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Effect of water vapor on coal ash slag viscosity under gasification condition

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ABSTRACT

The entrained flow gasification process employs a high temperature, high pressure slagging gasifier, in which the viscosity of the slag plays a key role in determining operating conditions. Many studies have focused on the viscosity of slag under the reducing atmosphere, especially CO + CO_2 and CO + H_2. As an important component in the gasification syngas, the effect of water vapor on the slag viscosity temperature properties is not yet clear. In order to keep the stable operation of the gasifier, the effect of water vapor on the viscosity temperature properties of the slag were studied in this work. Ash fusion temperatures (AFTs) decrease with the increasing water vapor proportion. Although mineral species do not change obviously, the content of SiO_2 in the ash decreases, and more amorphous substances forms when water vapor is added. The slag viscosity and temperature of critical viscosity (T_{CV}) also decrease with the introduction of water vapor, while the effect is not obvious due to the low solubility at ambient pressure. It is confirmed that water vapor weakens the melts network structure by breaking [Si–O–Si] bonds. Meanwhile, the network modifier, $[AlO_6]^{9-}$, increases with the increasing water vapor proportion. Besides, water vapor inhibits the growth of the crystal. As its proportion increases, the average particle size of crystals decreases, leading to the decrease of the slag viscosity and T_{CV}. The results provide a theoretical basis for the effect of water vapor on the slag viscosity and will be benefit for the operation of entrained flow gasification, especially for the coal water slurry gasification.

1. Introduction

Coal, as the main energy material, plays a dominant role in China's energy consumption and is an important guarantee for the rapid and stable development of the economy [1,2]. Coal gasification offers one of the most versatile and clean ways to convert coal into electricity, hydrogen, and other valuable energy products [3]. It can not only reduce the emission of harmful gases, but also can significantly increase the energy efficiency of coal. According to flow mechanics in the gasifier, coal gasification technologies are divided into fixed-bed (e.g., Lurgi and UGI), fluidized-bed (e.g., U-gas and KBR,) and entrained flow bed gasification (e.g., Shell, GE and OMB) [4,5]. In recent years, entrained flow gasification has become a predominant gasification technology in coal gasification due to its high throughput and feedstock flexibility.

The entrained flow gasifiers usually operate under a high temperature (usually higher than 1300 °C) and a high pressure [6]. Entrained flow gasifiers are slagging gasifiers. Under this condition, the evolution behavior of inorganic substances (minerals, ash and slag) in the coal at high temperature, especially the slag tapping, is a key factor for long-term running of an entrained flow gasifier. An appropriate slag viscosity property was required for the steady and reliable discharge of slag [7,8]. The high slag viscosity could cause slag blockage, while a low slag viscosity will result in rapid refractory wear [9]. According to the feedstock, entrained flow gasification includes pulverized coal gasification process (dry feed) and coal water slurry gasification process (slurry feed) [10]. For the pulverized coal process which features a membrane wall (such as the Shell gasifier), slag viscosity-temperature behavior is the key parameter to guide the smooth operation of the gasifier. It is generally accepted that slag viscosity should be 2.5–25 Pa·s at the slagging temperature when the temperature is between 1300 and 1500 °C [11]. At the same time, in order to prevent the rapid increase of slag viscosity caused by temperature fluctuations and the corresponding slagging problems in the gasifier, the slagging temperature should be higher than T_{CV}. Besides, the slag should be a glassy slag, of which the viscosity increases continuously as the temperature decreases. For the coal-water slurry gasifier (such as GE and OMB) [12], refractory lined are used for heat insulation, and the thermal resistance is mainly concentrated on the refractory brick layer. Basically, the slag viscosity is

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required in the range of 10–25 Pa·s under normal operation to ensure smooth slagging.

The slag viscosity-temperature characteristics are affected mainly by the chemical compositions of the coal slag. The other factors affecting slag viscosity-temperature characteristics are temperature, atmosphere and operating parameters of the gasifier [13]. According to the network theory of molten slag at high temperature, the coal ash chemical compositions are divided into three categories: network formers, network modifiers and amphoterics [14]. The network formers (e.g. Si^{4+} and Ti^{4+}), which become the polymers, increase the slag viscosity; the network modifiers (e.g. Na^{+}, K^{+}, Mg^{2+}, Ca^{2+} and Fe^{2+}) destroy the polymers, decreasing the slag viscosity; amphoterics (e.g. Al^{3+} and Fe^{3+}), which can play as network formers or network modifiers in different system [15]. Atmosphere is also an important factor, affecting the slag viscosity. It mainly attributes to reduction of the oxidation state of iron under high temperature. Under reducing atmosphere, a part of the iron that would normally be Fe^{3+} is reduced to Fe^{2+}. Fe^{3+} tends to enhance the three-dimensional structure of the melt and increases the slag viscosity [16]. However, Fe^{2+} is likely to disrupt the connectivity of network by providing non-bridging oxygen (NBO), lowering the slag viscosity.

