The effects of AAEM species on ignition temperature of a Loy Yang brown coal in O$_2$/N$_2$ and in O$_2$/CO$_2$ conditions

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Abstract

The ignition temperatures of a Loy Yang brown coal were investigated in a wire-mesh reactor where the secondary reactions of the evolved volatiles were minimised. Increase in the average particle ignition temperature of 21°C was observed for the brown coal when air (21% O₂ + 79% N₂) was replaced with a mixture of 21% O₂ + 79% CO₂. Experiments were also performed to determine the effects of Alkali and alkaline earth metallic (AAEM) species on ignition behaviour of coal in O₂/N₂ and O₂/CO₂ conditions. Water, ammonium acetate and sulfuric acid sequential extractions were carried out to classify the chemical forms of AAEM compounds and prepared the coal samples from the raw coal. An increase in the average particle ignition temperature of 55 °C both in air and in 21% O₂ +79% CO₂ was observed for H-form coal compared with that of raw coal. The average particle ignition temperature of water-washed coal sample indicated a minimum value and approximately decreased 30 °C both in air and in 21% O₂ +79% CO₂ than that of raw coal.

Combustion was also carried out for Na-exchanged coals and NaCl-loaded coals samples prepared from the brown coal. The average particle ignition temperatures of 0.05 M Na-exchanged coal decrease 48 °C and 42 °C than those of 0.05 M NaCl-loaded coal in air and in 21% O₂ +79% CO₂ respectively, which two samples having a close Na content. It is concluded that the Na in coal as carboxylates (-COONa) and as NaCl can both improve ignition characteristics of coal samples, but carboxylates (-COONa) shows more significant catalytic effect on average particle ignition
1 Introduction

Oxy-fuel combustion of coal is recognized one of the promising new technologies to reduce the emission of CO$_2$ from coal combustion [1-4]. Earlier studies [5-8] have shown some basic understanding about the behavior of coal under the oxy-fuel combustion conditions. An ignition delay of coal particles is widely recognized under oxy-fuel combustions compared with that under conventional air combustion conditions [2, 9]. The influence of heat transfer has been estimated and the delayed ignition and combustion is concluded by the higher heat capacity of CO$_2$ than that of N$_2$ due to the substitution of CO$_2$ for N$_2$ [2]. Our recent studies indicated that the thermal conductivity of gas atmosphere surrounding the particles, the structure of char and reactions involving the char (char-O$_2$ and char-CO$_2$) in different atmosphere can greatly influence the measured particle ignition temperature in a wire-mesh reactor [9]. The ignition temperature is also significantly affected by Alkali and alkaline earth metallic (AAEM) species in the brown coal [9-12]. In air condition, a 29°C ignition delay was observed for acid-washed coal (0.1 M sulfuric acid) compared with raw coal [9]. However, the effects of AAEM species on particle ignition temperature in oxy-fuel combustion conditions remain unclear.
Compared with bituminous coal, the presence of AAEM species in low-rank coal is always an important consideration in the utilisation of brown coal [13-20]. In the current pulverized-coal furnace, the high levels of inherent AAEM present in low-rank coals cause operational problems of slagging, fouling and particle agglomeration [13]. Meanwhile, the AAEM species in low-rank coal can also act as excellent catalysts for coal/char. A large number of studies have been carried out on the catalytic effects of AAEM species during pyrolysis or gasification of coal/char [14-17].

It was concluded by some researchers that the catalytic activity of alkali and alkaline earth salts correlates well with the first ionization energy of the metal: the lower the first ionization energy, the higher the catalytic activity [14, 18]. It was also widely known the influence of chemical form of AAEM on the catalytic activity. For example, our earlier investigation indicates that the Na loaded into the Loy Yang brown coal substrate as NaCl and as Na carboxylates (-COONa) can have very different catalytic effects on the char reactivity [15-17, 19]. As will be described in more details below, content of Na is the highest level among the AAEM species (e.g., Na, Ca, K and Mg) in Loy Yang brown coal. Generally, the Na species in coals exist in four main forms: as carboxylates, as soluble salts (NaCl), as intercalated groups and as aluminosilicate (clay) minerals [15, 20]. The Na species exist in a typical Victorian brown coal mainly in the front two forms. Although some investigations into the catalytic effects of AAEM species have been carried out [9-20], it is still not clear the effects of chemical forms of AAEM species on coal/char ignition behaviour. The purpose of this study is to systematically investigate the fates and roles of different AAEM compounds, especially Na species, on ignition temperature of coal particle.

