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Influence of coal blending on ash fusion property and viscosity

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ABSTRACT

Coal blending is a practical method to reduce ash percentage and improve fusion properties for gasifiers. High viscosity coal was investigated to improve its ash fluidity by blending with low viscosity coal. Both single coal and blended coal samples were studied to compare their ash fusion properties and viscosities. Thermodynamic calculations of slag contents were performed. Results revealed that the blended coals ash fusion temperatures differed little while their viscosities presented much difference. Viscosities of blended coal slags were similar at high temperature, however, the patterns of blended coal viscosity-temperature curve showed obvious divergence below 1450 °C. Thermodynamic calculations and X-ray diffraction results revealed that the content adequacy of mullite and quartz in the slag caused the solid phase separation from molten slag, which consequently resulted in the rapid increase in viscosity. The critical temperature and T_{25} of blended coals showed good linear dependence with blending ratio.

1. Introduction

Gasification is a potential coal application for its highly efficient process, green products and low pollution. Adequate fusion properties and low ash percentage of coal are recommended to improve the economic benefit of gasification. For a membrane wall entrained flow gasifier, flow properties of coal slag will greatly influence the heat transfer, mass transfer and chemical reactions between the slag and the wall. Slag should be excreted from the gasifier to keep the facility running, and the operation temperature should be controlled to protect the slag layer protection [1]. To evaluate the slag flowing condition, ash fusion temperature (AFT) and viscosity had been applied to measure slag fluidity change of temperature. The former characterizes the ash temperature from shrinking to melting, while the latter is often used to estimate the flowing behavior of ash in a gasifier. Critical temperature (T_{cv}) is important in industrial application for the operation temperature should be set higher than critical temperature [2]. In order to meet the slagging standard, coal ash viscosity should be less than 25 Pa·s when leaving the gasifier. T_{25}, the temperature of slag at 25 Pa·s, is also an essential operation parameter of gasifiers which ensure the continuous flow of slag.

Coal ash is mainly consisted of SiO_2 and Al_2O_3 with alkali metal, alkaline earth metal and transition metal oxide. At high temperature, slag is separated into the liquid phase metal cations and solid phase which is mainly consisted of aluminosilicate and metal cations [3–6]. With alkali metal and alkaline earth metal depolymerizing the aluminosilicate structure and transition metal oxide separable from liquid phase, the interaction between slag contents results in the complexity of fusion properties. Due to this theory, each type of anion does a contribution to the activity of the whole system. SiO_2 can form three-dimensional network structure due to its ionic potential, and pure silica is Newtonian fluid with very high viscosity. Al_2O_3 holds the similar effect in the network for Al^{3+} can substitute for the Si^{4+} polyanions to form polyanions of $[AlO_4]^{5-}$ tetrahedrons [7]. Three-dimensional network structure of aluminosilicate is likely to be disconnected by the addition of the basic oxides such as alkali metal oxides. Kong et al. [8] found that the addition of calcium was able to decrease the —Si—O—Si— bond and excessive calcium can cause composition changing of solid phase from aluminosilicate to anorthite. Kim et al. [9] revealed that effect of MgO on depolymerization was similar to CaO, but the effect could be limited under strong basic oxides environment. Addition of monovalent basic metal oxide to aluminosilicate can be more effective for it can eliminate the bridging tendency that still connects two tetrahedral occurring in alkaline earth cations

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[10]. Besides Li_2O and Na_2O, K_2O performs the contrary effect due to its induction of $[AlO_4]^{5-}$, which leads to the viscous of the slag [11].

The conventional solution, adding fluxing agents such as limestone, could generate more ash content in gasifier especially with a high AFT and high ash content original coal, and this is considered both expensive and impracticable for high ash content coals. Under such circumstances, coal blending may both reduce cost and compensate for undesirable characteristics of such kind of coal. Qiu et al. [12] obtained the mineral transformation of fusion blended coal ash, and found the non-linear change of fusion temperature and blending ratios. Shen et al. [13] found that the AFT of blended coals initially decrease and then increase with blending ratio. Bryant et al. [14] focused on the TMA method to investigate the difference of fusion temperature, which is undetectable using conventional AFT measurement. Bai et al. [15] also investigated the blending effects on coal reactivity. A lab-scale drop-tube furnace had been setup to examine the ash deposit properties between blended and single coals in air environment [16]. Blending of coal and petroleum coke was also reported to investigate the influence of vanadium adding to flow property [17].

