



Effect of circulating ash on sulfur conversion characteristics in the coal polygeneration process



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ABSTRACT

Sulfur transformation in the polygeneration process of Xinzhou high-sulfur coal employing a circulating ash heat carrier was studied using a fixed bed reactor. Circulating ash was effective in capturing the gaseous sulfur, along with ~80% of H₂S, 59% of COS, 55% of CS₂, and 48% of SO₂. Sulfur mass balance calculations revealed that 30.88% of the total sulfur content was retained in the circulating ash at 600 °C. The sulfur retention capacity of the ash was promoted by an increase in temperature, an increase in the ash to coal mass ratio, and a decrease in ash particle size. Sulfur captured in the circulating ash released lower quantities of SO₂ than the sulfur remaining in the char during combustion. Furthermore, CaO and Fe₂O₃ played a dominant role in the sulfur retention of the circulating ash, and the sulfur retention capacity of Fe₂O₃ was superior to that of CaO during pyrolysis. X-ray diffraction results indicated that the sulfur captured by CaO and Fe₂O₃ was converted into CaS and FeS. However, FeS was easily oxidized to Fe₂O₃, accompanied by the emission of SO₂, while CaS tended to be oxidized to CaSO₄ during combustion.

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1. Introduction

In recent years, direct coal combustion has been the cause of great public concern due to its poor energy conversion efficiency and contribution to air pollution [1]. Thus, to address these points and render coal a more efficient fuel, a polygeneration process coupled to a moving bed coal pyrolysis technique with circulating fluidized bed (CFB) combustion was proposed. In this process, the coal pyrolysis heat source was a high-temperature circulating ash accumulated from the CFB cyclone. The char and circulating ash were subsequently returned together to the CFB boiler for combustion. This combined process allows the polygeneration of gas, tar, power, and heat [2,3].

To date, a number of studies have focused on the development of the pyrolysis/combustion polygeneration process [4,5]. However, a comprehensive understanding of the distribution and conversion characteristics of sulfur in this process is still required. The circulating ash contains sulfur fixation sorbents, which are derived from two sources, namely the adventitious Ca-based additives used to capture the pollutant gases in the CFB boiler, and the remaining alkaline minerals following coal combustion. A number of studies have found that the alkaline mineral matter in coal can not only catalyze the coal conversion reactions, but can also trap released gaseous sulfur to maintain a high level of sulfur distribution in the char [6–10]. Liu et al. [11] studied the role of mineral matter in coal pyrolysis and found that the reaction of

alkaline mineral matter with sulfur-containing gas to form sulfide seriously hindered sulfur removal from coal. In recent years, researchers have further studied the utilization of alkaline mineral additives for sulfur retention in coal pyrolysis. Guan et al. [12] found that 95% of the gaseous sulfur evolved from raw coal was captured in char as CaS through the use of CaO and Ca(OH)₂ additives. In addition, Khan [13] concluded that the addition of CaO and Fe₂O₃ significantly reduced H₂S yields, while MgO had little effect on the evolution of gaseous sulfur. During the subsequent combustion of the pyrolyzed solids in the CFB boiler, various forms of sulfur were ultimately present in the two streams, namely gaseous sulfur species and mineralized sulfur in ash. Several reports on the oxidation of CaS have been published, with Xiao et al. [14] reporting that the major product of CaS oxidation below 970 °C was CaSO₄, while the solid-solid reaction between CaS and CaSO₄ was reinforced at 970–1150 °C, accompanying the evolution of SO₂. In addition, Qiu et al. [15] found that the conversion of CaS to CaSO₄ reached a maximum at 920 °C with <60% sulfidation observed for the desulfurization residues. Thus, the existence of alkaline mineral matter in circulating ash affects sulfur conversion during pyrolysis, which in turn affects sulfur evolution during the subsequent combustion process. A key factor in developing an optimized desulfurization scheme applicable to such a polygeneration process is the ability to predict and control sulfur evolution in pyrolysis and combustion processes. In addition, the extent of gaseous sulfur captured by the circulating ash depends to a large extent on the reaction conditions. However, the effects of different alkali constituents in the circulating ash on sulfur retention have not yet been studied in detail.

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Table 1
Proximate and ultimate analyses along with sulfur contents (wt%) of the SX coal.

Proximate analysis (ad)				Ultimate analysis (daf)					Sulfur content (daf)		
M	A	V	FC	C	H	N	S	O*	S _p	S _s	S _o *
0.75	13.06	33.73	52.46	82.64	5.42	1.21	3.11	7.62	1.11	0.34	1.66

*: by difference; ad: air dried basis; daf: dry and ash-free basis; M: moisture; A: ash; V: volatile matter; FC: fixed carbon; Sp: pyritic-S; Ss: sulfate-S; So: organic-S.

Table 2
Ash composition (wt%) of the circulating fluidized bed boiler ash.

Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	P ₂ O ₅	SO ₃	TiO ₂	SiO ₂
33.23	2.46	5.03	1.11	0.53	0.16	0.13	0.73	0.86	55.76

The objective of this study is to investigate the key technical factors that influence the sulfur distribution in products and to analyze the sulfur retention capacity of circulating ash in coal pyrolysis. In addition, we aim to reveal the transformation mechanism of residual and captured sulfur in char/ash during the combustion process. The results of this study are expected to provide powerful theoretical evidence for the future industrial development of pyrolysis/combustion grading conversion technology.

