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Investigating a high vanadium petroleum coke ash fusibility and its modification



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ABSTRACT

Petroleum coke (petcoke), especially high vanadium (V) petcoke, has been produced increasingly because of the growing consumption of petroleum oil. Petcoke ash fusibility is closely related to ash slagging, which has an important impact on the clean and efficient utilization of petcoke. This study investigates a high V petcoke ash fusibility and its modification by coal blending and flux addition at reducing atmosphere. X-ray diffraction (XRD) and scanning electronic microscopy (SEM) were used to determine the crystalline minerals and surface morphology of high-temperature ash slag, respectively. The ash fusion process was predicted by thermodynamic equilibrium calculations. The results show that Shengli Oilfield petcoke (SL) has a high ash fusion temperature (AFT), whereas coal blending and flux addition can effectively decrease the AFT of SL, which may be ascribed to the mineral transformations during ash fusion process. The synergistic effects of high-melting vanadium trioxide (V_2O_3) and coulsonite (FeV_2O_4) result in the high AFT of SL. When SL blends with Shenmu (SM) coal and Qi coal (QC), the formation of low-melting andradite ($Ca_3Fe_2Si_3O_{12}$) and the decrease of V_2O_3 contribute to the progressive decline of AFT. When the addition of flux calcium oxide (CaO) reaches 10%, the low-melting calcium orthovanadate ($Ca_3V_2O_8$) formed under reducing atmosphere decreases the AFT. With increasing CaO content, the content of V_2O_3 and FeV_2O_4 decreases while that of $Ca_3V_2O_8$ and $Ca_3Fe_2Si_3O_{12}$ increases gradually, which further leads to a decrease in the AFT.

1. Introduction

The production of petcoke has been steadily increasing with the trend of processing crude oils. Furthermore, there is gradual more high-sulfur petcoke due to the quality deterioration of crude oils [1]. In general, high-sulfur petcoke is considered as a fuel for burning, which inevitably causes undesirable emissions [2]. Petcoke gasification technology can produce high quality syngas ($H_2 + CO$) to address the hydrogen deficiency in hydroprocessing units [3,4]. Meanwhile, the process provides superior environmental performance since the inherent sulfur in petcoke is mainly converted to H_2S [5,6]. However, in comparison to high reactive coals, such as lignite, the low gasification reactivity of petcoke greatly restricts its utilization in some actual gasifiers [7,8]. There are three gasification technologies, viz. fixed bed, fluidized bed, and entrained flow gasifiers, of which the fixed and fluidized bed gasifiers appear to be unsuitable for petcoke gasification because of their lower operating temperatures [9]. The entrained flow gasifier operated at high temperatures has been becoming a promising gasification technology with the advantages of high output, high thermal efficiency, and high carbon conversion efficiency [10,11]. It is

well known that the behaviors of ash fusion and flow at high temperatures play a key role in affecting the stable operation of gasifiers [12]. Continuous slag tapping is crucial for entrained flow gasification [13]. Thus, the ash slagging temperature of feedstock is required to be below the operating temperature of entrained flow gasifiers [9].

The ash composition of coal generally consists of Si, Al, Ca, Fe, K, and Na, whereas petcoke ash is mainly composed of V, Ni, Si, Al, and Ca. The mass percentage of V in petcoke ash usually accounts for 20% and sometimes even higher [14]. The large ash compositional differences between petcoke and coal may cause unpredictable slagging/fouling problems under gasification conditions because the transformation behavior of V at high temperatures is quite different from the general ash composition [15]. Frandsen et al. [16] investigated the fate of V in the thermal conversion calculations. V_2O_3 was the major stable V-bearing species below 1477 °C at reducing atmosphere. Li et al. [17,18] related the thermodynamic calculations to experiments to study the transformation of V during petcoke gasification. It was demonstrated that V_2O_3 crystalline phase was the dominant V-bearing minerals that formed in the process of gasification, which closely resembled the study of Nakano et al. [19]. Wang et al. [20] studied the

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influence of V_2O_5 on the transformation of minerals at reducing atmosphere. The formation of $Ca_3V_2O_8$ occurred at high temperatures. When the temperature was higher than 1400 °C, V_2O_3 was the only V-bearing species. There also have been some investigations focused on the effect of V on the ash fusibility at reducing atmosphere. Wang et al. [20] and Li et al. [21] pointed out that the AFT significantly increased with increasing vanadium pentoxide (V_2O_5) content. The flow temperature (FT) was higher than 1450 °C when the addition of V_2O_5 reached 25%. Although the role of V_2O_5 in ash fusibility is widely studied, very little information is available for petcoke ash fusion characteristics.

In general, high V petcoke has a high AFT (its FT even exceeds 1500 °C) [14], which inevitably limits its application in entrained flow gasifiers. Coal blending and flux addition are considered to be the effective methods to decrease the AFT of petcoke. Moreover, co-gasification of petcoke with coal provides a superior choice for the utilization of petcoke because the advantageous attributes of high alkali metal and large surface area of coal make up the shortage of low gasification reactivity of petcoke via synergetic effects [22,23]. In this work, fundamental experiments are carried out to investigate a high V petcoke ash fusibility and then explore its modification behavior by coal blending and flux addition, which are expected to provide some available information for entrained-flow gasification of high V petcoke.

