Combustion behaviour of ultra clean coal obtained by chemical demineralisation
F. Rubiera¹*, A. Arenillas¹, B. Arias¹, J.J. Pis¹, I. Suárez-Ruiz¹, K.M. Steel² and J.W. Patrick²

¹ Instituto Nacional del Carbón, CSIC. Apartado 73. 33080-Oviedo. Spain
² School of Chemical, Environmental and Mining Engineering. Nottingham University. University Park. Nottingham, NG7 2RD. UK

Abstract
The increasing environmental concern caused by the use of fossil fuels and the concomitant need for improved combustion efficiency is leading to the development of new coal cleaning and utilisation processes. However, the benefits achieved by the removal of most mineral matter from coal either by physical or chemical methods can be annulled if poor coal combustibility characteristics are attained. In this work a high volatile bituminous coal with 6% ash content was subjected to chemical demineralisation via hydrofluoric and nitric acid leaching, the ash content of the clean coal was reduced to 0.3%. The original and treated coals were devolatilised in a drop tube furnace and the structure and morphology of the resultant chars was analysed by optical and scanning electron microscopies. The reactivity characteristics of the chars were studied by isothermal combustion tests in air at different temperatures in a thermogravimetric system. Comparison of the combustion behaviour and pollutant emissions of both coals was conducted in a drop tube furnace operating at 1000 °C. The results of this work indicate that the char obtained from the chemically treated coal presents very different structure, morphology and reactivity behaviour than the char from the original coal. The changes induced by the chemical treatment increased the combustion efficiency determined in the drop tube furnace, in fact higher burnout levels were obtained for the demineralised coal.

Keywords: Coal demineralisation; nitric acid; hydrofluoric acid; char reactivity; drop tube furnace
Introduction

Worldwide demand for energy will continue to increase in the future primarily due to the economic growth and industrialisation of the developing nations. Fossil fuels will account for most of this energy demand. Currently, coal totals 25% of all kinds of energy in the world, with 50% for the developing Asian countries. According to a report by the US-DOE [1], coal is projected to retain the largest market share of electricity generation. The widely distributed and abundant coal reserves, the political stability of coal exporting countries, the relatively low price of coal supply along with awareness on stable access to oil and natural gas in the future, are the most recurrent quoted advantages for the continuing use of coal. There is, however, a growing environmental concern on the deleterious effects caused by the use of fossil fuels such as acid rain (NO\textsubscript{x}, SO\textsubscript{2}), greenhouse effect (CO\textsubscript{2}, N\textsubscript{2}O), and the release of trace elements, among others. In this respect many industrialised nations are introducing tighter regulations to control emissions of pollutants [2]. After the Kyoto Protocol the world’s developed countries are placing particular focus on the reduction of fossil fuels in general, but coal is seen as the main fuel to be reduced because it emits the greatest amount of CO\textsubscript{2} per energy unit when it is burnt. The goal for developing nations, where coal consumption will increase, and industrialised countries, will be to maximise development while minimising gases emissions. This can be achieved by a more efficient use of coal in the emerging clean coal technologies that incorporate gas turbines. In these systems the high temperature combustion gases must be cleaned and the ash particles removed before they enter the gas turbine to avoid problems of erosion, corrosion and fouling. This cleaning process has encountered many difficulties and limits the overall efficiency of a generating plant system. On the other hand, heat loss due to the endothermic decomposition reactions of the mineral matter can be significant [3]. Ultra clean coal (UCC) is defined as a very low ash coal (<1 wt%) with various potential uses such as carbon feedstock for the production of aromatic chemicals and materials instead of oil, carbon source for the silicon smelting industry, and for fabrication of carbon anodes to replace petroleum coke [4]. The main application of UCC, however, would be as a fuel for its use in advanced power
generation technologies such as direct firing in gas turbines [5]. In this case ultra clean coal with very low ash levels will have to be used to avoid damage of the gas turbine blades [6]. Therefore, in recent years significant effort has been made to produce clean coal products in order to reduce both pollutant emissions and ash content. Physical cleaning techniques cannot reduce coal mineral components to very low levels, and chemical demineralisation has to be used for this purpose [7]. Leaching with nitric acid [8], hydrofluoric acid [9], caustic soda in the Gravimelt process [10], mixtures of hydrofluoric/hydrochloric acids [11], calcium hydroxide/hydrochloric acid [12], sodium hydroxide/hydrochloric acid [13] and different acids [14] have been utilised. Then, evaluation of the combustion behaviour of coal after demineralisation has to be conducted [15-18], as the advantages of using such cleaning processes can be cancelled out if poor coal reactivity performance is attained.

