Fluidized Bed Combustion of Coal Char Particles under Oxyfiring Conditions

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1. Introduction

Production of energy from fossil fuel combustion results in the emission of greenhouse gas species, with the most significant fraction being CO₂. The constant increase in greenhouse gas emissions has resulted in the development of new technologies with lower emissions and technologies that can accommodate capture and sequestration of carbon dioxide. Oxyfiring (or oxyfuel) technology can produce an almost pure CO₂ outlet stream, by using pure oxygen instead of air for fuel combustion [1]. Flue gas is partly recycled back into the furnace to control the combustion temperature. In this way the costs of CO₂ separation from the flue gas can be substantially reduced. Although most of the research activity in oxyfiring has concentrated on pulverized coal boilers, recently the application of this technology to circulating fluidized bed (CFB) coal boilers has been examined [2-6]. CFBs appear to be particularly suited for oxyfiring conditions because of the fuel flexibility and better temperature control (which allows to reduce significantly the amount of recycled flue gas). The feasibility of CFB coal oxyfiring has been successfully demonstrated in pilot-plant tests [2-6], and no particular technological barrier appears to exist for implementing this technology in the near-term.

However, a number of issues still need to be addressed in more detail to obtain a more fundamental understanding of the changes between oxyfiring and conventional air-fired combustion [1]. One of these issues regards the combustion characteristics of coal in an O₂/CO₂ atmosphere. In fact, it has been suggested that under these conditions (and especially at the high temperatures experienced in pulverized fuel combustion) carbon gasification by CO₂ might contribute significantly to the char mass loss [1]. In this work, combustion of single coal char particles in a lab-scale fluidized bed under simulated oxyfiring conditions was studied. The burning rate of the particles was followed as a function of time by continuously measuring the outlet CO and O₂ concentrations. Some preliminary evaluations on the significance of homogeneous CO oxidation in the reactor and of carbon gasification by CO₂ in the char particle at the relevant operating conditions are also reported.

2. Experimental

2.1. Apparatus

A circular stainless steel atmospheric bubbling fluidized bed reactor 40mm ID and 1m high was used for the experiments (Fig. 1). The gas distributor was a 2mm thick perforated plate with 55 holes 0.5mm in diameter disposed in a triangular pitch. A 0.6m high stainless steel column, containing a number of steel nets for gas preheating and mixing, was placed under the distributor. The fluidization column and the preheating section were heated by two semicylindrical electric furnaces. The temperature of the bed, measured by means of a thermocouple placed 40mm above the distributor, was kept constant by a PID controller. Temperature variations during the runs were always within ±1°C of the set point. A stainless steel circular basket could be inserted from the top to retrieve char particles from the bed.
Fig. 1 Experimental apparatus: 1) gas preheating section; 2) electrical furnaces; 3) ceramic insulator; 4) gas distributor; 5) thermocouple; 6) fluidization column; 7) gas suction probe; 8) stack; 9) cellulose filter; 10) membrane pump; 11) gas analyzers; 12) personal computer; 13) manometer; 14) digital mass flowmeters.

Gases were fed to the column via two high-precision digital mass flowmeters/controllers (accuracy ±1% full scale). Each flowmeter/controller was calibrated with a bubble flowmeter. Gases were supplied from two cylinders containing carbon dioxide and oxygen. The top section of the fluidization column was left open to the atmosphere and the exit gas was sucked by a hood. A stainless steel probe was inserted from the top of the column to convey a known fraction (0.06m³/h) of the exit gas directly to the gas analyzers. A high efficiency cellulose filter was inserted in the line to avoid dust entrainment into the analyzers. The probe, 2mm ID, was positioned 0.6m above the distributor, approximately at the axis of the column. The absence of any gas leakage and/or suction to/from the surrounding environment in the sampling probe and line was carefully checked.

A NDIR analyzer (accuracy ±1% full scale) was used for on-line measurement of CO and a paramagnetic analyzer (accuracy ±2% full scale) for O₂ concentration in the exhaust gases. The measuring range of the O₂ analyzer was 0 – 10% (v/v) and for CO 0-1000ppmV. Data from the analyzers were logged and further processed on a PC.

2.2. Materials
A Snibston bituminous coal was selected as the test fuel. Table 1 reports the fuel properties. The fuel particles were first devolatilized by dropping them in the fluidized bed with N₂ at 850°C. After 5min, char particles were retrieved from the bed and machined into almost spherical particles with an average size of ~6-7mm (Fig. 2A). The particles were preprocessed in air for 8h in the fluidized bed at ambient temperature and 0.3m/s to smoothen the particle surface. Some tests were performed with a thin (250μm OD) thermocouple inserted inside the particle to measure its temperature during the oxy-combustion test (Figs. 2B-C). The bed material consisted of 180g of quartz sand, corresponding to an unexpanded bed height of 0.1m. Sand was double sieved in the 500 – 600μm particle size range. The minimum fluidization velocity was 0.13m/s. The particle density of the quartz sand was 2560kg/m³, and the bed voidage at minimum fluidization was 0.44.
Tab. 1 Properties of Snibston coal.