Except for the difference of the feedstock and inner wall for pulverized coal gasifier and coal water slurry gasifier, the compositions of the syngas also varied a lot. For most of the gasifier, the main components of the syngas are CO, CO_2, H_2 and H_2O, while the proportion of each component is different. For example, in Shell gasifier, the ratio of CO, CO_2, H_2 and H_2O in syngas is 62.2%, 2.3%, 31.6% and 4.0%, respectively. In Texaco gasifier, the percentage of CO, CO_2, H_2 and H_2O is 35.4%, 15.5%, 34.4% and 14.7%, respectively [17]. In OMB gasifier, the syngas consists of 37.68% CO, 11.83% CO_2, 26.54% H_2 and 23.95% H_2O [18]. It can be concluded that water vapor is an important component in the gasification syngas. According to statistics of the syngas in the coal-water slurry gasification, the water vapor content in the gasifier and the slagging outlet is about 10–20%. Therefore, it is necessary to investigate the influence of water vapor on the slag viscosity behavior.

In this work, a typical coal in the coal-water slurry gasification was selected. The slag viscosity-temperature characteristics under different atmosphere (without and with different proportions of water vapor) were studied. X-Ray diffraction (XRD) was used to analyze the mineralogical compositions of the ash at high temperatures. The slag structures were characterized by Nuclear Magnetic Resonance Spectrometer (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Besides, solid phases in the slag during cooling were investigated by Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX).

2. Experimental

2.1. Sample

A bituminous coal in coal water slurry gasification, Yanzhou coal (denoted as YZ coal, Shandong province, North China), was selected in this work. The coal sample was crushed and ground to less than 75 μm. The proximate and ultimate analyses of the coal were performed according to GB/T212-2008 and GB/T476-2001, and the results are listed in Table 1. The coal ash was prepared at 815 °C in a muffle furnace based on GB/T 1574-2007. X-ray fluorescence (XRF) (Bruker S8 Tiger, Germany) was used to characterize the chemical compositions of the ash, as listed in Table 2. The coal ash was rich in calcium oxide and iron oxide, but the contents of silicon oxide and aluminum oxide were low.

Table 1
Proximate and ultimate analyses of YZ coal.

Proximate analysis (wt%, ad)				Ultimate analysis (wt%, ad)				
Moisture	Ash	Volatile	Fixed Carbon	Carbon	Hydrogen	Oxygen[a]	Nitrogen	Sulfur
5.47	5.46	34.63	54.44	74.46	4.45	8.82	0.91	0.43

ad: air dry base.
[a] By difference.

Table 2
Chemical compositions of YZ ash (wt%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5
15.08	8.55	22.30	33.59	2.37	12.49	0.05	0.79	0.35	0.02

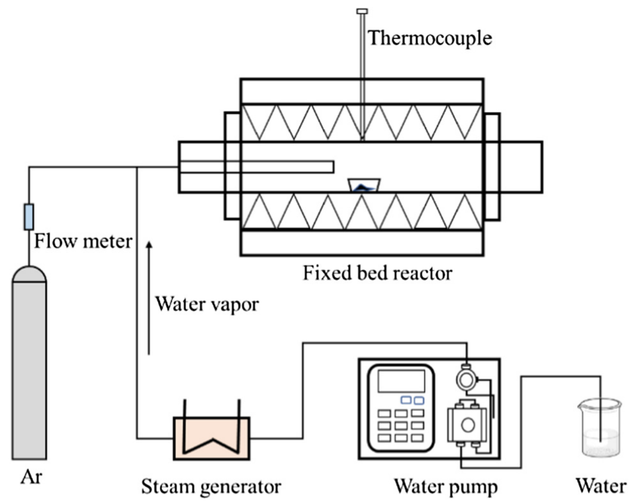

Fig. 1. A schematic diagram of water vapor generator.

2.2. Water vapor generator

A small fixed bed reactor which combined with a micro water pump (AP0010, Sanotac, China) was used to generate water vapor, and a schematic diagram is given in Fig. 1. The reactor was heated by a heating belt and the temperature was kept at 150 °C to ensure that water can be completely vaporized. A K-type thermocouple and a digital temperature controller (XMTD-2001, 0–399 °C) were used to control the temperature. The flow rate of water was accurately controlled by the micro metering pump which provided a flow rate from 0.001 ml/min to 10 ml/min with an accuracy of ± 0.5% [19]. Because the composition of the reducing atmosphere at various temperatures would be affected by possible water gas shift reaction (Eq. (1)), an argon gas (Ar) was selected to carry the water vapor. The total flow rate of the mixture gas was 700 ml/min, and the proportion of water vapor was 10%, 15% and 20%, respectively. In this work, ideal gas equation (pV = nRT) was used to calculate the amount of liquid water.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$