Therefore, in this work the combustibility characteristics of a very low ash bituminous coal obtained after chemical demineralisation with aqueous HF followed by aqueous HNO₃ were evaluated. To this end devolatilisation tests were carried out in a drop tube furnace (DTF) and the isothermal reactivities in air at different temperatures of the chars obtained from the parent and cleaned coal samples were compared. Structural changes of the chars were also observed by optical and scanning electron microscopies. In addition, the combustion behaviour of the raw and demineralised coal samples was also evaluated by burnout tests in a drop tube furnace, with simultaneous monitoring of pollutant emissions.

**Experimental**

Demineralisation tests were carried out on the 1-2 mm size fraction of a high volatile bituminous coal, HW. Experiments were performed with a coal sample size of 30 g and a solution volume of 100 ml, and carried out in a 500 ml Teflon beaker. The demineralisation process is based on that patented by Lloyd and Turner [9], which utilises HF. This process was modified to include HNO₃ as the first process was developed for coals with low levels of pyrite, which is unreactive towards
HF. In this work coal HW was treated with 25% HF for 8 hours at 60 °C, washed with hot distilled water, and soaked in 25% HNO₃ for 16 hours at 60 °C and finally washed with hot distilled water. A more complete description of the cleaning procedure and its optimisation is given elsewhere [19]. Table 1 shows the chemical and petrographic analyses of the initial untreated sample of coal HW and those of the treated coal sample, HW-D. Another sample treated only with HF (HW-HF) was obtained and is also included in Table 1 for comparison purposes.

Combustion and devolatilisation tests were conducted in a drop tube furnace with a reaction chamber of 40 mm i.d. and a maximum length of 1700 mm. Sized coal (38-150 µm) was fed by a rotary mechanism and introduced with the primary air into the reaction zone. The heating compartments were controlled to maintain a temperature of 1000 °C over the reactor height, and this was confirmed by measuring the axial temperature profile with a thermocouple. A particle residence time of 2 s was maintained in the experiments. Devolatilisation tests were carried out under nitrogen and various excess air ratios were used in the combustion tests. The reaction products were quenched by aspiration into a stream of nitrogen using a water-cooled probe. The solids were removed by filtration and the exhaust gases during combustion were analysed for O₂, CO, CO₂, N₂O and NOₓ (NO+NO₂).

The pyrolysis chars were subsequently oxidised isothermally in air at various temperatures between 450 and 600 °C in a thermogravimetric analyser (TGA). A sample mass of approximately 5 mg was used, the chars were heated under 50 ml min⁻¹ of nitrogen from room temperature at 15 °C min⁻¹ up to 1000 °C, and held at this temperature for 10 min. Thereafter, the chars were cooled to the desired temperature and air was admitted into the system. The burnoff or carbon conversion (X) is defined as the ratio of the mass loss (m₀⁻m) relative to the initial mass of carbon contained in the raw char (m₀) on a dry ash-free basis. The mass of the sample after completion of the test was taken as that of the ash.

Coal samples for conventional petrographic analysis were prepared following a modified procedure of the ISO 7404/2 standard. Maceral analysis and vitrinite reflectance determinations were carried
out using a MPV Combi Leitz microscope according to ISO 7404/3 and ISO 7404/5, respectively. The structure and optical texture of the derived chars was conducted in a Zeiss Axioplan microscope in reflected white light and also using crossed polars and a 1λ retarding plate. The morphological surface of the chars was examined with a Zeiss DSM 942 scanning electron microscope.

Results and discussion

Modification in the chemical and technological properties

Table 1 shows that demineralisation using the HF/HNO₃ two-stage leaching sequence modified the proximate and ultimate analyses of the treated coal, HW-D. There is a great reduction in ash and sulphur contents, which are much lower than those of the sample treated only with aqueous hydrofluoric acid, HW-HF. A marked oxidation was produced in HW-D in comparison with HW-HF, and this was caused by the treatment with 25% HNO₃, which is a strong oxidising agent. The nitrogen content also experienced a great increase due to nitrification of the sample with incorporation of nitro groups, -NO₂, as it has been found in previous FTIR studies on these samples [20]. Oxidation also produced a complete loss of fluidity of HW-D, as inferred from its nil Free Swelling Index. The sample treated in HF still shows some signs of plasticity with a FSI value of 1. A calorific value loss of 13.6% was attained after demineralisation with HF/NO₃.

