Oxy-combustion of high rank coals

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Abstract
One of the ways to face the abatement of CO₂ emissions in power plants is the combustion of coal using oxy-fuel technology. In this case coal would be burned in an O₂/CO₂ atmosphere and the flue gas would consist mainly of CO₂ which after condensation of water could be quasi-ready for storage. Most of the work related to oxy-fuel combustion has been applied to high volatile coals. In this study run of mine and single seam coals ranging in rank from low volatile bituminous to meta-anthracite have been burned under oxy-fuel combustion conditions.

A drop tube furnace (DTF) operated at 1300 °C with oxygen concentration in CO₂ ranging from 0 to 30 % has been used to prepare the chars. The results have been compared with those of conventional combustion in air using the same DTF. Characterisation of chars included measurement of reactivity in a thermobalance at 550 °C, determination micropore surface area by CO₂ adsorption at 0°C and the petrographic examination.

The results indicated similar conversion under O₂/CO₂ and O₂/N₂ atmospheres for equivalent O₂ concentration in the lowest rank members of the series whereas highest conversion under oxy-fuel combustion conditions were obtained for the highest ranked coals. The characteristics of the chars (CO₂ Surface area and reactivity) were similar up to 10% oxygen concentration in the reacting gas and further increase in oxygen resulted in loss of porosity and reactivity. 10% O₂ in CO₂ is also the threshold for observing a significant drop in particle size. Optical microscopy revealed that the semi-anthracites still retained certain plasticity as seen by the development of devolatilisation voids.

Keywords: Oxy-combustion, char microscopy, char reactivity, CO₂ capture

1. Introduction

Oxy-fuel pulverized coal combustion is one of the most promising technologies to be considered if it is assumed that coal combustion is going to maintain its role in the production of energy in the forthcoming years. Indeed coal has proven a significant stability in supply and costs that is very appreciated by the agents having to design economic politics. Nevertheless the utilization of coal necessarily pass through finding an economic way to capture CO₂ in order avoid the emission of greenhouse gases. Oxy-fuel combustion consists on burning the fuel in a nitrogen-free atmosphere (O₂/CO₂ mixtures) so that the flue gas consist of vapour easily condensable and CO₂ ready for compression and storage. The main arguments in favour of oxy-fuel technology are typically listed as: it is a technology essentially similar to the current pulverised coal technology, it might be retrofitted in existing plants and it brings about a simultaneous reduction of SOₓ and NOₓ whereas the arguments against are mainly the high price for
the Oxygen separation unit and the uncertainty on the effect of air-leaks (Anheden et al., 2005).

The way in which the higher specific heat of CO₂ and the lower volume occupied by this gas affect heat transfer and residence time still must be determined for different types of coal (Buhre et al., 2005). Studies comparing performance under O₂/CO₂ and O₂/N₂ reacting atmospheres have shown to certain extent contradictory results. Liu et al (2005) reported percentages about 30% O₂ in CO₂ to reach similar burnout as in air and accordingly Alvarez et al (2005) found lower conversions under O₂/CO₂ than under O₂/N₂ for equivalent oxygen concentration. Overall the explanations provided for lower oxy-fuel burnouts compared to conventional combustion dealt with the higher specific heat of CO₂ which lowers flame temperature whereas the longer residence time has been considered as responsible for higher conversions (Elliot et al., 2005).

Most of the studies carried in oxy-fuel atmosphere dealt with the behaviour of low rank or high volatile bituminous coals (Chui et al., 2003; Elliot et al., 2005, Liu et al., 2005) in which large amounts of volatile matter are emitted during the early devolatilization steps. This study follows that of Borrego et al. (2007) and focus on the behaviour of low volatile fuels including a petroleum coke. Various O₂/CO₂ proportions have been tested and the results are compared with those of conventional combustion in air.

2. Experimental

The selected fuels were Spanish high rank coals from El Bierzo coal mining area. The area essentially produces anthracites although significant differences in maturity still exist between different beds. A typical steam blend from the area was used and also some of the single coals comprised in the blend. A petroleum coke in the range of volatile matter content was also used for comparison. Proximate, Ultimate and Petrographic analyses were performed according to the appropriate ISO standards.

Coal chars were prepared in a drop tube reactor at 1300 °C under air and under five different O₂/CO₂ oxy-fuel atmospheres (0 to 30% Oxygen). The reactor is a furnace which surrounds two concentric alumina tubes (70 and 50 mm inner diameter, 1.30 and 1 m long, respectively). The reacting gas (600 Lh⁻¹) was injected at the bottom of the outer cylinder and was preheated while flowing upwards. When at the top of the outer cylinder, the gas was forced onto the inner tube through a flow straightener, and the gases flowed downwards and left the reactor through a water-cooled collection probe. The fuel particles were entrained (1 g min⁻¹) by a jet of non-preheated gas of the same composition than the reacting gas (300 Lh⁻¹) to a water-cooled injection probe placed on top of the inner tube. The estimated residence time of the particles in the reactor was 0.3s. The chars left the reactor through the collection probe, and an extra nitrogen flow was added to the exhaust gases in order to quench the reaction and improve the collection efficiency in the cyclone. Burnout was calculated with the ash tracer and assuming that ashes do not suffer further transformation in the reactor using the expression

