KINETIC AND MASS TRANSFER DATA FROM COMBUSTION OF BIOMASS CHARS IN A FLUIDIZED BED

N. RANGEL* and C. PINHO
CEFT/DEMec - Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal
*Corresponding author: nrangel@fe.up.pt, telephone +351 225081400, fax +351 225081440

Keywords: combustion, fluidized bed, kinetic constant, Sherwood number

Abstract
The purpose of this paper is to compare the method to obtain the kinetic constant and the Sherwood number of biomass chars burning in a fluidized bed, based on the measured burnout time, with the method based on the instantaneous overall combustion resistance. Several equations were published in literature to calculate the burn out time of batches of char particles in fluidized bed combustors. Such equations are functions of unknown diffusive parameters, or both unknown diffusive and kinetic data, as the following equation:

\[ t_q = \frac{\rho_c d_i^2}{96\varepsilon^c Sh D_G} + \frac{\rho_c d_i}{24k_c c_0} + \frac{m_c}{12\varepsilon c A U} \]

Reworking the previous equation it is clear that plotting the batch burnout time as a function of the initial particle diameter, the Sherwood number can be calculated from the slope and the kinetic constant \( k_c \) from the intercept at the origin,

\[ t_q = \frac{m_c}{12\varepsilon c A U} \frac{1}{d_i} = \frac{\rho_c}{96\varepsilon^c Sh D_G} d_i + \frac{\rho_c}{24k_c c_0} \]

On the other end through the equation for the instantaneous overall resistance to combustion,

\[ \frac{1}{K} = \frac{d}{Sh D_G} + \frac{2}{k_c} \]

the same parameters could be obtained through an alternative path.

The tests were carried out in an electrically heated bed of silica sand fluidized with air. The average initial diameters of char particles were in the range 1.8-3.6 mm. Burn out times of batches of char particles from biomass were measured and the values were introduced into the model. The obtained integrated values for Sherwood number and kinetic constant were then compared with corresponding instantaneous values.

The results show that for the tested chars the Sherwood numbers obtained by either method are similar; the kinetic constants obtained from the measure of the burnout time have lower values and the justification for such difference is then presented.
1- INTRODUCTION

Waste and virgin biomass are natural resources that can be combusted efficiently in fluidized bed reactors contributing to reduce the emissions of greenhouse gases to atmosphere. Energy from biomass, excluding food crops, is achieving a worldwide recognition as a suitable renewable energy source [1, 2]. For designing and construction of fluidized bed combustors it is necessary to know kinetic and mass transfer parameters for a large variety of biomasses.

The purpose of this work is to compare average values of Sh and $k_c$ over all combustion process, to the instantaneous values obtained elsewhere by the method of overall combustion resistance [3] at 50% of carbon conversion, which may be considered representative of the overall reactivity of the char [4].

2- MATERIALS AND METHODS

Wood chars of *Millettia stuhlmannii* (Jambirre), *Afzelia quanzensis* (Chanfuta) and *Pterocarpus angolensis* (Umbila) of Mozambican origin were burned in an electrically heated fluidized bed reactor in batches of 1.5 g of particles with average initial diameters of 3.6, 2.8, 2.2 and 1.8 mm, at bed temperatures of 750, 820 and 900 ºC, and fluidization conditions of 1.5 $U_{mf}$. These chars were obtained by carbonization of wood samples in a fixed bed with a nitrogen flow at heating rate of 0.5 ºC/s and maintained at pyrolysis temperature of 850ºC for 15 minutes. The bed temperature was measured by a K-type thermocouple with 3 mm in diameter, and controlled with a PID temperature controller. The inert material of the bed was silica sand in the size range of 250-315 µm, with a static height of 150 mm. The bed container was a refractory steel tube with ID 80.8 mm.

The tested sizes of char particles are in the typical range of 1-10 mm commonly used for biomass combustion, Lu and Baxter [5]. The density of the particles and the proximate analysis are in Table 1.