Morphology of the chars obtained after devolatilisation in the DTF

The outer surface of the chars from the raw coal, HW, and from the treated sample, HW-D, was observed by SEM. It can be seen in Figure 1 that the particles from the pyrolysed raw coal, HW, are of cenospheric type, presenting a swollen structure and plastic features with some degasification holes on their outer surface. The formation of these structures is typical of high volatile bituminous coals with plastic properties, as it is the case of HW. In contrast, the char particles from HW-D display rather different structures as can be seen in Figure 2. In general most of the particles show
an angular shape, with large fissures and microcracks on the surface. For a given particle, signs of softening and non-plastic structures can be distinguished in different zones of the char surface. Some devolatilisation holes were also observed but their size is smaller than those observed on the char from the raw coal, HW.

The predominant structures of the HW char, shown by optical microscopy, are cenospheres -tenui and crassospheres- (Figure 3a). These type of structures are characterised, according to the ICCP classification scheme [21], by the presence of <25% unfused material and a porosity higher than 80% for the tenuispheres and higher than 40% for the crassospheres. Network morphotypes (tenui and crassinetwork) with less than 25% of unfused material and a porosity higher than 40% were also found as it is shown in Figure 3b. These chars are less abundant than the cenospheres. Mixed porous and mineroid type particles (the latter with more than 50% mineral matter) were also distinguished (Figure 3c) but this was more the exception as they were present in a minor proportion. Most of the chars from the parent coal, HW, present anisotropy, and the optical texture of the walls resembles a fine-grained mosaic. The development of primary and secondary porosity on the char walls is also characteristic in these chars.

The type of char structures developed by the treated HW-D sample is different to that described for HW. Thus, the predominant morphotypes were chars of type similar to that described for inertoid structures in the ICCP classification, and network (mainly crassinetwork) as can be seen in Figures 4a and 4b, respectively. Less abundant were cenospheres (mainly crassispheres, Figure 4c). Scarce fusinoids and mixed dense char types were also found. Mineroid structures were not identified according to the very low mineral matter content of its parent sample. The majority of these char structures are isotropic and only cenospheres develop an anisotropic texture similar to that described for the HW sample. Occasionally some network morphotypes also display anisotropic texture. Finally, chars in these samples are characterised by a low development of devolatilisation vacuoles, which confirms the SEM observations.
Isothermal reactivity in air of the char samples

Gasification temperatures in the range 450-600 °C were used to ensure kinetic control, without diffusional constraints. The gasification rate on the basis of char consumption can be defined as:

\[
R_c = -\frac{dm}{dt} = \frac{1}{1-X} \frac{dX}{dt} = k(CO_2, T)Sc(X) = k_s(T)Sc(X)
\]

(1)

where \( k(CO_2, T) \) is the rate constant, which is a function of the oxygen concentration and temperature, and \( Sc(X) \) is the term related to the variation of carbon active sites with conversion within the char. In this work air was used as the gasifying agent and the oxygen partial pressure was kept constant, thus its effect was included into the constant \( k_s(T) \). The reaction rate constant, \( k_s \), can be expressed in Arrhenius form, and taking logarithms the following expression is obtained:

\[
\ln \left( \frac{1}{1 - X} \frac{dX}{dt} \right) = \ln[k_{so} Sc] - \frac{E_a}{RT}
\]

(2)

where \( k_{so} \) is the pre-exponential coefficient and \( E_a \) is the activation energy. The Arrhenius plots for both chars at different conversion levels are shown in Figure 5. Activation energies at each conversion degree were calculated from these plots. For char HW-D there is a transition from kinetic control regime (Zone I) to chemical kinetic/internal diffusion regime (Zone II), between 550 and 600 °C, thus the activation energies for char HW-D were calculated in the rectilinear region of chemical control (Zone I). The parameters, \( E_a \), and \([k_{so} Sc]\) at different char conversion degrees are given in Table 2 (uncertainties in \( E_a \) expressed as 95% confidence intervals). The activation energy values correspond well with previously published values [22-24]. Assuming that the term \( Sc \) is proportional to the N_2-BET surface area (which may not be true as the active surface area is different than the surface area determined either in N_2 or in CO_2), the pre-exponential coefficients at 0% conversion, \( k_{so}|_{X=0} \), can be calculated. The specific surface areas, \( Sc \), at \( X=0 \) present values of 41 m^2 g^{-1} and 383 m^2 g^{-1}, for chars HW and HW-D, respectively, and the calculated pre-exponential factors being 44 g m^{-2} s^{-1} and 14 g m^{-2} s^{-1} for HW and HW-D, respectively. These values of the chars pre-exponential factors seem to contradict the structural ordering revealed by the anisotropic optical texture presented by char HW, as the pre-exponential factor decreases with an increase in
char structural ordering. However, under the conditions of chemical control the possible catalytic effect of mineral impurities can be of utmost importance. The presence of catalysts produces an increase of the pre-exponential factor. Therefore, while char HW-D was obtained from a highly demineralised coal and no catalytic effects are expected in this char, the catalytic activity of the mineral matter of char HW seems to play a major role in this case. However, the effect of surface area of char HW-D, which is also related to its lower degree of structural order, is predominant in the overall char reactivity.

