Evaluation of Ash Deposition Behavior and Fine Particle Formation from Combustion of Low-rank Coal Impregnated with Molasses in DTF

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ABSTRACT : In recent years, many countries have invested enormous efforts to tackle increasingly harsh environmental problems, especially the greenhouse effect. The addition of biomass into coal is regarded as a promising technology to mitigate CO₂ emissions. However, the costs related to retrofitting injection systems and unstable combustion inhibit this option. Therefore, this thesis developed a two-in-one fuel that impregnates molasses into the holes of low-rank coal (LRC), which can be directly applied to existing boilers. However, due to the existence of alkali and alkaline earth metals (AAEMs) in molasses, the impregnation of molasses into the coal pores possibly lead to the ash deposited on the surface of the heat exchanger, thus reducing the heat exchange efficiency. Besides, a part of fine particles will emit into the atmosphere, resulting in a series of air pollutions. Thus, the investigation of ash deposition and fine particle formation is a significant topic to promote heat exchanger efficiency and protect the environment.

In this study, three fuels, Berau coal, Berau coal impregnate with 10wt% and 20wt% molasses were selected. Experiments are carried out in drop tube furnace (DTF) under the combustion temperature of 1300°C and the ash probe temperature of 800°C with access air. The fuel is fed at a rate of 0.45g/min for 10min. The properties of the ash depositions are analyzed.

Key words : Low-rank coal, molasses, ash deposition

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1. Introduction

Coal, as rich and important fossil energy on the earth, is the basis for human survival. Although coal still occupies a vital position in the world’s energy structure and plays a positive role in promoting economic and social development, the consumption of coal is decreasing in the next 20 years.

Among the abundant reserves of coal, low-rank coal accounts for nearly half of the total reserves [1]. In terms of high-rank coal, the price is more expensive and the supply in coal-fired power plants is unstable compared with low-rank coal. LRC is being more favored by thermal power plants. However, due to the high moisture content of low-rank coal, the increasing emissions of carbon dioxide will cause more severe climate change [2]. There is no doubt that the use of low-rank coal harms the environment, especially the greenhouse effect and air pollution. Therefore, the development of clean and efficient technology is a key research topic. It is reported that the above problems can be effectively alleviated by the blending of biomass with coal [3]. Biomass can be classified into solid, liquid, and gaseous fuels according to existing form [4]. Biomass is a renewable and environmentally friendly fuel with large reserves. Except for coal, natural gas and oil, biomass is the fourth largest energy source in the world, it plays a critical role in the entire energy system [5, 6]. The content of sulfur and nitrogen element as well as the ash in biomass are low. The objective of this research is to find the problems of fouling and fine particle formation from combustion of Low-rank Coal Impregnated with Molasses. Under the guidance of theoretical research, a systematic study on the morphology, element distribution and mineral phases of fouling produced from different samples (Beru coal, impregnated with 10 wt% and 20 wt% molasses) to reveal the factors affecting ash deposition.

2. Experimental Sections

2.1 Sample Preparation

In this study, there are three types of fuels were synthesized by immersing the coal sample in different proportional molasses, Beru coal, Beru coal immersed in 10wt% and 20wt% molasses solution. The synthetic process is as follows: Firstly, coal sample is grounded and sieved to get coals with a particle size of less than 75μm. It was then placed in a muffle furnace and treated at 105°C for 24h to remove moisture from the coal holes. Secondly, it is necessary to formulate molasses solutions with different mass ratios. Thirdly, the dried coal is then immersed in a molasses solution. It should be noted that the mass of coal is equal to the water quality in the molasses solution. In the following section, the above fuels are denoted as Beru coal, 10% CM(Berau coal impregnate with 10 wt% molasses), 20% CM(Berau coal impregnate with 20 wt% molasses) respectively.
Table 1. Sample information of fuels

