion of biomass is considered carbon neutral, because it does not contribute to CO₂ emissions, since during its combustion it releases the same amount of carbon dioxide that was stored by the plant during its growth (Demirbas, 2004; Klason and Bai, 2007). Some of the characteristics of the biomass like high moisture content, irregular shape and low bulk and energy density are some of the reasons why its transport, handling and storage is complicated (Kaliyan and Morey, 2009; Mediavilla et al., 2009). Transforming this bulky biomass material into a denser one (pellets) would improve its handling properties as well as reduce transportation and storage costs (Mani et al., 2006).

The process of biomass combustion can be divided into different stages: drying, pyrolysis, gasification and combustion itself. 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 char combustion 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 fixed bed combustion of carbonized pellets made from Cytisus striatus.

To carry out research experiments in order to find out the diffusive and kinetic parameters that control the combustion process, small batches of char particles are thrown into a laboratory scale fixed bed reactor heated up by an electrical resistance. The combustion characterizing parameters were obtained either from fluidized bed or from fixed bed combustion experiments of batches of these char particles. The fixed bed is assumed an isothermal well mixed reactor, with the reacting char particles at the same temperature $T_p$ and the oxygen concentration at the reactor exit assumed as the average bed oxygen concentration, $C_\infty$. 
2. COMBUSTION TIME OF BATCHES OF CARBON PARTICLES

In general terms, either complete combustion of carbon to CO$_2$ or the incomplete combustion to CO should be comprehended. Then, an overall combustion resistance for a single and spherical carbon particle can be given by (Ross and Davidson, 1982; Pinho and Guedes de Carvalho, 1984; Rangel and Pinho, 2011; Pereira and Pinho, 2013)

$$\frac{1}{K_{glw}} = \frac{d}{i \; Sh \; D_e} + \frac{1}{k_c}$$

(1)

where $d$ is the burning particle diameter, $Sh$ the Sherwood number, $D_e$ the oxygen diffusivity in the burning gas and $k_c$ the reaction rate constant for the heterogeneous reaction (C+1/2O$_2$→CO) that occurs at the surface of the particle; $i$ is a factor that takes the value 1 when the CO combustion to CO$_2$ takes place closer to the particle surface or 2 when this gaseous phase reaction takes place away from the particle surface. This definition of the overall combustion resistance can be applied either to a fluidized bed combustor or to a fixed bed combustor.

To analyze the combustion of batches of carbon particles in a fixed bed it is assumed that the burning particles are all at the uniform bed temperature $T_p$; that the molar concentration of oxygen is known and uniform throughout the bed $C_{o2}$, that the conditions of the comburent air are known at the bed entrance and that the combustion reactor is a well-mixed one and the combustion gases composition inside it is identical to the bed exit conditions.

In order to determine the burning time, $t_{\varphi}$, of a batch of particles is necessary to perform a balance to the oxygen consumed in the process. The carbon consumption of one of the particles composing the bed is connected to its mass reduction, in kmol/s of C which is equal to the consumption of O$_2$ in kmol/s,

$$-\rho_c \pi d^2 \frac{d}{dt} (d) = \pi d^2 K_{glw} \eta \; C_{o2}$$

(2)

with $\rho_c$ the carbon density, $M_c$ the carbon molecular mass and $K_{glw}$ the overall reaction constant, that is given by Eq. (1). In this equation it has been introduced a correction factor, $\eta$, to have into account the burning rate reduction when compared to the isolated particle. In fact, the bed stacking and the competition between particles for oxygen lead to a reduction of the reaction rate.