Combustion behaviour of the raw and demineralised coals evaluated in a drop tube furnace

Comparison of the burnout performance of the parent and treated coal samples was evaluated by conducting combustion tests in a drop tube furnace at 1000 °C, a fixed residence time of two seconds and different excess air ratios. The emissions of SO₂ and NOₓ were also measured during these tests and were expressed as mg of pollutant per gram of fuel burned. It can be observed in Figure 6a that the combustion efficiency of the demineralised coal, HW-D, was higher than that of the original coal, HW, in the range of excess air ratio studied. There is, however, a distinct behaviour in the combustion of both coals; HW is very sensitive to oxygen availability showing a rapid increase in burnout with excess air ratio, i.e., combustion efficiency increases from 79% under sub-stoichiometric conditions (0.95 excess air ratio), to 94% for 37% excess air. The burnout reached by coal HW-D is not affected in the same way, increasing from an already initial high value of 92% at stoichiometric conditions, to 96% for an excess air of 39%. At the temperature of operation of 1000 °C used in this work, diffusion into the pore structure can represent a significant mechanism during char gasification. Therefore, higher combustion efficiency is expected for coal HW-D whose devolatilisation char presents a high surface area. Under more drastic conditions (higher excess air), its burnout does not increase in the extent shown by coal HW. This is ascribed to efficient use of the oxygen available by HW-D even at stoichiometric conditions.
With regard to gaseous compounds emissions in the DTF tests, it can be seen in Figure 6b that there is an increase in NO specific emissions for both coals with excess air ratio as it could be expected. This increase is attributed to the increased oxidant atmosphere and to the increasing burnout of the chars that still contain nitrogen. At higher excess ratios the NO emissions are higher for coal HW-D in accordance with its higher nitrogen content caused by the nitric acid demineralisation treatment. On-going research is being conducted [25] and preliminary results indicate that through optimisation of the acidic treatment conditions ultra clean coals with low nitrogen content can be obtained. The SO₂ specific emissions are displayed in Figure 6c; the most important feature extracted from this figure is the clear and favourable decrease in SO₂ emissions produced by the acid leaching treatment of coal HW-D, which removed most of the pyritic sulphur.

**Conclusions**

Chemical treatment of a high volatile bituminous coal using two-stage leaching sequence with HF/HNO₃ produced an important diminution (95%) in the ash content. The chars obtained after rapid devolatilisation in a drop tube furnace of the raw and demineralised coal samples developed very different structures; the chars from the original coal presented anisotropy while those from the treated coal developed isotropic texture.

The combustion behaviour of the demineralised coal evaluated in the drop tube furnace compared favourably well with that of the parent coal. The SO₂ and NO emissions followed different trends. An important diminution in the SO₂ levels was achieved but the treatment with nitric acid produced an increase in NO emissions.

**Acknowledgements**

Work carried out with a financial grant from the European Coal and Steel Community (Project 7220-EA-017).
References


