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The formation of deposits and their evolutionary characteristics during pressurized gasification of Zhundong coal char

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ABSTRACT

The characteristics of deposits formed on stainless steel substrate (boiler tube) during pressurized gasification of Zhundong coal char with excessively high Na content were investigated in this work. The occurrences of alkali and alkaline earth metallic species in raw coal and its derived chars were determined by a sequential extraction method. The morphology, mineralogy and chemical compositions of deposits and bottom ash produced during the gasification of Zhundong coal char at 800, 1000 and 1200 °C were analyzed by X-ray diffraction and scanning electron microscopy combining energy dispersive X-ray spectrometer. Results show that water-soluble and ammonium acetate solution soluble sodium and potassium in raw coal tended to be converted to hydrochloric acid solution soluble form during Zhundong coal pyrolysis. Rising pyrolysis temperature increased the content of water-soluble calcium by enhancing the decomposition of $CaCO_3$ and organically bonded calcium. During the gasification of Zhundong coal char, the released inorganic species, especially Na, Ca, Cl and S, could condense and/or agglomerate as sticky fine particles, resulting in fouling and slagging on the probes. Specifically, after Zhundong char gasification at 800 °C, alkali and alkaline earth metallic species-bearing minerals loosely clung on the probes as silicate or aluminosilicate. During char gasification at 1000 °C, a Na-S-O and/or Na-S deposit layer with a thickness of ca. 2 μm was formed on the probe No. 1 at 514 °C, while abundant Ca-Mg-Si-O and few Na_2SO_4 crystals were accumulated on the probe No. 2 at 771 °C. During Zhundong char gasification at 1200 °C, the minerals deposited at low temperature region (599 °C) were mainly composed of agglomerated and sintered alkali and alkaline earth metallic species-bearing compounds (mainly NaCl, KCl and Ca-Mg-Si-O). However, only few isolated particles were observed on the probe with temperature higher than 924 °C. Residual alkali and alkaline earth metallic species in bottom ash could form low-melting eutectics, such as $NaAlSiO_4$ and $Ca_2Al_2SiO_7$.

1. Introduction

Zhundong coal is mined from the coal field located in Xinjiang province, China, with a potential coal reserve up to 3.9×10^{11} tons [1]. The coal features high calorific value, high volatile, low ash and sulfur contents [2]. However, its utilization, such as combustion and gasification, usually gives rise to severe fouling and slagging problems in the equipment and downstream processes [3,4] due to the high proportion of alkali and alkaline earth metallic species (AAEMs), especially sodium and calcium [5,6], in Zhundong coal (the so-called high-basic coal). Currently, the cascade upgrading of low-rank coal, which combines drying, pyrolysis and gasification technology, is under rapid development. This process could produce substantial syngas and tar with high industrial value [7]. Furthermore, some inorganic matter, such as AAEMs, halogen and toxic trace elements in raw coal, is considered to be released from coal matrix during pyrolysis, therefore alleviating fouling and slagging in the equipment and mitigating negative environmental impacts during the downstream char gasification [8,9]. Therefore, it is an effective way to improve coal utilization efficiency by coupling coal pyrolysis with char gasification. However, owing to the lack of systematic investigation on the deposition features of AAEMs, the fouling and slagging behavior during pressurized char gasification is still unclear.

The release of inorganic elements, e.g., Na, Cl and S, has been widely studied during coal pyrolysis. Organically bonded sulfur and chloride species are considered to be released at low temperature [10]. Meanwhile, part of the AAEMs, especially the soluble alkali metal species, could be released as alkali metal atoms and/or oxides and subsequently react with other volatiles species to form alkali metal-bearing substances, such as alkali chloride and sulfate [11,12].

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Although part of the volatile and harmful substances could be released into the gas phase during pyrolysis, there were still a significant amount of harmful substances retained in char. However, most of the previous work focused on the quantitative analysis of the released AAEMs and S, Cl species, while studies on the deposition and fouling behaviors of alkali metal-bearing minerals are insufficient during coal or char gasification. Generally, multiple factors could affect the transformation and deposition behaviors of minerals, such as thermal conversion and deposition conditions [13,14], occurrences of active minerals as well as the characteristics of char. Particularly, fuel thermal conversion conditions, such as temperature and atmosphere, are believed to be the decisive factor governing the transformation and deposition of minerals [15]. The diffusion and transformation of inorganic minerals is certainly enhanced with rising temperatures [15,16], therefore, the mineralogy, morphology and sintering characteristics of minerals are diversified under different temperatures. Among those minerals, various forms of AAEMs in char play an important role in the evolution and interaction of minerals. As reported in previous studies [17,18], water-soluble and organically bonded alkali metal species in Zhundong coal are considered to be the most harmful because of their high contents and highly volatile characteristics. The volatilized Na- and K-bearing species could either adhere to and react with fly ash particles or sulfate to form sticky low-temperature eutectic [19,20], resulting in fouling and corrosion in equipment. However, the insoluble AAEMs, i.e., AAEMs combined with the aluminosilicate, are difficult to volatilize [21]. Therefore, getting insight into the evolutionary behaviors of HCl soluble AAEMs under different temperatures are significant to the high-basic coal char gasification.