\[ \text{Burnout (\%)} = 1 - \left[ \frac{\text{Ash}_{\text{coal}}}{100 - \text{Ash}_{\text{coal}}} \right] \times \left[ \frac{100 - \text{Ash}_{\text{char-comb.}}}{\text{Ash}_{\text{char-comb.}}} \right] \times 100 \]
The surface area of micropores (<2 nm in diameter) was calculated using the Dubinin-Radushkevich (D-R) equation from CO₂ adsorption data at 273 K, which were obtained using a Micromeritics ASAP 2020. The Brunauer-Emmett-Teller (BET) theory was applied to the N₂ adsorption data at 77 K to obtain the surface area on selected samples. The surface area data were calculated on an ash-free-basis considering a value for the ashes of 0.8 m²/g⁻¹. The rate of char combustion was isothermally recorded using a Perkin Elmer TGA7 thermal analysis system. A small quantity of char (13 mg) was homogeneously spread at the bottom of the platinum crucible and then heated up to 550 °C under a nitrogen flow (35 cm³ min⁻¹) at a heating rate of 25 °C min⁻¹. After weight stabilisation, nitrogen was replaced by air at the same flow rate and the temperature was maintained until combustion was completed. At this low temperature and using such small sample sizes, bed effects in the thermobalance can be ruled out and the kinetic control of the reaction is ensured. The reactivity was calculated as $R = 1/m_0(dm/dt)$ where $m_0$ is the initial ash-free mass of coal. Samples were embedded in polyester resin and polished for petrographic examination under incident polarised light. Also the maximum reflectance of the particles was measured.

2. Results and Discussion

The chemical and petrographic analyses of the samples are shown in Table 1. PC is the petroleum coke with very low ash content and significant sulphur content. Its volatile matter is in the range of the values from the coals. BL is a blend of anthracites with an average vitrinite reflectance of 3.30 % and values for volatile matter and elemental composition intermediate between those of the highest rank individual coals (B4 and B5) and the anthracite B1. According with recent ISO classification of coals (ISO 11760:2005), all the samples are vitrinite-rich with moderate to low sulphur contents and moderate to high ash contents. Sample B2 contains around 15% of natural coke, which is common in the area due to intrusive rocks. Samples from anthracite C, B and A intervals, ordered by increasing reflectance are represented (ISO 11760:2005), which are roughly equivalent to the semianthracite, anthracite and metaanthracite categories in the ASTM classification system (ASTM D388-99; 2004).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Ash db %</th>
<th>VM daf %</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>Rr</th>
<th>V vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL</td>
<td>29.0</td>
<td>8.9</td>
<td>93.21</td>
<td>3.17</td>
<td>1.20</td>
<td>2.00</td>
<td>1.43</td>
<td>3.30</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>0.4</td>
<td>9.1</td>
<td>90.41</td>
<td>4.14</td>
<td>2.04</td>
<td>0.13</td>
<td>3.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>15.5</td>
<td>9.9</td>
<td>91.36</td>
<td>3.67</td>
<td>1.34</td>
<td>1.99</td>
<td>2.01</td>
<td>2.44</td>
<td>99.4</td>
</tr>
<tr>
<td>B2</td>
<td>14.1</td>
<td>8.3</td>
<td>93.3</td>
<td>3.2</td>
<td>1.2</td>
<td>1.4</td>
<td>0.9</td>
<td>2.81</td>
<td>84.6*</td>
</tr>
<tr>
<td>B3</td>
<td>45.8</td>
<td>9.9</td>
<td>87.6</td>
<td>2.9</td>
<td>2.9</td>
<td>6.2</td>
<td>2.2</td>
<td>3.35</td>
<td>98.7</td>
</tr>
<tr>
<td>B4</td>
<td>18.2</td>
<td>3.0</td>
<td>96.03</td>
<td>1.16</td>
<td>0.41</td>
<td>1.37</td>
<td>0.87</td>
<td>5.13</td>
<td>98.3</td>
</tr>
<tr>
<td>B5</td>
<td>23.8</td>
<td>4.8</td>
<td>95.10</td>
<td>1.11</td>
<td>0.48</td>
<td>1.80</td>
<td>1.32</td>
<td>5.14</td>
<td>99.1</td>
</tr>
</tbody>
</table>

VM= Volatile matter; Rr=random vitrinite reflectance; V=vitrinite; L=liptinite; I=inertinite. db= dry basis; daf=dry-ash-free basis, vol= volumen. *=15.2 % of natural coke