<table>
<thead>
<tr>
<th>Ash Chemical (wt%)</th>
<th>Berau coal</th>
<th>10% CM</th>
<th>20% CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>1.19</td>
<td>1.24</td>
<td>1.25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.55</td>
<td>12.60</td>
<td>11.90</td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.79</td>
<td>27.04</td>
<td>25.47</td>
</tr>
<tr>
<td>CaO</td>
<td>6.61</td>
<td>9.8</td>
<td>10.63</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>39.80</td>
<td>37.06</td>
<td>34.44</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.80</td>
<td>6.11</td>
<td>9.54</td>
</tr>
<tr>
<td>Na₂O</td>
<td>/</td>
<td>0.26</td>
<td>0.48</td>
</tr>
<tr>
<td>Other oxides</td>
<td>4.25</td>
<td>5.88</td>
<td>6.61</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ash Fusion Temperature (°C)</th>
<th>Berau coal</th>
<th>10% CM</th>
<th>20% CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>DT</td>
<td>1169</td>
<td>1182</td>
<td>1144</td>
</tr>
<tr>
<td>ST</td>
<td>1281</td>
<td>1214</td>
<td>1173</td>
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<tr>
<td>HT</td>
<td>1315</td>
<td>1285</td>
<td>1234</td>
</tr>
<tr>
<td>FT</td>
<td>1323</td>
<td>1313</td>
<td>1306</td>
</tr>
</tbody>
</table>

2.2 Experimental Facility and Method

In this study, DTF is used to carry out the combustion experiments. The schematic diagram and the real setup is shown in Fig. 1. The system consists of the following components: feeder, air pre-heater, main reactor, ash probe collector, cyclone, fine particle filter, vacuum pump, and high-pressure oxygen and nitrogen tank.

Fig. 1. Schematic diagram of DTF.

2.3 Experimental method

The above three types of fuels, including Berau coal, 10% CM and 20% CM are selected for combustion experiments in DTF. Before the experiment, fuels should be grounded and sieved. The particle size (< 75 μm) will be chosen as samples. Then the samples are heated at 105 °C for 24h in muffle furnace to dry moisture.

In the experiment, the feed rate of each fuel is around 0.45 g/min. The feed time is 10 min. The ratio of air to fuel is 1.4 to ensure that the fuel can be completely burned. The air preheater temperature is set to 900 °C. The combustion temperature and the ash probe temperature are 1300 °C and
800°C respectively. After the experiment, the ash deposits and fine particles from different samples are stored to analyze the morphology changes and elemental distribution of ash deposits and fine particles by a series of analytical methods.

3. Results and Discussion

3.1 The characteristics of deposits through DTF experiment

After feeding for 10min, the close-up view of the fouling deposits from these three samples is shown in Fig. 2. The inspection view of the deposits is taken by placing the camera on the front of the probe. It is observed that Berau coal, 10% and 20% CM have a similar deposits structure.

Fig. 2. Photograph of deposited fouling from different fuels.

Fig. 3. reveals the ash deposition rate as a function of different types of fuels. Here, it is particularly pointed out that the definition of the ash deposition rate is the ratio of the number of deposits to the total input ash. By analyzing the above figure, in the case of Berau coal, 10% CM and 20% CM, the ash deposition rate increases with the increase of molasses. 20% CM has the highest deposition rate because it contains a large amount of biomass.

The deposition rate of the three fuels is greatly related to the distribution of elements. Thus, it is necessary to further analyze the morphology, elemental distribution and mineral phase of deposits to clarify the specific reasons that affect the degree of ash deposition. The SEM images and EDX results of deposits collected at 800°C are shown as Fig. 4 to Fig. 6.

Obviously, the microscopic morphology of the ash deposits of the three fuels at the high and bottom layer is different. As far as the shape and particle size of Berau coal is concerned, the shape at the top layer is flaky, which may be because the ash is melted and accumulated so that the particles are larger than that of the bottom layer. In contrast, the degree of particle melting at the bottom layer is light.

The deposits shapes and size of 10% CM, 20% CM similar, that is, the degree of melting at the upper layer is more serious
than that of the bottom layer. In terms of the deposits at the top layer of different fuels, the degree of particle melting from 10% CM and 20% CM is the most serious.

![Fig. 4](image1.png)

Fig. 4. Typical SEM images and EDX results of deposits from Berap coal.

![Fig. 5](image2.png)

Fig. 5. Typical SEM images and EDX results of deposits from 10% CM.