<table>
<thead>
<tr>
<th>Parent wood</th>
<th>A. quanzensis</th>
<th>M. stuhlmannii</th>
<th>P. angolensis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate analysis (% w/w, as received)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>0.8</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>10.7</td>
<td>5.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Ash</td>
<td>14.0</td>
<td>3.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>74.5</td>
<td>87.5</td>
<td>89.9</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>735.1</td>
<td>607.2</td>
<td>464.5</td>
</tr>
</tbody>
</table>

The burning time of the batches was registered in intervals of 1 s by the program LabVIEW, as well as the molar concentration of CO$_2$ at bed exit that was measured by a non-dispersive infrared analyser. The criterion to consider complete combustion of the batch was the molar concentration of CO$_2$ in burned gases to reach 0.5%. Other approaches such visual observation or measurement of the bed temperature can be adopted to obtain experimentally the burnout time of the batches.

The burnout time of batches was thoroughly used in the study of combustion of carbon particles in fluidized bed [6, 7]. Equation 1 retrieved from another work [8] predicts the burnout time $t_q$ of a batch of particles knowing a set of invariable parameters during the combustion such as density of the carbon $\rho_c$ (shrinking model), initial particle diameter $d_i$, molar concentration of oxygen at the bed inlet $c_{i0}$, diffusivity of oxygen in air $D_G$, the
fluidization velocity \( U \), cross section area of the reactor \( A_t \), and the mass of carbon in the batch \( m_c \).

\[
t_q = \frac{T_c d_i^2}{96c_0 ShD_G} + \frac{\rho_i d_i}{24k_c c_0} + \frac{m_c}{12c_0 A U}
\]  

(1)

The parameters that vary during combustion are the Sherwood number and kinetic constant \( k_c \) of the heterogeneous reaction at particle surface, assuming that carbon reacts to CO according to the reaction \( C+1/2O_2 \rightarrow CO \).

Working on Eq. (1) it is possible, knowing the measured burnout time of the biomass batch, to calculate the Sherwood number from the slope and the kinetic constant \( k_c \) from the intercept.

\[
\left( t_q = \frac{m_c}{12c_0 A U} \right) \frac{1}{d_i} = \frac{\rho_i}{96c_0 ShD_G} d_i + \frac{\rho_c}{24k_c c_0}
\]

(2)

Through the equation for the instantaneous overall resistance to combustion, Eq. (3), the same parameters could be obtained for comparison [3].

\[
\frac{1}{K} = \frac{d}{ShD_G} + \frac{2}{k_c}
\]

(3)

3- RESULTS AND DISCUSSION

Plotting Eq. (2) it is possible to obtain a Sherwood number \( Sh \) and a \( k_c \) from the slope and intercept of the regression lines, respectively, for all chars and bed temperatures tested, Figure 1.

Figure 1: Plot of \( t_q = m_c (12c_0 A U) \) versus \( d_i \) for chars of a) A. quanzensis, b) M. stuhlmannii, and c) P. angolensis.
Table 2 shows the average values of Sh and $k_c$ over the total combustion time. The linear regressions have coefficients of correlation R-squared in the range 0.87-1.00, Table 2. The above Sherwood numbers obtained from the burnout time equation are compared in Figure 2 with the instantaneous values for 50% of conversion. There is a good agreement between the compared values, as shows the deviation band of ± 15%.

The average kinetic constants obtained over total combustion time $k_c$ are smaller than those obtained for 50% of conversion $k_{c,0.5}$. The corresponding ratios are quantified in Table 2 and Figure 3 shows that the ratio $k_c/k_{c,0.5}$ decreases with the increase of $k_{c,0.5}$. In other words, the discrepancies between these two methodologies are more evident at higher bed temperatures, and consequently for higher kinetic constants, because of the greater weight of the particle heating time in such conditions. During the particle heating time, its temperature is lower than the bed temperature inside which the particle is immersed, resulting in lower reaction rates and this effect appears in the average reaction rate constant obtained over the total combustion time as lower particle reactivity.