Figure 1 shows the burnouts achieved by the various coals under the oxy-fuel conditions tested. Generally it is expected that at the high heating rates and temperature in the reactor the volatile yields would be higher than the proximate volatiles. The burnouts
for the CO₂ char ranged between 0 and 12%, which are values in the range of proximate volatiles. Considering the low volatile matter content and the high ash content of some of the samples, some lower values of CO₂ char burnouts than those of proximate volatiles could indicate transformations of the mineral matter. In any case the low burnout values at high heating rates reflects the difficulties of anthracite to loose volatiles in such short residence time. The petroleum coke data are not plotted in Figure 1 because the low mineral matter content of the PC introduces large uncertainty in the ash tracer. Indeed for the various conditions tested the ashes of the PC chars varied between 1 and 2 and this represented burnouts between 60 and 80%. Figure 1 also shows rather similar yields for 0 and 5% O₂ content chars indicating that this amount of oxygen was not enough to promote significant combustion. The burnout trends did not follow the vitrinite reflectance sequence as observed by the higher burnouts of B3 compared to B1 and B5 compared to B4. Only B5, the highest rank anthracite with moderate ash content, exhibited sistematically lower burnouts at any conditions tested. The mineral matter appears to exert a possitive effect in the combustion of anthracites as it represents imperfections in the structure probably facilitating the diffusion of oxygen (Menéndez et al., 1994). The Only an appreciable difference is observed for the lowest rank anthracite (B1). Burnouts close to 90 % were achieved with 30% O₂ in CO₂.

The comparison of the yields under oxy-fuel and conventional combustion atmospheres is shown in Figure 2 in which the burnouts under air (21%O₂ in N₂) are plotted versus the burnout data for 21%O₂ in CO₂. The results indicate rather similar burnouts for most of the samples under both operating conditions except for the highest rank anthracites that show better performance under oxy-fuel atmosphere. This is a different result to

![Figure 1](image_url)

**Figure 1.** Burnout of the oxy-fuel combustion experiments in relation to oxygen concentration in the reacting gas.
that observed for high volatile bituminous coals using the same device and conditions (Alvarez et al., 2005) in which lower burnouts for oxy-fuel chars were observed.

\[ \text{Figure 2. Burnout under air (21%O}_2\text{ in N}_2\text{) and under oxy-fuel atmosphere (O}_2\text{/CO}_2\text{) with similar oxygen concentration.} \]

The reactivity of the oxy-chars shown in Figure 3 indicated that oxygen did not modify the reactivity of the chars up to contents over 10% O\text{ in CO}_2\text{ and a significant drop in reactivity was first observed for the 21% O}_2\text{ oxy-char. No variation in reactivity was observed for the petroleum coke char. The variation of surface area of both micro and mesopores was also evaluated through the N}_2\text{ and CO}_2\text{ adsorption isotherms of selected chars. The oxy-chars essentially contained micropores as seen by the surface areas based on N}_2\text{ adsorption, which were always below 20 m}^2\text{g}^{-1}. The evolution of CO}_2\text{ surface areas is shown in Figure 3. According to the reactivity results the significant drop in surface area occurred for the oxy-char prepared with 21% O}_2\text{ in CO}_2\text{. The lowest values in S}_\text{CO}_2\text{ were those of the lowest reflecting anthracite that still retained certain plasticity as seen by the appearance of the chars.} \]

As in the case of the burnouts CO}_2\text{ surface areas and reactivity were compared for the char prepared in air and the oxy-char prepared with similar amount of oxygen (Figure 4). The reactivities were slightly higher for the oxy-fuel coal chars whereas lower for the oxy-fuel petroleum coke char compared to their air counterparts. Accordingly the CO}_2\text{ surface areas were also higher for the oxy-fuel coal chars compared to their air counterparts.}
Figure 3. Variation of reactivity and micropores surface area for the oxy-chars prepared under different oxygen concentrations.

Figure 4. Relationship between reactivity and micropore surface area of chars obtained under similar oxygen concentration (21%) in O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres.

The aspect of the chars was examined with an optical incident light microscope. The images characterizing the different types are shown in Figure 5. The lowest rank anthracite still retained certain plastic properties as shown by the devolatilization voids observed, which is in agreement with the lowest surface area of its chars. Nevertheless plasticity was rather limited because the particles maintain a sub-angular shape. Under the experimental conditions used in this work the anthracite with a vitrinite reflectance of 2.81% hardly exhibit plasticity. The highest rank anthracites did not show any fusion sign and the passage through the reactor mainly resulted in an enhanced order in their structure and combustion through the structural planes. The petroleum coke oxy-char had an strongly anisotropic texture of small domains and in the reactor shrinkage cracks were generated which facilitated the combustion.
Conclusions

The comparison of combustion behaviour of low volatile coals under air and under oxy-fuel atmosphere with equivalent oxygen concentration revealed higher burnouts under oxy-fuel atmosphere. The chars generated had overall similar characteristics although trends for slightly higher reactivity and micropores surface area were observed.

High mineral matter content appeared to facilitate the combustion of the anthracites offering discontinuity surfaces through which combustion can progress.

The lowest rank anthracite having about 10% volatile matter and 2.44 % vitrinite reflectance still retained certain plastic properties at the time-temperature conditions at which the particles were submitted whereas the highest rank anthracites (VM~4% and R_r~5%) did not fuse in the reactor but enhanced the degree of order of their carbonaceous structure.

No specific difficulties are envisaged for the use of high rank coals with oxy-fuel technology and enhanced yields could be expected compared to conventional combustion conditions.

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