<table>
<thead>
<tr>
<th>Proximate analysis, % (as received)</th>
<th></th>
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<tbody>
<tr>
<td>Moisture</td>
<td>14.6</td>
</tr>
<tr>
<td>Ash</td>
<td>4.0</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>35.2</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>46.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate analysis, % (dry and ash free basis)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>81.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>10.8</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.0</td>
</tr>
<tr>
<td>Char density, kg/m$^3$</td>
<td>1040</td>
</tr>
</tbody>
</table>

2.3. Procedures

In all the tests performed in this experimental campaign the inlet oxygen concentration was smaller than 10% (v/v), because these are the relevant local O$_2$ concentrations near a burning particle in a fluidized bed under oxyfiring conditions. If low oxygen concentrations are used (< 2% v/v), it is known that the particle temperature can be assumed approximately equal to the bed one [7]. Since some tests were performed with a higher O$_2$ concentration, in these tests a thermocouple was inserted inside the particle to measure its temperature.

The experiments were performed in a fluidized bed at 850ºC, atmospheric pressure, with a fluidization velocity of 0.3 m/s, which corresponds to bubbling/slugging conditions. An inlet gas mixture was introduced in the bed made of CO$_2$ and O$_2$ in the combustion tests and only CO$_2$ in the gasification tests; O$_2$ concentration assumed the values 1, 2, 4.5 and 8 % (v/v). The test consisted in the injection of one char particle, of known mass and diameter, in the fluidized bed and in the continuous measurement of CO and O$_2$ concentrations at the outlet. In order to obtain the char burning rate during the tests, a balance on oxygen and carbon in the reactor was carried out:

\[
\dot{m}_{\text{in},O_2} + \dot{m}_{\text{in},CO_2} \times \frac{32}{44} = \dot{m}_{\text{out},O_2}(t) + \dot{m}_{\text{out},CO_2}(t) \times \frac{16}{28} + \dot{m}_{\text{consumed}} \times \frac{32}{44} 
\]

(1)

\[
\dot{m}_{\text{in},CO_2} \times \frac{12}{44} + \dot{m}_{\text{consumed}}(t) = \dot{m}_{\text{out},CO_2}(t) \times \frac{12}{28} + \dot{m}_{\text{out},CO}(t) \times \frac{12}{28} 
\]

(2)

Fig. 2 A) Coal char particles used for the experiments; B) and C) char particle with thermocouple inside.
where $\dot{m}_{i}^{\text{in}}$ or $\dot{m}_{i}^{\text{out}}$ is the mass flow rate of species $i$ that enters or exits the reactor and $\dot{m}_{\text{C consumed}}$ is the carbon consumption rate, all in g/s. Combining these two equations gives:

$$\dot{m}_{\text{C consumed}}(t) = \frac{12}{32} \left[ \dot{m}_{\text{in}}^{\text{O}_2} - \dot{m}_{\text{out}}^{\text{O}_2}(t) \right] + \frac{3}{14} \dot{m}_{\text{CO}}^{\text{out}}(t)$$  \hspace{1cm} (3) \hspace{1cm}

By integrating the curve obtained with Eq. (3) between time zero and the end of the test it is possible to calculate the total mass of carbon consumed during the test:

$$\dot{m}_{\text{C consumed}} = \int_{0}^{t_f} \dot{m}_{\text{C consumed}}(t) \, dt$$  \hspace{1cm} (4) \hspace{1cm}

Assuming that the spherical particle burns according to a constant density shrinking particle model, the char particle diameter as a function of time is given by:

$$d(t_f) = \left[ 6 \left( \dot{m}_{\text{C initial}} - \int_{0}^{t_f} \dot{m}_{\text{C consumed}}(t) \, dt \right) / \pi \cdot \rho_{\text{char}} \right]^{1/3}$$  \hspace{1cm} (5) \hspace{1cm}

The reactions that can occur during the oxy-combustion process are:

- $\text{C(s)} + \text{O}_2 \rightarrow \text{CO}_2$ \hspace{1cm} (A)
- $\text{C(s)} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}$ \hspace{1cm} (B)
- $\text{C(s)} + \text{CO}_2 \rightarrow 2 \text{CO}$ \hspace{1cm} (C)
- $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$ \hspace{1cm} (D)

where (A) and (B) represent carbon combustion reactions, (C) carbon gasification by CO$_2$ and (D) homogeneous CO oxidation reaction. In order to check if reaction (D) occurred, a test was done in which a mixture of CO and O$_2$ was introduced in the fluidized bed (without the presence of a char particle) first at ambient temperature and then at 850°C, and the concentration of CO at the exit was measured in both cases. It was observed that at 850°C the concentration of CO at the exit significantly decreased when compared to ambient temperature, meaning that in the conditions of the tests reaction (D) is not negligible.