Coal ignition was always described as a continuous reaction process between the fuel and oxidizer, coal flashing was generally used to identify ignition [9,21]. Coal particles can ignite either homogeneously or heterogeneously depending on different reaction conditions, which including particle size, heating rate, final temperature, gas pressure and so on [22-25]. In practice, a clear
distinction between homogeneous and heterogeneous ignition is quite difficult or nearly impossible. If possible, it is clearly essential to study the ignition of coal/char particles in the absence of volatiles. In this work, the ignition temperatures of a Loy Yang brown coal were investigated in a wire-mesh reactor where the secondary reactions of the evolved volatiles were minimized. The cause of using wire-mesh reactor to check ignition temperature of coal particles can be also found elsewhere [9]. Briefly, the wire-mesh reactor features a relatively accurate control of particle time-temperature history compared with the other common methods, such as thermogravimetric analysis (TGA) and drop tube furnace, which are mainly based on the conventional measurement of the minimum gas temperature required for the ignition of coal/char particles [26-27]. On the other hand, the operated conditions of the TGA techniques (e.g., in terms of coal sample stacking and very slow heating rates) are quite different from those in industrial furnaces.

This study aims to evaluate the effects of different chemical forms of AAEM species on the ignition behaviour of a Victorian brown coal during air and oxy-fuel combustion. The ignition temperatures of different prepared coal samples were investigated in a wire-mesh reactor in the absence of significant secondary reactions of volatiles.

2. Experimental

2.1 Coal preparation

Samples of Loy Yang brown coal with a particle size between 106 and 150 μm were used in this study. The coal samples are hereafter termed as “raw coals” and their properties are listed in Table 1. The raw coal was also sequential extracted by water, ammonium acetate and sulfuric acid to
make three coal samples containing virtually different chemical forms of AAEM species. The details of washing sample preparation can be found elsewhere [15, 20, 28]. Briefly, the raw brown coal samples was stirred in ultrapure water for 24 h, then filtered and partially dried at low temperature (<35°C) to prepare the water-washed coal sample. The water-washed coal sample was then extracted in 0.5 M ammonium acetate solution for 24 h and partially dried at low temperature to obtain the ammonium acetate-washed coal sample. The ammonium acetate-washed coal sample was finally washed in 0.1 M sulfuric acid for at least 16h under nitrogen atmosphere and then washed with double-distilled water and dried at low temperature (<35°C) to prepare the H-form coal sample containing virtually no AAEM species.

The Na-exchanged and NaCl-loaded coal samples prepared from raw coal were also combusted in the wire-mesh reactor. The Na-exchanged and NaCl-loaded samples were prepared by adding the H-form coal samples into the 0.05 M, 0.1 M and 0.5 M solutions of sodium acetate and sodium chloride respectively. The mixtures were stirred under nitrogen atmosphere and then dried at low temperature (<35°C) to prepare the coal samples. The procedures of these treatments have been detailed elsewhere [28].

2.2 Ignition temperature determination in wire-mesh reactor

A wire-mesh reactor similar to that described by Gibbins and co-workers [29] and Li and co-workers [30, 31] was used in this study to determine coal ignition temperature. The details of experimental process can be seen in our recent work [9]. In this work, about 5mg coal sample distributed within a round working area of 20 mm diameter between two layers of wire mesh. The
distribution of coal particles approached almost that of “single particles”: the particles certainly existed as a single layer and did not come into significant contact with each other. The mesh was then heated up at a rate 10 K s\(^{-1}\) to 700 °C while a stream of O\(_2\)/N\(_2\) or O\(_2\)/CO\(_2\) mixture continually passed through the mesh at 4.0 L min\(^{-1}\) (measured under ambient conditions) to carry the evolved volatiles away. As soon as particles ignited, the heat released caused a sudden increase in mesh temperature and a decrease in the thyristor control voltage (i.e. a decrease in electrical power input into the system). This temperature is considered to be the particle ignition temperature. The particle ignition could also be observed visually. The detection of particle ignition by monitoring sudden mesh temperature increase agreed well with the visual observation of particle ignition. Each ignition temperature shown hereafter represents the average of up to ten repeats under each set of conditions.

