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Improvement of ash flow properties of low-rank coal for entrained flow gasifier

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HIGHLIGHTS

- Ash flow properties of low-rank coal with high Fe_2O_3 and CaO were detailed studied.
- The effect of kaolinite and coal GP with high SiO_2 was investigated.
- Mineral transformation and viscosity with kaolinite and coal GP were discussed.
- Coal blending method has a larger tapping temperature range.
- Coal blending method is superior in improving ash flow properties.

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ABSTRACT

In order to meet the demand of slagging for entrained flow gasifier, addition of refractory agent kaolinite and coal with high SiO_2 and Al_2O_3 contents was applied to improve ash flow properties of low-rank coal including fusion temperature and viscosity. The FACTsage software package was used to predict proportion of solid phase and minerals as a function of temperature. X-ray diffraction (XRD) analysis was carried out to identify the major crystalline phases in ash. The results show that the variation of ash fusion temperatures (AFTs) with addition of kaolinite is similar to that with addition of coal with high SiO_2 and Al_2O_3 contents. It first decreases with increasing amount of kaolinite addition and coal with high SiO_2 and Al_2O_3 contents, and then decreases and reaches a minimum value before increasing again. The location of ash composition in pseudoternary phase diagram and mineral changes in ash can be used to explain the variation of ash fusion temperatures of low-rank coal with addition of kaolinite or coal with high SiO_2 and Al_2O_3 contents. Viscosity of slag also increases with increasing additions of kaolinite and coal with high SiO_2 and Al_2O_3 contents. The sensitivity of slag viscosity to temperature excursion decreases with increasing of kaolinite addition and coal with high SiO_2 and Al_2O_3 contents, because the sensitivity of the SiO_2–Al_2O_3–'FeO'–CaO–MgO system to temperature excursions decreases with increasing kaolinite addition and coal with high SiO_2 and Al_2O_3 contents. Meanwhile, coal blending method has a larger tapping temperature range and shows a better effect on improving ash flow properties for entrained flow gasifier.

1. Introduction

Extremely large amount of low-rank coals are reserved underground in western China, especially in Xinjiang province. The future energy and chemicals supply depends on efficient and cost-effective utilization of these resources. Low-rank coals are well known for three distinguishing features which govern the gasification rate including high concentration of oxygen-containing functional groups, high proportion of transitional and macropores, and high dispersion of catalytic inorganic constituents [1]. Thus, coal gasification has been identified as one of the most viable technologies for chemical production from these low-rank coals.

Compared with fixed-bed and fluidized-bed gasification, entrained flow gasification operates at higher temperature with smaller particles, often achieves a high carbon conversion, and produces a high quality syngas with low methane and tar content [2,3]. Advantages of the entrained-flow gasifier are well summarized by Hotchkiss [4], and most prominent advantages are the ability to utilize nearly any type of coals with high throughputs per reactor volume and the simpler mechanical design with nearly 100% carbon conversion. Therefore, it is becoming more important and widely used than ever [5]. Koppers-Totzek, Texaco, Shell, Prenflo and GSP are the well-known gasification processes that operate with entrained-flow gaisfier. In the gasifier, the ash

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forming components melt, flow down from the walls of the reactor and finally leave the reactor as a liquid slag. Smooth operation of such gasifier depends strongly on steady and reliable removal of slag, which is largely determined on the flow behavior of the slag [6]. Two parameters are commonly used to characterize ash flow behavior: ash fusion temperatures and viscosity dependence on temperature. Besides, viscosity of slag directly affects the operation temperature of gasifier, life of refractory brick and heat loss, etc. To ensure the smooth tapping of slag, the slag viscosity must be sufficiently low at the temperature of tapping, typically less than 25 Pa s at temperatures between 1300 °C and 1500 °C [7].

Slag viscosity depends on ash chemistry, temperature, oxygen partial pressure (determined by the CO/CO_2 ratio in the gasifier), and the precipitation of solid phases [8–10]. Ash chemistry relies on the source of the coal and/or any additional carbonaceous feedstock that mixed with, such as other types of coal or petcoke. Low-rank coals in west of China are significantly rich in CaO and Fe_2O_3, which is a strong depolymerizing unit in silica based slags. Thus, it normally has a low viscosity due to the fluxing properties of the Ca and Fe minerals. Schobert studied flow properties of low-rank coal ash slags for slagging gasification [8]. Recently, Ilyushechkin et al. [9] and Zhou et al. [10] discussed flow properties of slag with various compositions according to the content of CaO and Fe_2O_3, and found that viscosity is always below 5 Pa s at 1300 °C for high calcium and high iron slags. At viscosities below 25 Pa s, slag flows down the gasifier walls and is discharged through the tapping device. However, if the slag viscosity drops below 2 Pa s, it may become too fluid and potentially cause some problems in the gasifier, such as excessive wear of refractory walls (e.g. GE and ConocoPhillips E-gas technologies) or excessive heat loss through water-cooled walls (e.g. Shell or Siemens technologies) [11,12]. The wear rate is a phenomenon which is determined by viscosity, solubility, temperature and amount of slag per unit of time. For given bricks and process conditions, the wear rate was mostly dependent on the slag viscosity. A slag with lower viscosity easily penetrates into refractory pores, and leads to more wear. Guo et al. has proved that the wear rate increased by 1.5 times as slag viscosity decreased from 10.0 Pa s to 4.0 Pa s [13]. To enable gasification (or co-gasification) of these low-rank coals for entrained flow gasifier, difficulties caused by the low slag viscosity need to be overcomed.

