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Research article

Viscosity fluctuation behaviors of coal ash slags with high content of calcium and low content of silicon

Xia Liu *, Guangsuo Yu, Jianliang Xu, Qinfeng Liang, Haifeng Liu

Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, Shanghai Engineering Research Center of Coal Gasification, East China University of Science and Technology, Shanghai 200237, China

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A B S T R A C T

This work aims to study the ash slagging behaviors of two specific coals, on account of a blocking problem of the slag discharge encountered when these coals were used in an industrial entrained-flow gasifier. Through the measurements of the ash fusion temperatures (AFTs) and the slag viscosities of the two coal samples, it was found that while the coal ashes had sufficiently low AFTs, they exhibited a strong viscosity fluctuation as well as a slag foaming and expansion. By comparing to the slagging behaviors of some artificial ash mixtures, it was ascertained that while the enrichment of sulfate in the coals ashes was responsible for the slag foaming and expansion, the viscosity fluctuation was attributed to a high content of calcium together with a low content of silicon in the coal ashes. With the help of X-ray diffraction (XRD) analysis and FactSage thermochemical modeling, it was found that the presence of a crystalline gehlenite phase during the slagging process for the two coal ashes was closely related to the slag viscosity fluctuation. The addition of silica to the coal ashes could virtually eliminate the slag viscosity fluctuation. The sand (a silica rich mineral) addition method had also been successfully used in the industrial gasifier.

1. Introduction

Entrained-flow gasification has the advantages of flexibility for a wider range of fuels, high energy efficiency, and low-carbon content in slag residue [1–2]. The operating temperature controlled in an entrained-flow gasifier is generally 50–200 °C higher than the fusion temperature (FT). At such a temperature, the mineral components in coal are molten and discharged as a slag from the bottom of the gasifier by gravity [3]. To guarantee a flow stability, the slag viscosity is usually required to be within the range of 5 to 10 Pa·s, and an upper limit may sometimes be 25 Pa·s [4–6]. Since the viscosity measurement of ash is expensive and time-consuming, the AFTs are widely used to assess whether a coal can be used as an appropriate feed for an entrained-flow gasifier [7–8]. In some cases, the AFT determination method is actually feasible for practical application [9–10]. However, it was observed from the industrial gasification operation that for some coals, even with the FT lower than the gasification temperature, their slags had a poor flowing stability [11]. The Yulin (YL) coal from Shaanxi province and Yangchangwan 1# (YCW1#) coal from Ningxia province were such two typical coals. These coals had lower AFTs, but they could not be directly used for the entrained-flow gasifiers because of the slag block problem, which ever caused the unplanned and troublesome shutdown a few times.

The dependence of the slag viscosity on the transformations of minerals phase has been investigated [12–14]. Xuan et al. [12] reported that the formation of some crystalline phases during the slagging process or the separation of a melt into two or more immiscible liquids during cooling could affect the viscosity of slag. Oh et al. [13] also investigated the relation between the slag viscosity and the formation of crystalline phase. However, the correlations between the viscosity and the heterogeneity of a molten slag are difficult to describe [14]. On the other hand, a great deal of effort has been done to investigate the complex decomposition, interaction and phase transformations of varying mineral components in the ashes during the heating [15–16]. The FactSage is a powerful software, which can calculate the equilibrium phase diagrams of a multicomponent system, based on the minimization of Gibbs free energy [17]. Several works were done with respect the phase transformations in different component systems by means of FactSage and other analysis methods such as high-temperature X-ray diffraction (HT-XRD) and scanning electron microscopy point count analysis (SEMPC) [18–21]. However, no studies have been reported on the viscosity fluctuation and its plausible relation to the occurrence of some crystalline phases.

In this study, we have investigated the slagging properties of two specific coals, because there was a slag blocking problem when these coals were used in an industrial entrained-flow gasifier. We have for

* Corresponding author.
E-mail address: lxia@ecust.edu.cn (X. Liu).

