



Ash fusion characteristics during co-gasification of biomass and petroleum coke

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ABSTRACT

In this study, the effect of biomass ash on petroleum coke ash fusibility was investigated at a reducing atmosphere. Some analytical methods, such as ash fusion temperatures (AFTs) analysis, X-ray diffraction (XRD), FactSage and scanning electron microscopy (SEM), were applied to determine the characteristics of ash fusion and transformation of mineral matters. The results indicated that AFTs were closely associated with ash mineral compositions. It was found that the formations of high melting point calcium silicate, vanadium trioxide and coulsonite resulted in the high AFTs of Yanqing petroleum coke (YQ). When blending with certain proportional pine sawdust (PS), corn stalk (CS), the AFTs of mixture could be decreased significantly. For PS addition, the formations of low-melting point calcium vanadium oxide should be responsible for the reduction of AFTs, whereas for CS addition the reason was ascribed to the formation of low-melting point leucite and the disappearance of high-melting V_2O_3 .

1. Introduction

The production of petroleum coke has increased rapidly with the growing demand for heavy oil processing. Meanwhile, the proportion of high-sulfur petroleum coke increases gradually owing to the quality deterioration of crude oil in refineries (Zhang et al., 2015). It cannot be used in the aluminum smelting industries, graphite electrodes for steel production as well as the nonferrous industries because of its high content sulfur. High-sulfur petroleum coke is only regarded as a kind of fuel (Liu and Li, 2014). Inevitably, it causes severe SO_2 emission under combustion conditions. Thus, it is urgent to seek feasible technical routes for the clean and efficient utilization of petroleum coke. Gasification can efficiently convert petroleum coke into syngas ($CO + H_2$) to meet the increasing demand for hydrogen by refineries and other applications (Jayaraman and Gokalp, 2015). Meanwhile, the sulfur inherent in petroleum coke is mainly converted to H_2S during the process. However, it should be noted that petroleum coke reactivity is very poor due to the high C/H ratio, high sulfur and the low content of combustible volatiles. The petroleum coke complete gasification needs a higher temperature, a longer processing time or catalyst additives, which will raise the cost of the industrial gasification (Liu et al., 2015; Nemanova et al., 2014).

Biomass, as a zero-emission renewable resource, has competitive advantages of high reaction activity and low pollutant emission (Wei

et al., 2017a). Furthermore, the inherent abundant alkali and alkaline earth metals (AAEMs) in biomass ash could be used as a natural catalyst to reduce the catalyst cost (Wei et al., 2017b). However, the industrialization of biomass gasification is seriously limited due to its shortcomings in supply stability, slagging, tar yield and energy density (Song et al., 2015). Co-gasification of biomass and petroleum coke is an effective option. The prominent complementary is reflected in reactivity, physicochemical property and AAEMs content between biomass and petroleum coke. These particular advantageous make co-gasification of biomass and petroleum coke achieve the comprehensive, clean and efficient utilization (Wei et al., 2017a,b).

The vast majority of researches on the co-gasification of biomass and petroleum coke have focused on the production mechanism of kinetics and the synergetic effect of their co-gasification (Nemanova et al., 2014; Edreis et al., 2014; Zhang et al., 2016). However, the effect of biomass on petroleum coke ash fusibility is rarely reported. In the process of gasification, the behaviors of ash fusion and flow become the important factor that affects the stable operation of gasifier. In order to make better utilization of biomass and petroleum coke, it is essential to understand the ash fusion characteristics during co-gasification of biomass and petroleum coke. The ash fusion temperature (AFT) is widely used to reflect fusibility, flow, rheological properties of ash or slag and the extent of slag formation during gasification (Song et al., 2009; Song et al., 2010). Despite its shortcomings, AFT is still the most acceptable

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way to predict the feedstock slagging tendency during gasification (Van Dyk and Waanders, 2007). It is also an important parameter for selecting the operating temperature for gasification. Therefore, to further develop their co-gasification technology, it is necessary to investigate the ash fusion characteristics of petroleum coke and biomass mixtures.

The ash compositions of petroleum coke contain abundant amounts of V, which are different from coal that consists of Si, Al, Ca, Fe, K, and Na (Li et al., 2017a). In general, petroleum coke has a high AFT (its FT even exceeds 1500 °C) because the behavior of V at high temperatures is quite different from the general ash composition (Bryers, 1995). Li et al. (2016, 2017b) demonstrated that V_2O_3 and FeV_2O_4 were the main V-bearing forms during petroleum coke gasification, which was consistent with the investigation of Nakano et al. (2015) that crystallized V_2O_3 and VFe_2O_4 phase were present in high temperature slag. Frandsen et al. (1994) studied the fate of V in coal at reducing conditions by thermal conversion calculation. They found that V_2O_3 was formed at less than 1477 °C. Wang et al. (2013) investigated the effect of V_2O_5 on the transformations of minerals under a reducing atmosphere. The results indicated that $Ca_3V_2O_8$ formed at high temperatures and V_2O_3 was the only V-bearing species over 1400 °C. Unfortunately, few researches about the petroleum coke ash fusion characteristics and its modification have been published.