Many of these studies on coal blending above have concentrated on the fusion properties and reactivities of blended coals. However, comparison researches of both fusion properties and viscosities of single coals and blended coals were seldom referenced. In this study, we focused on the effect of coal blending on improvement of fluidity of a high ash viscosity coal by blending with a low ash viscosity coal. The fusion temperatures and viscosities of both single coals and blended coals were measured. Empirical formulas of fusion temperature and critical temperature were derived to validate the accuracies of empirical predictions. Thermodynamic calculations and X-ray diffraction were performed to study the influence of blending ratio on coal slag phase transformation.

2. Experimental

2.1. Blended coals selection and preparation

In this study, coal blending experiments were undertaken by adopting two Chinese coals. One was from Guizhou province marked as H and the other was from Inner Mongolia province marked as L. Coal H was of low S/A ratio and high ash viscosity so that was not capable for direct gasification application. Coal H was blended with coal L with high S/A ratio and low ash viscosity to improve the flow properties and reduce ash percentage. The proximate, ultimate, and ash analysis of two single coals are shown in Table 1.

Coal samples were burned into ash in the muffle furnace at 815 °C according to the Chinese standard GB/T1574-2011 (similar to ISO 1171:2010 and ASTM D3174-12). Chemical composition of coal ash samples was analyzed by Thermo Advant' X X-ray Fluorescence Analyzer. Table 2 presents the ash content analyses of single coals and blended coals. Three blended coals with mass ratio of 1.5:1.0, 1.0:1.0 and 1.0:1.5 were adopted in this paper. These coals were marked as H1.5L1, H1L1 and H1L1.5.

2.2. Ash fusion measurements

Ash fusion temperatures were measured by a 5E-AF4000 fusion properties analyzer under a reducing atmosphere according to Chinese standard GB/T 219-2008. Coal ash was mixed by gummeline and then shaped into triangular ash cones. Ash cones were then placed into the analyzer and heated to 1500 °C at a rate of 5 °C/min for measuring. Four characteristic temperatures were measured for each coal ash: deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT). The measured deviation of the ash fusion test is ±40 °C.

2.3. Slag viscosity measurements

To prepare for the viscosity measurement, about 80 g of each blended coal ash was melted in a corundum crucible inside a high temperature chamber furnace. The temperature of furnace was set to 200 °C above its FT. We prevented collecting the slag sample around the crucible wall so that the effect of corundum dissolution into the samples could be reduced. The melting process could ensure that slag would melt and form a homogeneous liquid and avoid occasional slag overflowing during the viscosity test.

RV-DVIII viscosity measuring system produced by Theta Industries was employed for viscosity measurements. This device was consisted of a Brookfield DVIII Ultra programmable rheometer that was originally designed for room temperature use and a high temperature furnace manufactured by Thermalcraft Inc. The furnace employed a set of molybdenum disilicide heating elements as a heater, with a maximum temperature of 1650 °C. The viscometer had been calibrated with standard silicone oil at high temperature, and the measured deviation of the test was less than 1%.

During the measurement process, about 40 g of melted slag was transferred the sample into a cylindrical corundum crucible. The crucible was placed in the center of the furnace by three fluted corundum rods. To maintain the mild reducing atmosphere, we vacuumed the viscometer firstly and kept the atmosphere by injecting a gas mixture at a flow rate of 100 cm^3/min during the test, the volume ratio of the gas mixture is $CO:CO_2 = 60:40$. The slag sample in the crucible was placed to heat up from room temperature to the target temperature, about 200 °C above the previously determined ash fusion temperature. The heating rate was set to 10 °C/min below 1200 °C and 5 °C/min above its flow temperature. The furnace temperature was programmed to be held in target temperature for 30 min in order to stabilize the temperature variations and ensure the system to reach equilibrium. During that time, the spindle was immersed into the molten slag. Then the viscosity measurements were taken as the chamber cooling and spindle rotating. The cooling rate during the viscosity measurements was 2 °C/min. The initial rotational speed of the spindle in all test in this paper was set to 15 rpm. In order to obtain the slag morphology during the viscosity test, CO/CO_2 mixed gas was injected until room temperature to remain reducing atmosphere. X-ray diffraction (XRD) tests were performed on crushed slag sample after the test.

Table 1
Proximate, ultimate analysis of single coals (wt%).

	Proximate analysis (ad)				Ultimate analysis (ad)				
Sample	M	Ash	VM	FC	C	H	O	N	S
H	1.88	16.94	11.5	69.68	73.42	2.92	1.66	1.03	2.15
L	6.97	11.31	31.05	50.67	68.75	3.89	7.79	0.98	0.31