### 3. Results

In Fig. 3A the typical concentration curves of CO and O$_2$ at the exit of the bed are shown, for a combustion test with 2% O$_2$ at the inlet. The absence of peaks or changes in the slope of the CO curve reveal that no particle fragmentation occurred during the test. Using the data from these curves together with Eqs. (3) and (5) it was possible to determine the variation of the particle diameter with time. As stated previously, some of the combustion tests were performed with a thermocouple inserted in the char particle to measure its temperature during the test. Table 2 reports the results in terms of the peak temperature difference between the particle and the bed. For oxygen concentrations larger than 2% the error done by considering that the char particle has the same temperature as the bed can be larger than 10°C.

Another series of tests was performed at 850°C to quantify how important is reaction (C) during the tests. A typical outlet CO concentration profile obtained during a gasification test (100% CO$_2$) is shown in Fig. 3B. The gasification test clearly shows a much longer reaction time with respect to the combustion ones.
Figure 3  A) CO and O₂ concentration profiles during a typical oxyfiring char combustion test, $T = 850°C$, O₂ = 2% (v/v); B) CO concentration profile during a typical char gasification test, $T = 850°C$, CO₂ = 100% (v/v).

Figure 4A reports the carbon burning rate (calculated with Eq. (3)) as a function of the particle diameter for the oxyfiring combustion tests at different O₂ inlet concentrations. Results show that the combustion rate increases as the concentration of O₂ in the bed increases. This result can be expected both in the case of kinetically controlled and diffusion controlled combustion. Figure 4A also shows that the combustion rate increases almost linearly with the particle diameter, indicating that diffusion of oxygen through the particle boundary layer is likely to control (at least partially) the burning process, as it is the case during air combustion [7].

Figure 4B shows the carbon consumption rate as a function of time for the same gasification test shown in Fig. 3B. For this test the curve was not plotted as a function of diameter, since in these conditions the constant density shrinking particle model (and in turn Eq. 5) is likely not to apply anymore. By comparing Figs. 4A and 4B it can be clearly noted that the gasification reaction rate at 850°C is always slower than the combustion rate and that it is less dependent on the actual char particle mass (especially in the first half of the run, see Fig. 4B), denoting a significant contribution of the intrinsic kinetics on the reaction rate. Nevertheless, the gasification rate under high CO₂ bulk concentrations at 850°C is not negligible, contrary to what happens under typical air combustion conditions [7].

The carbon mass balance for the char particle was calculated as the initial carbon mass in the particle minus the total amount of carbon consumed. For the tests under oxyfiring combustion conditions this balance had an absolute error which was always less than 5%. On the other hand, for the gasification tests the error was in the order of 20% (the calculated consumed mass was smaller than the initial mass of carbon). This suggests that abrasion by attrition is important during the gasification tests and that part of the char probably exited the reactor as elutriated material without reacting.

**Tab. 2  Peak temperature difference between the char particle and the bed for different inlet oxygen concentrations.**

<table>
<thead>
<tr>
<th>Inlet O₂ concentration (% v/v )</th>
<th>Peak temperature difference (°C)</th>
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<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>4.5</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
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</tbody>
</table>

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**Fig. 4** Carbon consumption rates: A) as a function of particle diameter during oxyfiring char combustion tests at different O₂ concentrations, T = 850°C; B) as a function of time during a typical char gasification test, T = 850°C, CO₂ = 100% (v/v).

4. Conclusions

Results from the preliminary experimental tests showed that during oxy-combustion of coal in a bubbling fluidized bed at 850°C, besides the heterogeneous combustion reactions, the CO₂ gasification reaction and the homogeneous CO oxidation reaction are not negligible.

During coal oxyfiring the temperature of the particle is approximately equal to the bed temperature up to an oxygen concentration of 2%, for higher concentrations the temperature of the particle is considerably higher than the bed one.

The gasification reaction is always slower than the combustion reaction, and intrinsic kinetics is likely to control the gasification rate. During gasification conditions particle attrition phenomena appear to be more important than under combustion conditions.

5. Acknowledgements

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6. References