Through the reactor inlet side, there are $U_e A_i C_{o2}$ kmol/s of O$_2$ entering the reactor, where $U_e$ is the average inlet air superficial velocity, $A_i$ is the inlet cross section area and $C_{o2}$ is the inlet oxygen molar concentration. Through the reactor exhaust side there are $U_e A_i C_{o2}$ kmol/s of O$_2$ leaving the reactor, where $U_e$ is the average reactor outlet velocity and $C_{o2}$ is the molar concentration of oxygen in the exhaust. Because the laboratory reactor is assumed a well-mixed reactor, $C_{o2} = C_{o2}$. The difference between these two oxygen molar flow rates is the oxygen consumed in kmol/s,

$$U_e A_i C_{o2} - U_e A_i C_{o2} = N_p \left( -\frac{\rho_c \pi d^2 \frac{d}{dt} (d)}{2 M_c} \right)$$

(3)

where $N_p$ is the number of particles composing the batch of carbon particles with a total entrance mass of $m_c$,

$$N_p = \frac{6 \; m_c}{\rho_c \pi d_i^3}$$

(4)

for a particle of initial diameter $d_i$.

Taking the equations (1), (2) and (3), eliminating $K_{glw}$ and $C_{o2}$ between them, one obtains the following differential equation,

$$-\frac{3}{M_c} \; d^2 \frac{d}{dt} (d) = \frac{U_e A_i \rho_c}{2 \; M_c \eta i \; Sh \; D_e} \; d \; d(d) - \frac{U_e A_i \rho_c}{2 \; M_c \eta k_c} \; d(d) = U_e A_i C_{o2} dt$$

(5)

Integrating between the limits: $t = 0 \Rightarrow d = d_i$ and $t = t_{\varphi} \Rightarrow d = (1 - \varphi)^{1/3} d_i$, results the following expression for the burning time of a fraction, $\varphi$, of a charge $m_c$ of particles with initial diameter $d_i$.

$$t_{\varphi} = \frac{\rho_c \left[ 1 - (1 - \varphi)^{\frac{1}{3}} \right] d_i^2}{4 \; M_c \; Sh \; \eta i \; D_e C_{o2,x}} + \frac{\rho_c \left[ 1 - (1 - \varphi)^{\frac{1}{3}} \right] d_i}{2 \; M_c \eta k_c C_{o2,x}} + \frac{\varphi \; m_c}{M_e U_e A_i C_{o2,x}}$$

(6)
The first term, proportional to the square of the initial particle diameter, quantifies the weight of the mass transfer in the combustion process, while the second term, proportional to the initial particle diameter, takes into account the kinetics of the chemical reaction. The third term, which is not directly dependent on the initial particle diameter although it is indirectly under the required knowledge of the total mass of the load, is essentially function of flow conditions existing in the furnace.

The burned mass fraction is defined as \( \varphi = \frac{m_{cf}}{m_c} \) and the carbon consumed mass \( m_{cf} \) is determined through the integration of the CO\(_2\) concentration curve from the combustion beginning until \( t_{\varphi} \).

\[
m_{cf} = 12 \, \bar{V}_{art} \bar{n} \int_0^{t_{\varphi}} v_{CO_2} \, dt
\]

(7)

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. In this work the diameter of the sphere with the same volume of the particle and the shape factor sphericity \( \phi_c \) are used to obtain the equivalent initial diameter, \( d_i \) (Pereira and Pinho, 2014).

As far as the correction factor \( \eta \) is concerned, it represents in a simple way a combination of factors that take into account the difficulty affecting the oxygen diffusion inside the packed bed in its trajectory towards the carbon burning particles. These factors are: first in the case of wood or in general biomass particles the reduction of oxygen concentration due to its consumption by the volatiles released during the pyrolysis stage of the combustion process; a reduction of the particle surface area available for reaction because of the close contact existing among particles composing the fixed bed; the tortuosity of the path followed by the oxygen crossing into the bed of and further the obstructing effects of the ashes from the burning biomass particles. In the present work and similarly to mass transfer inside porous particles it will be considered that (Fogler, 2004)

\[
\eta = \frac{\varepsilon_b \delta}{\tau_b}
\]

(8)

where \( \delta \) is a factor accounting for the previous oxygen consumption in the gas phase by the volatiles released during the pyrolysis step, \( \varepsilon_b \) is the bed porosity and \( \tau_b \) is the bed tortuosity. In the present experimental situation as the particles under study are of char, its volatile content is about 4.5 % (w/w) and it can be assumed that \( \delta = 1 \). \( \sigma_c \) is the bed constriction factor and considers both effects, inter particle contact and ash restriction effects, but in the present work for lack of better information it will be considered also as \( \sigma_c = 1 \).