### 2.3 Quantification of AAEM

An inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to analyze the contents of AAEM species. The coal samples were dissolved in a fuming nitric acid and a hydrogen peroxide solution. The contents and different chemical forms of AAEM species in Loy Yang coal samples were shown in Table 2. Table 3 gives the Na contents of Na-exchanged and NaCl-loaded coal samples of Loy Yang brown coal.

### 2.4 BET determination of coal particle

An instrument of Micromeritics ASAP 2020 with single-point BET nitrogen adsorption method was used to determine the BET surface area of the samples. The widely used method was applied
in this study to determine the pore surface area of coal particle from gas adsorption isotherms which using N$_2$ at -196°C as adsorptive.

3. Results and discussion

3.1 Effects of indigenous AAEM on ignition temperature

In this work, experiments were carried out by using brown raw coal, water-washed coal, ammonium acetate-washed coal and H-form coal samples, which containing different chemical form of AAEM species. These four coal samples were termed as sample 1, 2, 3 and 4 respectively. As is shown in Fig. 1, brown raw coal (sample 1) indicates the average ignition temperatures of 447 °C in air and 471 °C in 21% O$_2$ + 79% CO$_2$ conditions. An increase in the average particle temperatures of 30 °C and 55 °C was observed for the ammonium acetate-washed coal (sample 3) and H-form coal (sample 4) respectively both in air and in 21% O$_2$ + 79% CO$_2$. This observation indicates that the particle ignition temperatures under the oxy-fuel combustion conditions for a given oxygen concentration (21% in this case) is higher than that under the conventional air combustion conditions. The data in Fig. 1 also show that the average ignition temperatures of water-washed coal (sample 2) decrease about 30°C than those of Loy Yang raw coal both in air and 21% O$_2$ + 79% CO$_2$, although the higher AAEM contents of raw coal was shown in Table 2. It was estimated that some inorganic minerals in brown coal was removed as well as water-soluble AAEM species and the coal surface area was also changed due to water-leaching when raw coal was washed by ultrapure water [32]. As is shown in Fig. 2, compared with raw coal (sample 1), the BET surface area of water-washed coal (sample 2) increases and those of ammonium acetate-washed and H-form coals (samples 3 and 4) decrease. Comparison of the data in Figs. 1 and 2 reveals a close correspondence between the ignition temperature and the BET surface area. However, the coal
samples (samples 3 and 4) represent the equivalent BET surface area but significantly different ignition temperature. It is clear that the content of AAEM and chemical form are important factors influencing the ignition of coal/char particles.

Mechanisms classified as electron-transfer theories have been also proposed to explain the action of catalysts in the ignition process [14]. In 1950, Long and Sykes [18] proposed that the presence of a catalyst resulted in a transfer of electrons to or from the carbon substrate causing a redistribution of π-electrons in the graphite structure, a weakening of the C-C bond at the edges of the graphite sheets and an increase in the C-O bond strength during oxidation. The formation of intercalation compounds might have very substantial effects on the electronic properties of the graphite substrate, which could influence the reactivity of carbon atoms on the surface.

3.2 Effects of oxygen concentrations on ignition temperature

Fig. 3 shows the average ignition temperature of Loy Yang raw coal and H-form coal as a function of O$_2$ concentration during the combustion in O$_2$/N$_2$ and O$_2$/CO$_2$ mixtures. As is shown in Fig. 3, both in O$_2$/N$_2$ and O$_2$/CO$_2$ combustion conditions, the average particle ignition temperature of two coal samples decrease with increasing O$_2$ concentration. The data in Fig. 3 also show that the particle ignition temperatures under the O$_2$/CO$_2$ combustion conditions for the given O$_2$ concentration (21%, 30% and 50% in this case) are higher than those under the O$_2$/N$_2$ combustion conditions. In order to have a better understanding the effect of oxygen concentration on ignition temperature of raw coal and H-form coal, this experiment was also carried out in 18% O$_2$ + 82% N$_2$ and 18% O$_2$ + 82% CO$_2$. The particles of H-form coal were observed to gradually oxidise when heated at 10 K s$^{-1}$ to 700 °C, but no obvious ignition was observed both in 18% O$_2$ + 82% N$_2$ and 18% O$_2$ + 82% CO$_2$. Particle ignition of brown raw coal in 18% O$_2$ + 82% N$_2$ could be measured by
thermocouple readings and also observed visually. However, ignition of raw coal in 18% O$_2$ + 82% CO$_2$ was still not observed. The average particle ignition temperature of raw coal increased to 465 °C in 18% O$_2$ + 82% N$_2$ compared with that in air.