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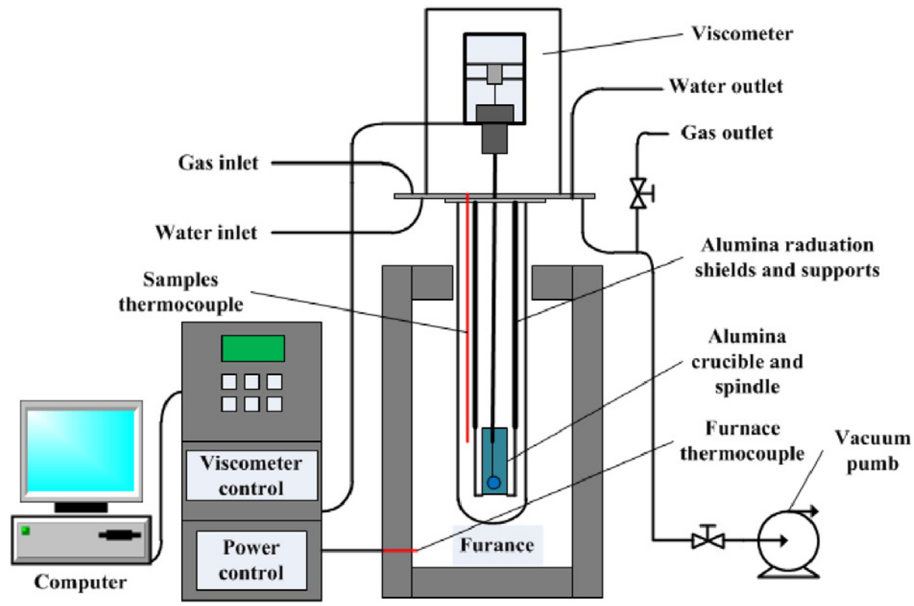

Fig. 1. Schematic diagram of high temperature rotational viscometer.

the first time observed the distinct slag viscosity fluctuation occurring for these two coals. A plausible reason for this phenomenon is discussed. Moreover, a method has been proposed by the addition of silica to the coal ashes or coals to successfully mitigate the viscosity fluctuation and solve the blocking problem in the industrial application.

2. Experimental

2.1. Coal ash samples

YL and YCW1# coal were used in this study. As described above, the direct use of them without additive suffered from the slag blocking problem. In order to find out the reasons and illustrate it sufficiently, Yangchangwan 2# coal (YCW2#) from Ningxia province and Nantun (NT) coal from Shandong province both well applicable in industrial entrained-flow gasifiers were also investigated by way of comparison. The coal ashes were prepared by combusting the coals in a muffle furnace (Germany, Nabertherm, LVT 15/11/P330) at 815 °C. The ash samples were ground to the particle sizes smaller than 0.2 mm for analysis. The chemical compositions of coal ashes were measured by X-ray fluorescence (America, Thermo Fisher Scientific ARL Advant'X Intellipower TM 3600). Although YCW1# and YCW2# were both from Yangchangwan coal field in Ningxia province, they were exploited at different time and different coal seam. Because the slag flow ability of them had a great difference, we did lots of repeated experiments including the ash fusion temperature and chemical compositions measurement. The results showed that there was no obvious relationship between these two coals, hence they could totally be treated as two different coal samples.

2.2. AFT measurement

The AFTs of the coal ashes were determined on a 5E-AFIII auto analyzer (Changsha KaiYuan Instruments Co. Ltd) under reducing atmosphere according to Chinese standard GB/T219-2008. With the programmed temperature rise, four characteristic temperatures including initial deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT), and FT were automatically recorded in a computer.

2.3. Slag samples

The slag samples used for viscosity-measurement experiments were prepared by the pre-melting of the coal ashes. The slags obtained after pre-melting were similar to those of the slags obtained from the industrial gasifier [21]. In this experiment, an 80– 100 g sample of coal ash was molten in a 255 ml corundum crucible in a high-temperature furnace. The crucibles were made of high purity Al_2O_3 (>99.9%) so that the interaction of slag with the crucible wall during the experiments could be ignored [20,22]. The ash samples were heated to a temperature 200 °C higher than the FT determined prior, and kept at this temperature for about 30 min to reach the equilibrium of the melting reactions as far as possible. The slag samples were recovered after the melt was cooled, and then crushed and ring-milled to the particle size smaller than 0.5 mm for viscosity measurement. Note that the coal ash could not be directly used for viscosity measurement because of a large shrink of ash sample powders during the melting process.

2.4. Viscosity measurement

The viscosity measurement was performed on a RV DVIII high temperature rotational viscometer (American firm Theta Industries). As shown in Fig. 1, this device was composed of a Brookfield DVIII ultra programmable rheometer, a high-temperature electrical furnace and a computer. The electric furnace could be heated up to 1700 °C. In each test, about 40 g of the slag sample was placed into a 66 ml cylindrical corundum crucible (purity, >99.9%), and then fixed at the center of furnace with a pedestal containing three fluted rods made of high-purity corundum. The set of pedestal and crucible was isolated from the wall of furnace with a high-purity corundum tube. After the sample crucible

Table 1
AFTs of coal ash samples.

Sample	AFT analysis/°C			
	DT	ST	HT	FT
YL	1148	1203	1214	1233
YCW1#	1228	1240	1241	1248
YCW2#	1160	1174	1176	1190
NT	1318	1351	1358	1370