Various authors [14–17] have expressed the flow properties of coal ash as a function of the oxides, i.e. SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, Na_2O and K_2O. The relationship between flow properties and ash compositions can be explained as follows: the acid oxide with high ionic potential are prone to form the polymers and lower the fluidity (e.g., the ionic potentials of Si^{4+}, Al^{3+}, and Ti^{4+} are 9.5, 5.9, and 5.9, respectively), while basic oxides with low ionic potential serve to terminate the formation of the polymers and increase the fluidity (e.g., the ionic potentials of Mg^{2+}, Ca^{2+}, Na^{+}, and K^{+} are 3.0, 2.0, 1.1, and 0.75, respectively). Huggins et al. [14] used the ternary equilibrium phase diagrams to study the effects of Fe_2O_3, CaO, and K_2CO_3 on the AFTs of coal ash. Gray et al. [15] studied the effects of acid and basic fluxes on the AFTs of coal ash. Vassilev et al. [16] investigated the influence of mineral and chemical composition of coal ashes on their fusibility. Song et al. [17] applied the thermodynamic computer package FactSage to study the effect of pure compounds (SiO_2, Al_2O_3, CaO, Fe_2O_3, and MgO) on the AFTs of coal ash.

With the aim of improving slag viscosity, fluxing materials are needed to obtain the proper viscosity at reasonable temperatures. Substances contained acid oxides like SiO_2, Al_2O_3 and TiO_2 seems to be the appropriate choice [18]. To increase the range of coals that can be processed in entrained flow slagging gasifiers, a common practice is to blend the feedstock with either additives or other coals with suitable composition to produce a feed with appropriate slag viscosity behavior. In this work, these two methods with additive and coal blending were both studied in order to improve to improve flow properties of selected low-rank coal ash. The variations of ash fusion temperatures and slag viscosity were investigated by ash fusion temperature detector and Theta high-temperature rotating viscometer. The FACTsage software package was used to calculate liquidus temperatures of coal ash, proportions of solid phase and mineral phase in slag as a function of temperature.

2. Experimental

2.1. Materials

For this study, one coal sample from Xinjiang was selected: YL (Yinli). The coal sample was ground to a particle size of less than 0.200 mm, dried at 105 °C for 24 h in N_2 atmosphere. Taken into account that SiO_2, Al_2O_3 and TiO_2 all have an increasing effect on slag viscosity, it is worthwhile to use the quartz (SiO_2), alumina (Al_2O_3) and titania (TiO_2)-containing substances. Kaolinite contains mainly SiO_2 and Al_2O_3 and GP (Gaoping) coal with high content of SiO_2 and Al_2O_3 were selected to blend with YL.

According to Chinese standards for coal analyses (GB/T212-2001, GB/T476-2001, GB/T213-2003, and GB/T214-1996), the proximate analyses, ultimate analyses, and total sulfur contents of samples were conducted, and the results were shown in Table 1. The ash compositions of materials were analyzed by X-ray fluorescence (XRF) according to ASTM D6349, and the results were presented in Table 2.

2.2. Measurement of AFTs

The ash fusion temperatures auto detecting system (KY company, China) was used to investigate the AFTs of coal ashes with addition of kaolinite and GP coal under CO/CO_2 (6:4) atmosphere according to the Chinese standard procedures (GB/T 219-2008). This procedure involves heating an ash cone at 15 °C/min up to 900 °C, and then changing the heating rate to 5 °C/min. During this process, the initial deformational temperature (IDT), softening temperature (ST), hemispherical temperature (HT), and fluid temperature (FT) were recorded according to the specific shapes of the ash cones.

2.3. Viscosity measurements

The viscosity of slags from blended coal (kaolinite with 6%, 12%, 18% and GP coal with 30%, 50%, 70%) was analyzed with a Theta high-temperature rotating viscometer (Theta Industries, Inc., USA) under a reducing atmosphere as measurement of AFTs. The test started from a higher temperature than liquidus temperature for keeping the sample totally melted. The maximum temperature of the viscometer is 1680 °C, which is high enough to melt most ash into slag. The alumina rotors and cylinder crucibles were used and the parameters for the rotor crucible combination were determined by the calibration with standard reference material 717A glass. The sample temperature was recorded using a type-B platinum thermocouple in an alumina pedestal and corrected using a previously determined temperature calibration experiment with a thermocouple inside the crucible filled with magnesium oxide.

2.4. Thermodynamic equilibrium calculations

FACTsage can be used for predicting multiphase equilibria, proportions of the liquid and solid phases, as well as phase transitions in a specified atmosphere and temperature for the heterogeneous slag systems [19]. In this work, FACTsage 6.3 with databases of