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# Fusibility characteristic and flow properties of semi-char from industrial circulating fluidized bed gasification

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ABSTRACT

The carbon conversion of fluidized bed gasification (FBG) has been restricted by the entrainment of high-carbon-containing semi-chars. Thus, the concept of FBG combined with combustion melting system was proposed to make effective use of the gasified semi-char. However, long-term running of the melting furnace was confined by severe slag plugging. The objective of this research is to understand the ash fusibility and flow properties of the semi-char, and provide some guidance for the design and operation of the integrated system. Two typical semi-chars from industrial circulating fluidized bed gasifier were chosen as raw materials, and the major results are as follows. The ash fusion temperatures (AFTs) of Liaocheng semi-char (LCSC) are about 100 °C lower than Suqian semi-char (SQSC), mainly caused by its higher basic element content. As the particle size increases, the AFTs of SQSC ash first increase sharply, and then rise smoothly, whereas no obvious differences are found for LCSC ash. The effect of atmosphere on ash fusibility was also studied. The AFTs appear in the order of oxidizing > inert > reducing, which should be related to the variations in $Fe^{2+}/Fe^{3+}$ ratios under different atmospheres. The viscosity-temperature curves show that the LCSC ash tends to form glassy slag when completely melted, which turns out to be plastic slags for SQSC ash, probably resulting from mullite crystallization. Heating stage microscopy has been considered an effective way to in situ observe the melting and crystallization process of ashes. The preliminary results indicate that dendrite particles tend to strengthen internal bonding in the molten slags, promote the formation of solid phases, and accelerate the growth in viscosity.

## 1. Introduction

Fluidized bed gasification ( FBG ) has been considered one of the most promising technologies for clean coal utilization because of its wide fuel diversity, low-cost operation and minor pollutant emission [1–3]. Unfortunately, massive amounts of high-carbon-containing semi-chars are entrained out by crude gas, which reduces the carbon conversion of FBG (< 90%). Thus, the concept of FBG combined with combustion melting system was proposed [4], which could effectively recover the residual carbons in the semi-char and avoid air pollution. Volume reduction could also be realized, as the mineral matters are melted to form liquid slags. However, long-term running of the melting furnace was confined by severe slag plugging problems. Thus, it appears imperative to understand the fusibility and flow properties of the semi-char for developing the integrated system.

Recently, plenty of researches have been carried out concerning the fusibility and flow properties of coal ashes and slags. The acid elements, e.g., Si, Al, and Ti, were found capable of raising the ash fusion temperatures (AFTs) of South African coals [5]. Song et al. [6] concluded that the AFTs first decreased, reached a minimum, and then increased again, when CaO, $Fe_2O_3$, and MgO were added in coal ashes. Chen et al. [7] investigated the ash fusion properties of coals rich in sodium. The results indicated that the AFTs decreased remarkably with increasing $Na_2O$ content, owing to the formation of eutectic Na-containing aluminosilicates. Kong et al. [8] evaluated the effect of $CaCO_3$ on the flow properties of slags. The viscosity behavior and slag type changed markedly with $CaCO_3$ addition due to the different solids formation processes. Song et al. [9] compared the flow properties of slag from Shell gasifier to the parent Huainan coal ash. The results indicated that the critical viscosity of slag were lower than that of coal ash. The slag from Texaco gasifier behaved as a Newtonian fluid above its liquidus temperature, which turned into non-Newtonian fluid below its liquidus temperature [10]. Schobert et al. [11] analyzed the flow properties of slags from slag-tapping fixed bed gasifier, and revealed that the viscosity under oxidizing condition was higher than that in reducing atmosphere. Hiesh et al. [12] concluded that the combination

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of experimental data from high temperature rotary viscometry with thermodynamic modeling results could improve the prediction accuracy of coal ash slag models.

When it comes to the semi-char, lots of literature regarding its physicochemical properties and reactivity have been published [13–16]. However, few studies about its ash fusibility were available. Li et al. [17] investigated the fusibility characteristic of the semi-chars from pilot-scale pressurized ash agglomerated fluidized bed gasifier, and found that the AFTs and sintering temperatures of Shenmu and Jincheng semi-chars were lower than the corresponding coals. The ash fusion and mineral transformation behaviors of the semi-char from an industrial circulating fluidized bed (CFB) gasifier have been investigated under oxidizing condition in our previous research [4]. Moreover, scarcely any work has been reported with reference to the flow properties of the semi-char.

In this study, two typical semi-chars derived from industrial CFB gasification were selected. The effect of particle size and reacting atmosphere on their ash fusibility was analyzed. Meanwhile, the flow properties of the two semi-chars were compared, and the crystallization processes were in situ observed by heating stage microscopy. This work aims to get a clear understanding of the fusibility and flow properties of the semi-chars and provide some guidance for the design and operation of the melting furnace.