![Fig. 6](image3.png)

Fig. 6. Typical SEM images and EDX results of deposits from 20% CM.

To further clarify the difference in the morphology of the upper and lower particles, the experiment further measured the element distribution of the upper and lower layers by EDX. The results show that the deposits from these three fuels mainly contain K, Ca, Al, Si, Fe, and trace elements of Mg and Na. As mentioned previously, the main reason of deposits is due to the formation of eutectic compounds with a low melting point (Si-Al-Fe-Ca-Mg-K-Na) under the combustion process. It has shown that co-combustion of coal with biomass, such as olive stones or wood, may lead to serious deposits problems due to the high content of K and Ca [7, 8].

As far as the elemental distribution of Berap coal, 10% CM and 20% CM is concerned, the contents of Ca and Fe increase with the increase of molasses content, which means that 10% CM and 20% CM are more likely to have eutectic compounds, leading to serious deposits. The results are shown in Fig. 4 to Fig. 6.

![Fig. 7](image4.png)

Fig. 7. XRD patterns of fouling mineral phase of three Types fuels.

The crystallization distribution of minerals is an index for exploring the melting behaviors of deposits. The mineral transformation of the three fuels was analyzed by XRD. At combustion temperature of 1300°C and probe temperature of 800°C, it can be seen that the mineral phases of deposits produced from Berap coal, 10% CM and 20% CM are identified as SiO₂, MgFeAlO₄ and Fe₂O₃ have strong intensity among these three fuels. With the impregnation of 10% and
20% molasses, the peak intensities of SiO₂ and aluminum-rich phase (MgFeAlO₄) in the mineral components lightly decrease. However, the intensity of Fe₂O₃ increased, as shown in Fig. 7. Meanwhile, SEM-EDX can be found that the composition of the mineral phase is associated with the ash chemicals. Quartz and aluminum-rich phase (MgFeAlO₄) have a higher melting point. Fe₂O₃ is a kind of fluxing agent, its presence will decrease the ash melting point and lead to a severe tendency of ash deposits [9-11]. EDX results indicate that Fe content increase with the impregnation of 10% and 20% molasses, which probably result in a higher deposits tendency.

3.2 The characteristics of fine particle formation from different types of fuels

The fly ash, usually coarse particles (>1 μm), can be captured by the dust removal equipment in the coal power plant after the combustion of coal and biomass. Relatively speaking, small particles, especially fine particles (<1 μm), are not efficiently trapped. The literature review has already discussed that the discharge of ultra-fine fly ash particles into the air will cause harm to the living environment of humans, animals and plants. Therefore, it is of great guiding to explore the formation mechanism of fine particles.

In this study, three types of fuels, Berau coal, 10% CM and 20% CM, were selected. The combustion experiment was carried out at 1300°C in DTF. The morphological characteristics and elemental distribution of particles with different modes (<1 μm, <2.5 μm, >10 μm) were described by SEM-EDX, the results are as shown in Fig. 8. (particle size <1 μm: 1-3, 1 μm < particle size <10 μm: 4-6, particle size >10 μm: 7-9)

It can be found from the SEM image that the morphology of the fine particles (<1 μm) produced from all fuels is spherical. The coarse particles (>1 μm) are mainly composed of irregular particles, as shown in Fig. 8. Some studies have pointed out that the morphology of the different size particles is related to different formation mechanism, fine particulate matters (<1 μm) are formed by the gasification condensation process. Coarse particulate matter (>1 μm) is formed by the coalescence of intrinsic mineral, the breakdown of external minerals and coal char [12-15].

The formation of particulate matters can be further understood by analyzing the characteristics of elemental distribution. EDX results show that Al, Si, K, Ca and Fe exist in coarse particles and fine particles in each fuel. However, the elemental distribution in coarse particles and fine particles is different. It is clear that the volatile elements K, S and Mg are rich in the fine particles (<1 μm) in each fuel. Al, Si, Ca and Fe are rich in the coarse particles, because the boiling point of Si, Al, Ca and Fe is 2355°C, 2327°C, 1484°C and 2750°C respectively, it is difficult to vaporize under testing temperature, thus, these elements are rich in coarse particles (>1 μm) [16]. The boiling point of K, S and Mg is 774°C, 445°C and 1090°C respectively, so these elements are easy to vaporize and condense to form fine particles (<1 μm). the gas phase, K, S and Mg, can interact to form K₂SO₄(g) and MgSO₄(g). When the gas phase, K₂SO₄(g) and MgSO₄(g), encounters the low temperature, it will condense into nuclei, K₂SO₄(s) and MgSO₄(s), resulting in
the formation of fine particles (<1 μm). The above results are consistent with the formation mechanism of fine and coarse particles.