2. Experimental

2.1. Coal and ash samples

High-sulfur bituminous Xinzhou coal from Shanxi province (SX coal) was employed in the study. The coal sample was crushed and sieved to give a particle size range of 0.075–0.106 mm. Table 1 shows the proximate and ultimate analyses along with the sulfur contents of the SX coal. Quartz sand and circulating ash were chosen as the solid heat carriers in this study. The circulating ash employed was collected from a 75 t/h CFB boiler. The ash composition of the circulating ash was analyzed by X-ray fluorescence spectrometry (XRF), and the results are shown in Table 2. All additives used in the study (i.e., CaO, Fe₂O₃, MgO, Ca(OH)₂, and KOH) were of analytical grade. Coal containing additives and their abbreviations are shown in Table 3.

2.2. Pyrolysis and combustion experiments

To investigate the conversion characteristics of sulfur in the polygeneration process on the laboratory scale, a horizontal fixed bed reactor was used (as shown in Fig. 1) for the pyrolysis/combustion two-stage experiment. Initially, coal samples were pyrolyzed together with the solid heat carrier under an inert atmosphere, and subsequently, the char and ash were combusted under air.

For the pyrolysis experiment, 5 g coal and the desired quantity of the solid heat carrier were positioned in the quartz tube (length: 440 mm, inner diameter: 19 mm), and the tube was placed in the electric furnace. Nitrogen was used as the carrier gas at a flow rate of 60 mL/min. A heating rate of 10 °C/min was used along with a holding time of 10 min after reaching the desired pyrolysis temperature. Tar and water released from the volatiles were cooled and collected in a cold trap. A sulfur determination analyzer was used for total sulfur determination in both the solid and liquid products. The sulfur distribution mass

Table 3
Sample details for the SX additive-containing coals.

Additive	CaO	Fe ₂ O ₃	MgO	NaOH	KOH
Mass fraction = 1%	SX1	SX4	–	–	–
Mass fraction = 3%	SX2	SX5	SX7	SX8	SX9
Mass fraction = 5%	SX3	SX6	–	–	–

balance was calculated by comparing the quantities of sulfur in char, solid carrier, and tar with the total sulfur present in raw coal. Sulfur distribution in the gaseous form was calculated based on the difference of these values. For the combustion experiment, char and ash after pyrolysis were combusted using an air flow of 120 mL/min, a heating rate of 15 °C/min, and a holding time of 90 min at the final desired temperature. The combustion residue was collected and its sulfur content was determined.

2.3. TG-MS experiments

Combined thermogravimetric mass spectrometry (TG-MS) experiments of SX coal and the mixture of SX coal with circulating ash were performed using a Setsys-Evolution thermal balance coupled with a Balzers Omnistar™ mass spectrometer. In each TG experiment, the sample (15 mg) was placed in a ceramic crucible and was heated from 20 °C to 800 °C at 30 °C/min under a flow of N₂ at 80 mL/min. The evolved gases were sampled automatically and analyzed by the MS system, with an electron impact source tuned at 40 eV and a mass range of 0–300 amu.

2.4. Analytical methods

Sulfate and pyritic sulfur contents were determined based on the GB/T 215–2003 standard method [16]. Sulfur was extracted from sulfate samples using a 5 mol/L HCl solution and the sulfur content was calculated based on the concentration of SO₄²⁻ in the filtrate. The resulting residue was then extracted with a 2 mol/L HNO₃ solution and the pyritic sulfur content was determined based on the concentration of Fe³⁺. During treatment with the HCl solution, the inorganic sulfide decomposed and was released as H₂S. Thus, only organic sulfur remained in the residual char washed by the HCl and HNO₃ solutions. The organic sulfur content was determined using the sulfur determination analyzer, and the sulfide sulfur content was calculated by subtraction of the sum of the organic, sulfate, and pyritic sulfur from the total sulfur content [17].

X-ray diffraction (XRD) patterns were collected on a D/max2500PC automatic powder X-ray diffractometer using CuKα radiation at 200 mA and 40 kV. Each sample was scanned between 10° and 80° 2θ at a scan speed of 5°/min.

The surface sulfur content in the char was determined by X-ray photoelectron spectroscopy (XPS) using an ESCALAB250 with AlKα source at a base pressure of 2.0 × 10⁻⁷ Pa. Calibration for binding energy calculations was carried out using the main C1s peak at 285 eV. The relative concentrations of sulfur forms were based on binding energy peak values at (163.3 ± 0.4), (164.1 ± 0.2), (166.0 ± 0.5), (168.0 ± 0.5), and (169.5 ± 0.5) eV for sulfides, thiophenes, sulfoxides, sulfones, and sulfates, respectively [18,19].

3. Results and discussion

3.1. Evolution of gaseous sulfur during pyrolysis

As shown in Fig. 2, compared to coal pyrolysis alone, a noticeable decrease in gas evolution intensity was observed for the four gaseous sulfur compounds upon the addition of circulating ash. Approximately 80% H₂S, 59% COS, 55% CS₂, and 48% SO₂ were captured by the circulating ash, as calculated by an area integration method using the Origin

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