## 2. Experiments

### 2.1. Raw materials

Two types of semi-char were collected from industrial CFB gasifiers. The principles and technological process of CFB gasification have been introduced in detail previously [18]. The gasifiers were established in Suqian city of Jiangsu province and Liaocheng city of Shandong province, China, respectively, to produce clean fuel gas for ferronickel smelting and alumina calcination. The gas-producing capacity of the first gasifier is 25,000 $Nm^3/h$, using a lignite as fuel; the other possess a capacity of 40,000 $Nm^3/h$, and the feedstock is a bituminous coal. Generally, both gasifiers operate at about 950 °C under atmospheric pressure, and the mixture of air and steam are employed as gasifying agents. The semi-chars were obtained from the bag dust collector and designated as SQSC and LCSC, respectively. The proximate, ultimate analyses and lower heating values of the two samples are listed in Table 1. The ash compositions and AFTs under an oxidizing atmosphere (21:79 $O_2/N_2$, volume ratio) are provided in Table 2.

### 2.2. Samples preparation

#### 2.2.1. Preparation of the semi-char samples of various particle sizes

A laser diffractometer (Mastersizer 2000, Malvern, Britain) was adopted to analyze the particle size distributions of SQSC and LCSC. The two samples were sieved and screened into five groups with different particle sizes, namely, < 25 μm, 25–38 μm, 38–53 μm, 53–75 μm and > 75 μm for SQSC, and < 6.5 μm, 6.5–10 μm, 10–18 μm, 18–25 μm and > 25 μm for LCSC.

#### 2.2.2. Ash preparation and high temperature treatment

Both SQSC and LCSC have considerably large carbon contents, which would presumably interact with the minerals at high temperature and affect the fusion properties of coal ashes [19]. To eliminate the effect of carbon, the SQSC, LCSC and semi-chars of various particle sizes were ashes at 815 °C in a muffle furnace according to Chinese standard GB/T 1574–2007. Briefly, the furnace was first heated from ambient temperature to 500 °C within 30 min and held for another 30 min. Then, the furnace was raised to 815 °C and remained for another 120 min. Subsequently, the ash samples were retreated at higher temperature under different conditions. Fig. 1 gives the schematic diagram of the horizontal tube furnace. A typical treatment procedure consists of the following steps. First, about 1 g ash sample was loaded in an alumina crucible and placed into the tube reactor. The temperature was then elevated to 750 °C at 15 °C/min. Finally, the heating rate was reduced to 5 °C/min, and the reactor was raised to prescribed temperature and held for 5 min. The treatment temperature was set at 1200 °C, 1300 °C, 1400 °C and 1500 °C. The SQSC ash was reprocessed under oxidizing, inert (pure $N_2$) and reducing (60:40 $CO/CO_2$, volume ratio) atmosphere, respectively. The ash samples after treatment were fetched out from the reactor and immersed instantly into ice water to inhibit phase transformation and crystal segregation. The quenched samples were dried at 105 °C, and ground to a size of < 100 μm for further analysis.

### 2.3. Analytical methods

#### 2.3.1. AFTs measurement

A variety of methods have been applied to evaluate the fusion properties of coal ashes, among which the AFTs measurement is mostly adopted. Despite its weakness in determining initiation of ash melting [20], the AFT measurement could provide valuable reference on ash fusibility of coal ashes. Besides, the AFT values could not be used solely to predict the flow properties, due to particle level deviations from practical system [21]. In this study, an ash fusion determinator (LECO, AF700, US) was chosen to analyze the AFTs of the ash samples. The process involves heating a sample cone from ambient temperature to about 1550 °C under different conditions. The cone was first heated to 750 °C at 15 °C/min, then the heating rate was reduced to 5 °C/min, and the temperature slowly rised to 1550 °C. Notably, the limit temperature of the analyzer is 1550 °C. That is, the AFTs above 1550 °C could not be obtained. The AFTs of SQSC and LCSC ashes of various particle sizes were evaluated in oxidizing atmosphere. The tests were performed under different conditions, e.g., oxidizing, inert and reducing, for SQSC and LCSC ashes.

#### 2.3.2. Characterization of the samples

The elemental compositions of SQSC and LCSC ashes of various particle sizes were detected by XRF spectrometry (Shimadzu, XRF-1800, Japan). Powder XRD (Bruker, D8 Advanced, Germany) was chosen to analyze the phase compositions of samples. Before test, the sieved ashes were placed in sample well, and the sample surface was flatted with a glass slip. The scanning was accomplished at a step size of 0.05° (2θ) between 2 θ values of 10° and 80° at a rate of 10° 2θ/min. A scanning electron microscopy (HITACHI, S-4800, Japan) was adopted to observe the surface morphology of the ash samples.

**Table 1**
Proximate and ultimate analyses of SQSC and LCSC.

| Sample | Proximate analysis (wt. %, ar) | | | | Ultimate analysis (wt. %, ar) | | | | | Lower heating value |
|---|---|---|---|---|---|---|---|---|---|---|
| | *M* | *V* | FC | *A* | C | H | O | N | S | $Q_{ar,net}$ (MJ/kg) |
| SQSC | 0.06 | 0.67 | 38.61 | 60.66 | 37.30 | 0.19 | 0.00 | 0.25 | 1.55 | 13.49 |
| LCSC | 0.68 | 1.98 | 63.56 | 33.78 | 63.46 | 0.75 | 0.00 | 0.43 | 0.91 | 22.74 |

Note: ar, as received basis.