Accordingly, the objective of this paper is to elaborate the morphology and mineralogy characteristics of AAEMs-bearing minerals during pressurized gasification of Zhundong char in a simulated bench-scale pressurized fixed-bed gasifier at different temperatures. During the gasification process, stainless steel substrates were placed at different position of the reactor to capture the mineral aerosol derived from the evaporation or volatilization of minerals in char. Bottom ash and deposits were analyzed for the morphology, elemental distribution, compositions and binding state. Besides, the evolution of minerals under different temperatures was simulated using FactSage based on the thermodynamic equilibrium. This work systematically clarifies the mineral deposition characteristics during char pressurized gasification at different temperatures. And it is expected to provide useful information for mitigating and eliminating slagging and corrosion in equipment during the utilization of high-basic coal.

2. Experimental section

2.1. Sample preparation

A typical high basic coal mined from Wucaiwan, Zhundong coalfield, (hereafter termed as W-coal) is used in this work. The coal was air-dried, crushed and sieved to obtain a sample with particle sizes between 0.9 and 2 mm. The proximate, ultimate and ash compositions analyses of the sample are presented in Table 1. W-coal is characterized by high volatile (27.01 wt%) and low ash content (6.24 wt%). Moreover, the contents of Na_2O, CaO and SO_3 in W-coal ash were up to 3.83, 23.15 and 19.77 wt%, respectively.

The contents of various chemical forms of Na, K, Ca and Mg in raw coal and its derived chars were determined by a sequential extraction method. Specifically, coal and char samples were ground and sieved to < 74 μm and then packed in an ion-exchange column and sequentially extracted for 6 h in each cycle using deionized water, ammonium acetate solution (1mol/L), and hydrochloric acid solution (1 mol/L), respectively. Subsequently, the concentration of AAEMs in the extracted solution was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Table 1
Analysis of W-coal, char and ash samples.

Samples	W-coal	800-char	1000-char	1200-char
Moisture (wt% ad)	11.81	0.84	0.52	0.96
Proximate analysis (wt% db)				
Volatile matter	30.63	4.86	3.76	1.99
Fixed carbon	62.29	86.55	86.24	87.53
Ash	7.08	8.59	10.00	10.48
Ultimate analysis (wt% daf)				
C	79.07	88.82	90.47	90.93
H	4.05	0.623	0.191	0.131
N	0.79	0.65	0.85	0.62
S_t	0.51	0.328	0.448	0.568
$O_{(diff.)}$	15.58	9.579	8.041	7.751
Elemental compositions of ash (wt%, ashed at 500 °C)				
SiO_2	25.56	22.20	19.31	22.07
Al_2O_3	12.55	12.67	10.29	11.18
CaO	23.15	28. 71	24.10	25.14
Na_2O	3.83	4.99	2.85	4.52
Fe_2O_3	2.88	2.86	2.83	2.76
SO_3	19.77	13.67	29.41	21.90
MgO	7.20	10.44	7.64	8.10
K_2O	0.36	0.36	0.34	0.35
Cl	0.96	1.86	0.99	1.38
Coal ash melting point/°C				
Deformation temperature (DT)	1155			
Softening temperature (ST)	1163			
Flowing temperature (FT)	1171			

Note: ad.: air dry basis; db.: dry basis; daf.: dry and ash free; diff.: by different.

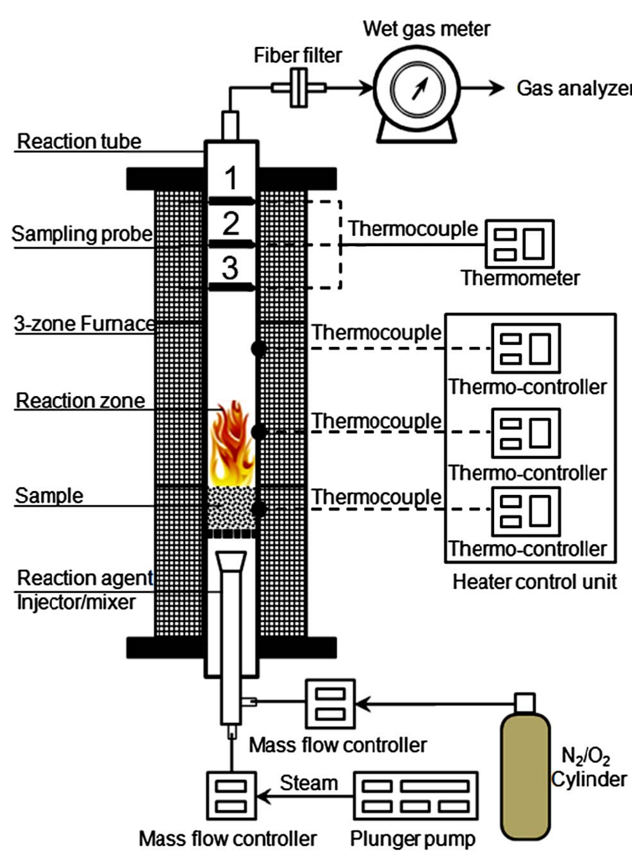

Fig. 1. Schematic diagram of pressurized fixed bed pyrolysis/gasification reactor.

2.2. Experimental apparatus and process

As shown in Fig. 1, gasification experiments were conducted in an electrically heated pressurized fixed-bed pyrolysis/gasification reactor.