### Table 2: Sh and $k_c$ values

<table>
<thead>
<tr>
<th>Wood char</th>
<th>$T_{bed}$ (°C)</th>
<th>$R^2$</th>
<th>Sh</th>
<th>$k_c$ (m/s)</th>
<th>$Sh_{0.5}$</th>
<th>$k_{c,0.5}$ (m/s)</th>
<th>$k_c/k_{c,0.5}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. quanzensis</td>
<td>750</td>
<td>0.99</td>
<td>1.36</td>
<td>0.166</td>
<td>1.64</td>
<td>0.257</td>
<td>64.4</td>
</tr>
<tr>
<td></td>
<td>820</td>
<td>0.98</td>
<td>1.29</td>
<td>0.207</td>
<td>1.56</td>
<td>0.500</td>
<td>41.3</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.97</td>
<td>1.37</td>
<td>0.275</td>
<td>1.50</td>
<td>1.968</td>
<td>14.0</td>
</tr>
<tr>
<td>M. stuhlmannii</td>
<td>750</td>
<td>0.99</td>
<td>1.19</td>
<td>0.169</td>
<td>1.37</td>
<td>0.337</td>
<td>50.2</td>
</tr>
<tr>
<td></td>
<td>820</td>
<td>1.00</td>
<td>1.42</td>
<td>0.194</td>
<td>1.48</td>
<td>0.491</td>
<td>39.5</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.99</td>
<td>2.00</td>
<td>0.224</td>
<td>1.77</td>
<td>0.666</td>
<td>33.6</td>
</tr>
<tr>
<td>P. angolensis</td>
<td>750</td>
<td>0.87</td>
<td>1.76</td>
<td>0.115</td>
<td>1.82</td>
<td>0.202</td>
<td>57.1</td>
</tr>
<tr>
<td></td>
<td>820</td>
<td>0.97</td>
<td>1.20</td>
<td>0.169</td>
<td>1.46</td>
<td>0.291</td>
<td>58.1</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.99</td>
<td>1.90</td>
<td>0.196</td>
<td>1.52</td>
<td>0.778</td>
<td>25.2</td>
</tr>
</tbody>
</table>

**Figure 2:** Comparison of Sherwood numbers. Instantaneous values at 50% conversion $Sh_{0.5}$ versus integrated values over burnout time $Sh$. 

1679
4- CONCLUSIONS

The tested chars have similar Sherwood numbers obtained by either method. On the other end, the kinetic constants obtained by the method based on the measurement of the burnout time vary from 14 to 64% of the corresponding values obtained by the method of instantaneous overall resistance, stressing the importance of the heating period on the overall burning behaviour.

The studied chars did not fragment during the combustion, so it would be of interest to extend this research to chars experiencing the phenomenon of fragmentation.

ACKNOWLEDGEMENTS

This work was supported in part by the grant SFRH/BPD/49250/2008 from Portuguese Foundation for Science and Technology (Fundação para a Ciência e a Tecnologia). The experimental data were collected by Neli P. Tomé throughout her MSc work at laboratory facilities of INEGI.

NOMENCLATURE

\( A_t \) Cross section area of the bed, m\(^2\)
\( c_0 \) Oxygen molar concentration at bed inlet, kmol m\(^{-3}\)
\( D_G \) Gas diffusivity, m\(^2\) s
\( d_i \) Initial diameter of char particles, m
\( k_c \) Kinetic constant, m s\(^{-1}\)
\( k_{c,0.5} \) Kinetic constant at 50% conversion, m s\(^{-1}\)
\( m_c \) Mass of carbon in a batch of coal particles, kg
\( Sh \) Particle Sherwood number
\( Sh_{0.5} \) Particle Sherwood number at 50% conversion
\( t_q \) Burnout time of a batch of particles, s
\( U \) Superficial air velocity, m s\(^{-1}\)
\( \rho_c \) Mass of carbon per unit volume of particle, kg m\(^{-3}\)
REFERENCES