3.3 Effects of Na acetate and Na chloride on ignition temperature

As was shown in Fig. 1 and Fig. 3, the average ignition temperatures of H-form coal much increased when AAEM species was removed from raw coal. It was concluded that AAEM species have an important catalytic effect on brown coal than bituminous coal mainly due to a significant amount of AAEM species in brown coal, especially Na [33]. To gain a better understanding of the effects of Na on coal ignition, experiments were also carried out using the coal samples of Na-exchanged and NaCl-loaded, which were prepared H-form coals in the solutions of sodium acetate and sodium chloride respectively.

Fig. 4 shows the average ignition temperature of Loy Yang Na-exchanged and NaCl-loaded coal samples in air and in 21% O$_2$ + 79% CO$_2$. The average particle ignition temperatures decrease with increasing Na content of coal samples. As is shown in Table 3, the samples 3 and 6, prepared by 0.05 M solutions of sodium acetate and sodium chloride respectively, indicates a close Na content. However, the average particle ignition temperatures of Na-exchanged coal (samples 3) decrease 48 °C and 42 °C than those of NaCl-loaded coal (sample 6) in air and in 21% O$_2$ + 79% CO$_2$ respectively. Furthermore, Table 3 shows a equivalent Na content of sample 3 and much lower content of the other AAEM species (e.g., Ca, K and Mg) compared with Loy Yang raw coal. A close particle ignition temperature was observed between sample 3 and brown raw coal. Comparison of the data in Fig. 4 and Table 3 reveals that sodium acetate has a more significant effect on ignition temperature of coal particles than sodium chloride. It was estimated that catalyst
effects of alkali metal correlate with pH value of solution: the higher the solution pH value, the stronger catalyst effects [33-35].

4 Conclusions

The effects of chemical forms of AAEM species on ignition behaviour of a Loy Yang brown coal was investigated in a wire-mesh reactor. The following main conclusions can be drawn.

(1) Compared with the average particle ignition temperature of Loy Yang raw coal, an increase of 30 °C for the ammonium acetate-washed coal and 55 °C for H-form coal was observed respectively both in air and in 21% O₂ + 79% CO₂. A 30 °C decrease in average particle ignition temperature was also measured by thermocouple readings for the water-washed coal sample.

(2) Na in coal as carboxylates (-COONa) and as NaCl can both improve ignition characteristics of coal samples, but carboxylates (-COONa) shows more significant catalytic effect on average particle ignition temperature under our experimental conditions.

(3) The average particle ignition temperature of coal samples decreases with increasing O₂ concentration. The particle ignition temperatures under the O₂/CO₂ combustion conditions for the given O₂ concentration (21%, 30% and 50% in this work) are higher than those under the O₂/N₂ combustion conditions.

ACKNOWLEDGEMENTS

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Australia and Prof. Qin Shuai at China University of Geosciences in Wuhan, China.

REFERENCES


TABLES.

Table 1 Properties of the Loy Yang raw coal samples studied.

<table>
<thead>
<tr>
<th>sample</th>
<th>Ultimate analysis (wt.%, daf)</th>
<th>Proximate analysis (wt.%, db)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>Loy Yang brown coal</td>
<td>68.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Table 2 Contents of Alkali- and Alkaline-Earth Metals in Loy Yang Coal Samples Studied

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na, % (db)</td>
<td>0.347</td>
<td>0.268</td>
<td>0.041</td>
<td>0.016</td>
</tr>
<tr>
<td>K, % (db)</td>
<td>0.025</td>
<td>0.018</td>
<td>0.009</td>
<td>n/d[^a]</td>
</tr>
<tr>
<td>Ca, % (db)</td>
<td>0.070</td>
<td>0.053</td>
<td>0.038</td>
<td>0.012</td>
</tr>
<tr>
<td>Mg, % (db)</td>
<td>0.172</td>
<td>0.128</td>
<td>0.088</td>
<td>0.001</td>
</tr>
</tbody>
</table>