Table 1. Main characteristics of the parent and cleaned coal samples

<table>
<thead>
<tr>
<th></th>
<th>HW</th>
<th>HW-D</th>
<th>HW-HF</th>
<th>HW (38-150 µm)</th>
<th>HW-D (38-150 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate Analysis</strong> (wt %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash (db)</td>
<td>6.2</td>
<td>0.3</td>
<td>2.2</td>
<td>5.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Volatile Matter (daf)</td>
<td>37.0</td>
<td>41.6</td>
<td>33.6</td>
<td>37.7</td>
<td>38.8</td>
</tr>
<tr>
<td>Fixed Carbon (daf)</td>
<td>63.0</td>
<td>58.4</td>
<td>66.4</td>
<td>62.3</td>
<td>61.2</td>
</tr>
<tr>
<td><strong>Ultimate Analysis</strong> (wt %, daf)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>82.4</td>
<td>70.9</td>
<td>81.3</td>
<td>81.4</td>
<td>70.9</td>
</tr>
<tr>
<td>H</td>
<td>5.9</td>
<td>4.2</td>
<td>5.0</td>
<td>6.3</td>
<td>5.7</td>
</tr>
<tr>
<td>N</td>
<td>2.0</td>
<td>5.3</td>
<td>1.8</td>
<td>1.9</td>
<td>4.8</td>
</tr>
<tr>
<td>S</td>
<td>2.9</td>
<td>1.3</td>
<td>2.7</td>
<td>2.8</td>
<td>1.3</td>
</tr>
<tr>
<td>O</td>
<td>6.8</td>
<td>18.3</td>
<td>9.2</td>
<td>7.6</td>
<td>17.3</td>
</tr>
<tr>
<td>Calorific Value (kcal kg⁻¹)</td>
<td>7761</td>
<td>6705</td>
<td>7856</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Free Swelling Index</td>
<td>6.5</td>
<td>0</td>
<td>1</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td><strong>Petrographic Analysis</strong> (vol %, mmf)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vitrinite</td>
<td>71.7</td>
<td>80.9</td>
<td>-</td>
<td>79.5</td>
<td>76.1</td>
</tr>
<tr>
<td>Liptinite</td>
<td>11.7</td>
<td>7.1</td>
<td>-</td>
<td>9.8</td>
<td>10.8</td>
</tr>
<tr>
<td>Inertinite</td>
<td>16.6</td>
<td>12.1</td>
<td>-</td>
<td>10.7</td>
<td>13.1</td>
</tr>
<tr>
<td>Mean Random Reflectance (%)</td>
<td>0.74</td>
<td>0.74</td>
<td>-</td>
<td>0.83</td>
<td>0.82</td>
</tr>
</tbody>
</table>

¹ by difference
Table 2. Variation of the activation energy, $E_a$, and $[k_{so} \text{ Sc}]$ with char conversion degree

<table>
<thead>
<tr>
<th>X (%)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$[k_{so} \text{ Sc}] \times 10^{-3}$ (s$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$[k_{so} \text{ Sc}] \times 10^{3}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>108 ± 13</td>
<td>4.6</td>
<td>107 ± 25</td>
<td>5.9</td>
</tr>
<tr>
<td>10</td>
<td>112 ± 7</td>
<td>11.2</td>
<td>107 ± 16</td>
<td>8.0</td>
</tr>
<tr>
<td>20</td>
<td>117 ± 7</td>
<td>28.3</td>
<td>110 ± 19</td>
<td>14.5</td>
</tr>
<tr>
<td>30</td>
<td>118 ± 7</td>
<td>35.4</td>
<td>111 ± 16</td>
<td>21.4</td>
</tr>
<tr>
<td>40</td>
<td>116 ± 10</td>
<td>30.3</td>
<td>113 ± 12</td>
<td>34.1</td>
</tr>
<tr>
<td>50</td>
<td>116 ± 10</td>
<td>34.1</td>
<td>116 ± 6</td>
<td>57.3</td>
</tr>
<tr>
<td>60</td>
<td>113 ± 11</td>
<td>23.9</td>
<td>118 ± 3</td>
<td>76.0</td>
</tr>
<tr>
<td>70</td>
<td>115 ± 10</td>
<td>33.1</td>
<td>117 ± 10</td>
<td>74.6</td>
</tr>
<tr>
<td>80</td>
<td>111 ± 15</td>
<td>19.5</td>
<td>122 ± 7</td>
<td>204.4</td>
</tr>
<tr>
<td>85</td>
<td>116 ± 11</td>
<td>42.5</td>
<td>127 ± 5</td>
<td>424.8</td>
</tr>
<tr>
<td>90</td>
<td>105 ± 17</td>
<td>10.6</td>
<td>128 ± 4</td>
<td>595.8</td>
</tr>
</tbody>
</table>
Figure 1.

Combustion behaviour of ultra clean coal obtained by chemical demineralisation

F. Rubiera et al.
Figure 2.

Combustion behaviour of ultra clean coal obtained by chemical demineralisation

F. Rubiera et al.
Figure 3.

Combustion behaviour of ultra clean coal obtained by chemical demineralisation

F. Rubiera et al.
Figure 4.

Combustion behaviour of ultra clean coal obtained by chemical demineralisation

F. Rubiera et al.
Combustion behaviour of ultra clean coal obtained by chemical demineralisation

F. Rubiera et al.
Figure 6.

Combustion behaviour of ultra clean coal obtained by chemical demineralisation

F. Rubiera et al.