The porosity of the bed of particles can be determined through (Benhahia and O’Neill, 2005),

\[
\varepsilon_b = \left( 0.1504 + \frac{0.2024}{\phi_p} \right) + \frac{1.0814}{\left( \frac{d_i}{d_{cf}} + 0.1226 \right)}
\]

(9)

while the bed tortuosity can be calculated by means of (Lanfrey et al., 2010),

\[
\tau = \frac{1.23 \left( 1 - \varepsilon_b \right)^{1/3}}{\varepsilon_b \phi_p}
\]

(10)

where \( \phi_p \) is the sphericity of the particles composing the burning bed

\[
\phi_p = \frac{\pi^{1/3} \left( 6 \, V_p \right)^{1/3}}{A_p}
\]

(11)

being \( A_p \) the surface area of a particle and \( V_p \) its volume.
3. EXPERIMENTAL SETUP AND MEASUREMENTS

The experimental setup consisted of a cylindrical combustion chamber with 80 mm internal diameter (Fig. 1). An external 3.12 kW electrical resistance was heating the bed just above the distributor. Insulation was made with Kaowool ceramic blanket. The mass flow rate of the supplied air was measured by an orifice plate flow meter using an Omega Engineering differential pressure transducer model PX143. This combustor could work both as a fluidized bed or as a fixed bed reactor.

A 4 mm internal diameter stainless steel probe sampled the combustion gases leaving the reactor through the converge nozzle. The CO₂ 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.

Cytisus striatus was the species chosen for this work to find out its behavior in fixed bed burning. Batches of 20 g of carbonized pellets of different sizes were burned using an operating fixed bed temperature of 800 °C. The sizes tested were 4.79, 4.82, 5.62 and 5.69 mm in equivalent diameter defined by the sphericity and the Sauter diameter. The tests were repeated twice. The mass flow rate of the supplied air was 19.2 g/min in all the experiments. For each burning test the bed temperature, the pressure differential in the air orifice plate flow meter and the molar CO₂ and O₂ concentrations in the exhaust combustion gases were continuously measured and recorded.

![Experimental setup diagram](image)

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

<table>
<thead>
<tr>
<th>Cytisus striatus</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density (kg/m³)(^{(1)})</td>
<td>729.1</td>
</tr>
<tr>
<td>Moisture(^{(2)})</td>
<td>6.0</td>
</tr>
<tr>
<td>Ashes(^{(3)})</td>
<td>5.5</td>
</tr>
<tr>
<td>Volatile matter(^{(4)})</td>
<td>4.1</td>
</tr>
<tr>
<td>Fixed carbon(^{(5)})</td>
<td>84.4</td>
</tr>
</tbody>
</table>

\(^{(1)}\) obtained with mercury porosimetry technique; \(^{(2)}\) EN 14774-3: 2009; \(^{(3)}\) EN 14775: 2009; \(^{(4)}\) EN 15148: 2009; \(^{(5)}\) ASTM D 3172:97

As an example Figure 2 shows, for \(d_i = 4.79\) mm and \(d_i = 4.82\) mm, the measured evolution of the molar concentration of CO₂ in the exhaust gas from the reactor while operating in fixed bed conditions. The consumption rate of carbon was obtained from the integration of these curves.
4. RESULTS AND DISCUSSION

The first experiments were carried out in the reactor working as a fluidized to get information on the kinetic parameters of the biochar being tested. This approach was adopted because of the expertise of some team members with this type of reactor and the testing followed the methodology adopted in previous works (Pereira and Pinho, 2013; Pereira and Pinho, 2014). For these fluidized bed experiments the same biochar particle size, carbonized *Cytisus striatus* pellets, and operating bed temperature, were used, as intended for the fixed bed experiments.