Despite a few shortcomings, the AFT is a valuable guide for predicting ash slagging tendency during gasification [24]. The AFT provides not only detailed information on the softening and melting behavior of ash, but also the indication on the progressive melting of ash to slag [25]. The AFTs of petcoke mixed with different ratios of coal and flux CaO are investigated. Two characterization methods of XRD and SEM are used to investigate the crystalline minerals and microstructure of high-temperature ash slag, respectively. Thermodynamic equilibrium calculations by FactSage are also employed to predict the ash melting process, which is to compare and then validate the experimental results.

2. Experimental

2.1. Characteristics of raw materials

The typical high V petcoke from Shengli Oilfield, China, Shenmu coal from Shanxi Province, China, and Qi coal from Hebei Province, China, were selected for this study. Their proximate and ultimate analysis under air-dry basis are listed in Table 1. Petcoke ashing was performed at 700 °C for 24 h based on the American Society of the International Association for Testing and Materials (ASTM-International) standard designation D4422-13, Standard Test Method for Ash in Analysis of Petroleum Coke [26]. Two kinds of coal ashes were prepared at 815 °C for 2 h according to the Chinese standard procedures [27] (GB/T 1574–2007). Table 2 shows the chemical composition of three ash samples. To investigate the modification behavior of petcoke AFT by coal blending and flux addition, SM and QC were mixed with SL at the mass ratio of 10, 20, 30, 40, 50, and 60 wt%, respectively. SL was also blended with 5, 10, 15, 20, and 25 wt% flux CaO. The mixture was dried at 105 °C for 24 h in nitrogen atmosphere after blending sufficiently.

Table 1
Proximate and ultimate analysis of samples.

Samples	Proximate analysis(wt%, ad)			Ultimate analysis(wt%, ad)				
	M	A	V	C	H	O	N	S
SL	0.67	0.80	9.81	88.80	3.61	1.38	1.14	3.60
SM	0.84	13.17	22.98	76.62	4.29	1.96	1.26	1.86
QC	2.24	7.88	31.37	77.63	4.81	5.59	1.06	0.79

SL, Shengli Oilfield petcoke; SM, Shenmu coal; QC, Qi coal.

2.2. Measurements of AFTs

The ash fusion temperature analyzer developed by KY Corporation, China was used to determine the AFTs of mixed ash samples. The measurements were carried out under reducing atmosphere following the Chinese standard procedures [28] (GB/T 219–2008), which provided a valuable guide for the slagging of gasification [20]. In the procedure, the ash cone with a specific geometry was heated up to 900 °C at 15 °C/min and then changed to 5 °C/min. The shape variation of an ash cone was recorded with video camera. Four characteristic temperatures of ash, i.e., deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT), and FT, were recognized and recorded automatically with the accuracy of 1 °C. Repeated AFT tests were performed.

2.3. Quenching experiments

Quenching experiments were carried out to obtain high-temperature ash slag samples. The experimental temperature ranges from 1000 to 1300 °C, with the interval of 100 °C. The ash sample (1.0 g) filled in corundum crucible was heated in an electricity tube furnace under reducing ($CO/CO_2 = 6:4$ [12,20]) atmosphere. Fig. 1 shows the schematic diagram of the furnace apparatus. The thermal profile was set according to the AFT test. After reaching the scheduled temperature and residence time (15 min), the ash slag sample was immediately taken out and quenched in ice water to inhibit crystal segregation and phase transformation.

2.4. Characterization and testing

The chemical composition of petcoke and coal ash samples was analyzed by X-ray fluorescence spectrometry (XRF) with a Rh target X-ray tube (50 kV, 40 mA) from Shimadzu, Japan. The mineral composition of quenched ash slag samples was examined by a RIGAKU D/max-rB X-ray power diffractometer using Cu Ka radiation (40 kW, 100 mA, $K_{\alpha 1} = 0.15408$ nm). The samples were scanned with a 0.01° step size over the 2θ range of 10–80° at 4° 2θ /min scanning speed. Moreover, a JSM-7001F scanning electron microscopy was used to observe the surface morphologies of the quenched ash slag samples.

2.5. Thermodynamic equilibrium calculations

FactSage thermodynamic equilibrium modeling was used to calculate the solid phase component and liquid phase change with multiple components of V_2O_5 -NiO-SiO₂-Al₂O₃-Fe₂O₃-CaO-MgO-TiO₂-SO₃-K₂O-Na₂O-P₂O₅. The original mineral composition of metal elements in petcoke ash (ashed at 700 °C) and coal ash (ashed at 815 °C) was not taken into account in FactSage [17]. The mixed ash sample (1.0 g) was chosen as input data for equilibrium calculations and all the metal elements studied were assumed to get into equilibrium freely. FToxid and FactPS database were chosen for the phase formation data. However, FactSage did not have the database to deal with the interactions between VO_x and slag [29]. Calculations were carried out under reducing ($CO/CO_2 = 6:4$) atmosphere at 0.1 MPa. FactSage was based on Gibbs free energy minimization. Thus, when the total Gibbs energy of system reached its minimum value, all possible chemical reactions (homogeneous and heterogeneous) would reach equilibrium and only stable chemical species and phases remained [30]. It should be noted that the phases formed at equilibrium concentrations below 0.01 wt% were ignored in calculations.

3. Results and discussion

3.1. AFTs of ash samples

The AFTs of petcoke and coal ash samples under reducing

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