In summary, according to SEM-EDX analysis, the fine particles (<1 μm) are rich in K, Mg and S, and these elements will undergo different degrees of gasification and condensation at testing temperature [14], then it will react with S in the gas phase to form K₂SO₄(g), MgSO₄(g). Consequently, condensation occurs at low temperatures to form fine particulates(<1 μm). Most silicon-aluminum materials or minerals will decomposition or break down to form coarse particles (>1 μm) [17].

Fig. 8. SEM images and EDX results (average data) of fine particles. (A: Berau coal, B: 10%CM, C: 20%CM).

From the above SEM-EDX analysis, the morphology and elemental distribution of the particulate matter produced by these three fuels have some in common. It was found that the SEM image showed that the microscopic morphology of the fine particles (<1 μm) was a regular spherical shape in each fuel, the morphology of the coarse particles (>1 μm) consists of irregular flaky particles, which are due to different formation mechanisms. EDX also indicates that K, S and Mg are easily gasified and condensed to form fine particles in each fuel. While Si, Al, Ca and Fe are refractory elements, which are enriched in coarse particles. The results of SEM-EDX is correspondence with the formation mechanism of fine and coarse particles.

Except the common in these three fuels, there are existing some differences. It is obvious that the ash chemicals have big difference, K and S in the ash of 10% CM and 20% CM are higher Berau coal, which is due to the high contents of S and K in the ash. Studies have shown that fuels containing large amount of aluminum-silicon may capture more fine particles, thus decreasing the fine particle emissions [18], because the aluminum-silicon materials in the coarse particles can react with Fe or AAEMs to form a liquid phase or eutectic compound, which can promote the conversion of Fe and Ca into coarse particles, thus reducing the emission of fine particles [18].

4. Conclusions

In this thesis, three fuels, Berau coal, 10% CM and 20% CM were selected, and experiments were carried out in DTF at a combustion temperature of 1300°C and ash probe temperature of 800°C. The properties of the deposits and fine particles produced by the combustion of the three fuels were further investigated and compared. The
following conclusions were obtained:

(1) As far as the ash deposition was concerned, it was found that 20% CM showed the most serious deposition tendency, followed by 10% CM, Berau coal. SEM-EDX, XRD and theoretical model analysis indicated that CaO and Fe₂O₃ are the main factors affecting the deposition propensity. Because CaO or Fe₂O₃ can react with SiO₂ and Al₂O₃ under high temperature to form a low melting point eutectic, resulting in serious deposits tendency. Also, as for the ash deposition of the bottom and top layer, the particle size of deposits at the top layer is larger than the bottom layer.

(2) In terms of the fine particle formation, it was obvious that there was a certain similarity between the morphology and elemental distribution of the fine and coarse particles from each fuel. Firstly, the morphology of the fine particles is a regular spherical, the coarse particles is irregular. Secondly, the EDX results showed that K, S and Mg are rich in fine particles (<1 μm), because the boiling points of K and S are low, so it is easy to be gasified and condensed to form fine particles. While the boiling points of Si, Al, Ca and Fe were higher than other elements, it is difficult to volatilize under testing temperature. Thus, the coarse particles (>1 μm) were rich in Si, Al, Ca and Fe.

Through DTF fouling deposition experiment and fine particle formation experiment, correlation between AAEMs and fouling and fine particle formation was confirmed. To control these problems, introduction of various additives can be considered. Particularly, aluminum-silicon additives, which are known to reduce fouling and capture fine particles, are suitable because biomass has a high content of alkali metal component.

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References

[5] H. Long; X. Li; H. Wang; J. Jia; “Biomass resources and their bioenergy potential