The aims of this work are to investigate the ash fusion characteristics during co-gasification of biomass and petroleum coke. Moreover, in order to better understand the influence of calcium-containing minerals in biomass on petroleum coke ash fusibility, quantitative investigation was conducted by blending calcium oxide with petroleum coke ash. Meanwhile calcium oxide is usually used as a flux addition to regulate the fusibility of coal. The ionic potential of Ca^{2+} (20 nm^{-1}) is lower than 25 nm^{-1} , which combines with oxygen and then decrease the amount of Si-O combination force to some extent. FactSage, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were applied to investigate the ash melting process and the modification mechanisms of petroleum coke ash by the addition of biomass ash, which is expected to provide some available information for further developing petroleum coke and biomass co-gasification technology.

2. Materials and methods

2.1. Characteristics of raw material

The typical high V petroleum coke from Yanqing Petrochemical Company (YQ), China, corn stalk (CS) from Taiyuan, Shanxi Province, China and pine sawdust (PS) from Heilongjiang Province, China, were used for this study. The samples were crushed and sieved to less than 0.2 mm. Prior to the experiment, all the samples were dried at 105 °C for 24 h to eliminate the disturbance of moisture. Their proximate and ultimate analyses are presented in Table 1. Flux calcium oxide (CaO) was provided by Fuchen Chemical Reagents Factory, Tianjin, China.

2.2. Ash preparation

Petcoke ash was prepared according to the American Society of the International Association for Testing and Materials (ASTM-International, 2013) standard designation D4422-13, Standard Test Method for Ash in Analysis of Petroleum Coke. The petroleum coke

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
YQ	1.43	0.69	11.71	89.44	3.85	1.51	1.31	3.89
PS	0.68	0.38	84.3	51.12	6.6	41.06	0.1	0.06
CS	9.21	5.08	66.42	46.86	6.22	37.61	9.22	0.091

sample was heated to 700 °C within 60 min and then held at 700 °C for 24 h in a muffle furnace. Biomass ash was prepared following the Chinese standard method (GB/T28731, 2012). Biomass was heated to 250 °C at the rate of 5 °C/min and kept for 1 h. Then the temperature was increased to 550 °C and kept for 2 h. Table 2 shows the chemical compositions of ash samples. The prepare procedures of samples mixtures of petroleum coke and biomass or CaO were prepared as follows. Biomass ash was put into YQ ash at the mass ratio of 10, 20, 30, 40 and 50%, respectively. Similarly, flux calcium oxide (CaO) was added into petroleum coke ash with various ratio of 5, 10, 15, 20, 25, and 30%. The mixture was placed in a vacuum oven at 105 °C for 24 h in nitrogen atmosphere after blending sufficiently.

2.3. Quenching experiments

A quenching experiment was performed to investigate the changes of compositions and surface morphology of ash at elevated temperatures. The ash samples were prepared at different temperatures in a horizontal electricity tube furnace under a reducing ($CO/CO_2 = 6:4$ (Wang et al., 2013; Kong et al., 2013)) atmosphere. To keep the same conditions, the thermal profile was set based on the AFTs test. To prevent crystal segregation and phase transformation, all ash samples were immediately pulled out and quenched in ice water.

2.4. Measurement of AFTs

The AFTs of mixture samples were carried out by the ALHR-2 ash fusion temperature analyzer. The measurements were performed under a reducing ($CO/CO_2 = 6:4$) atmosphere following the Chinese standard method (GB/T219-2008). The procedure is as follows, the ash cone was first heated to 900 °C at 15 °C/min, and then changed to 5 °C/min. The shape change of ash cone was recorded by video camera. Four characteristic temperatures of ash (deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT)) were determined and recorded automatically with the accuracy of 1 °C. Repeated experiments were performed.

2.5. Ash analytical methods

A wavelength-dispersive sequential X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan) with a Rh target X-ray tube (50 kV, 40 mA) was used to analyze the chemical compositions of petroleum coke and biomass ash samples. The mineral compositions of the quenched ash slag were analyzed by a RIGAKU D/max-rB X-ray powder diffract-meter with Cu Ka radiation (40 kV, 100 mA, $Ka1 = 0.15408\text{ nm}$). The samples were scanned with a step size of 0.02° at $4^\circ/\text{min}$ over the 2θ range $5\text{--}80^\circ$. The surface morphology of the ash samples was examined by a JSM-7001F scanning electron microscope.

2.6. Thermodynamic equilibrium calculations

FactSage 6.2 was applied to calculate the solid phase component and liquid phase change at different temperatures with multiple composition of $V_2O_5\text{-NiO-SiO}_2\text{-Al}_2O_3\text{-Fe}_2O_3\text{-CaO-MgO-TiO}_2\text{-SO}_3\text{-K}_2O\text{-Na}_2O\text{-P}_2O_5$. FactPS and FToxid databases were chosen for phase formation data and FToxid was first to avoid selecting duplicate compounds. FToxid calculations were carried out in a mild reducing ($CO/CO_2 = 6:4$) under atmospheric pressure. The calculation method of FactSage is based on Gibbs' energy minimization. Thus, at a given temperature and composition range, all possible reactions (homogeneous and heterogeneous) will reach thermodynamic equilibrium and there are only stable chemical species and phases (Bunt and Waanders, 2010). In addition, phases formed at concentrations below 0.01% were ignored in the calculation process.

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