[^a]: n/d: not detected

Sample 1 was Loy Yang raw coal. Sample 2 was prepared by washing raw coal in ultrapure water. Sample 3 was prepared by sequential washing raw coal in ultrapure water and ammonium acetate. Sample 4 was also termed as H-form coal and prepared by sequential washing raw coal in ultrapure water, ammonium acetate and sulfuric acid.
Table 3 Contents of Na in Loy Yang Coal Samples Studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>LY,%(db)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>0.347</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.016</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0.323</td>
</tr>
<tr>
<td>Sample 4</td>
<td>0.752</td>
</tr>
<tr>
<td>Sample 5</td>
<td>1.479</td>
</tr>
<tr>
<td>Sample 6</td>
<td>0.375</td>
</tr>
<tr>
<td>Sample 7</td>
<td>1.191</td>
</tr>
<tr>
<td>Sample 8</td>
<td>3.860</td>
</tr>
</tbody>
</table>

*n/d: not detected

Sample 1 was raw coal. Sample 2 was also termed as H-form coal sample and prepared by sequential washing raw coal in ultrapure water, ammonium acetate and sulfuric acid. Sample 3, 4 and 5 were prepared by adding the H-form coal sample into the 0.05 M, 0.1 M and 0.5 M solutions of sodium acetate respectively. Sample 6, 7 and 8 were prepared by adding the H-form coal sample into the 0.05 M, 0.1 M and 0.5 M solutions of sodium chloride respectively.
List of Figure Captions

**Figure 1.** Average ignition temperatures of Loy Yang raw coal and three sequential extracted coal samples under air and 21% O\(_2\) + 79% CO\(_2\) combustion conditions. Sample 1 was Loy Yang raw coal. Sample 2 was prepared by washing raw coal in ultrapure water. Sample 3 was prepared by sequential washing raw coal in ultrapure water and ammonium acetate. Sample 4 was also termed as H-form coal sample and prepared by sequential washing raw coal in ultrapure water, ammonium acetate and sulfuric acid. Note that the scale of x-axis is not linear. The error bars indicate one standard deviation.

**Figure 2.** BET specific surface area of Loy Yang raw coal and three sequential extracted coal samples. Sample 1 was Loy Yang raw coal. Sample 2 was prepared by washing raw coal in ultrapure water. Sample 3 was prepared by sequential washing raw coal in ultrapure water and ammonium acetate. Sample 4 was also termed as H-form coal sample and prepared by sequential washing raw coal in ultrapure water, ammonium acetate and sulfuric acid. Note that the scale of x-axis is not linear.

**Figure 3.** Average ignition temperatures of Loy Yang raw coal and H-form coal under O\(_2\)/N\(_2\) and O\(_2\)/CO\(_2\) combustion conditions. The error bars indicate one standard deviation.

**Figure 4.** Average ignition temperatures of Loy Yang brown coal samples of Na-exchanged and NaCl-loaded under air and 21% O\(_2\) + 79% CO\(_2\) combustion conditions. Sample 1 was Loy Yang raw coal. Sample 2 was also termed as H-form coal sample and prepared by sequential washing Loy
Yang raw coal in ultrapure water, ammonium acetate and sulfuric acid. Sample 3, 4 and 5 were prepared by adding the Loy Yang H-form coal sample into the 0.05 M, 0.1 M and 0.5 M solutions of sodium acetate respectively. Sample 6, 7 and 8 were prepared by adding the Loy Yang H-form coal sample into the 0.05 M, 0.1 M and 0.5 M solutions of sodium chloride respectively. Note that the scale of x-axis is not linear. The error bars indicate one standard deviation.
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Figure 3. Average ignition temperatures of Loy Yang raw coal and H-form coal under $O_2/N_2$ and $O_2/CO_2$ combustion conditions. The error bars indicate one standard deviation.
Figure 4. Average ignition temperatures of Loy Yang brown coal samples of Na-exchanged and NaCl-loaded under air and 21\% O_2 + 79\% CO_2 combustion conditions. Sample 1 was Loy Yang raw coal. Sample 2 was also termed as H-form coal sample and prepared by sequential washing Loy Yang raw coal in ultrapure water, ammonium acetate and sulfuric acid. Sample 3, 4 and 5 were prepared by adding the Loy Yang H-form coal sample into the 0.05 M, 0.1 M and 0.5 M solutions of sodium acetate respectively. Sample 6, 7 and 8 were prepared by adding the Loy Yang H-form coal sample into the 0.05 M, 0.1 M and 0.5 M solutions of sodium chloride respectively. Note that the scale of x-axis is not linear. The error bars indicate one standard deviation.