According to the mathematical model adopted for the treatment of the fluidized bed combustion experiments (Pereira and Pinho, 2013; Pereira and Pinho, 2014), the obtained results, as show in Fig. 3, clearly show that the combustion of these biochar pellets is diffusively controlled. The heterogeneous reaction rate constant $k_c$ is very high and the kinetic term on the overall reaction rate constant, as defined by Eq. (1) tends to zero.

Considering that the operating conditions in fixed bed combustion conditions are even more convenient for mass transfer control, the information obtained in the fluidized bed experiments was used for the analysis of the fixed bed combustion experiments. As such, the second term in Eq. 6 is null and this means that the plotting of the burning time $t_\varphi$ as a function of $d_i^2$ will be a straight line. By doing that, from the slope of the linear tendency, the Sherwood number $Sh$ for fixed bed combustion conditions can be determined. In Fig. 4 it is plotted $t_\varphi$ vs $d_i^2$ for different mass burned fractions and the corresponding trend lines are shown.
The correction factor $\eta$ has been determined by the combination of Eqs. 8 to 11 yielding values between 0.205, for $\varphi=30\%$ and 0.203, for $\varphi=70\%$. This small decrease in value is related to the decrease in porosity and the increase in tortuosity of the bed, as combustion progresses.

In Table 2, and for the burned mass fractions of 30, 50 and 70 %, are represented three sets of Sherwood numbers, the $Sh^a$ determined from the slopes of the trend lines of Fig. 4, $Sh^b$ for a packed bed according to Incropera and DeWitt (2002) and $Sh^c$, also for packed bed, according to Levenspiel (1998). The $Sh^a$ are average values for the combustion life time since its beginning up to the corresponding burned mass fraction under consideration.

<table>
<thead>
<tr>
<th>$\varphi$ (%)</th>
<th>$Sh^a$</th>
<th>$Sh^b$</th>
<th>$Sh^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>12.25</td>
<td>11.67</td>
<td>6.715</td>
</tr>
<tr>
<td>50</td>
<td>8.69</td>
<td>11.16</td>
<td>6.472</td>
</tr>
<tr>
<td>70</td>
<td>7.07</td>
<td>10.59</td>
<td>6.216</td>
</tr>
</tbody>
</table>

Through the observation of the results presented in Table 2 it can be concluded that the experimentally obtained Sherwood numbers for the fixed combustion process $Sh^a$ are of the same order of magnitude of those determined by means of two correlations from the literature (Levenspiel, 1998; Incropera and DeWitt, 2002) which in a certain way justifies the methodology adopted in the present work. The diminishing of the Sherwood number throughout the combustion process is clear from this table and is also shown with more detail in Fig. 5. Work is still being carried out to clarify the reasons for the evolution of $Sh$ with the progress of the combustion process. Besides further work will also be carried out with other different types of biomass, namely using biochars with finite values for the heterogeneous reaction rate constant $k_c$, i.e. when there is competition between mass transfer and kinetics for the control of the combustion process.
5. CONCLUSIONS

A mathematical model for the batch combustion of solid biomass particles in packed was developed. To assess its validity, packed bed combustion of biochar made from Cytisus striatus pellets was analyzed. Prior to this, combustion experiments for this type of biochar, were carried out in fluidized bed and it was found that the combustion of this type of char was diffusionally controlled. Extending this conclusion to the treatment fixed bed combustion results, mass transfer data, in terms of the Sherwood number, were then obtained and compared with two correlations found in the scientific literature. The closeness of the Sherwood numbers obtained from the packed bed combustion experiments and the literature correlations are an indication of the suitability of the proposed mathematical model. However, further experiments are still required to widen the range of applicability of the model, either in terms of the type of tested chars or in terms of bed operating conditions.

5. ACKNOWLEDGEMENTS

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6. REFERENCES


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