



# Sulfur transformation during the pyrolysis of coal mixed with coal ash in a fixed bed reactor



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## HIGHLIGHTS

- The coal ash could capture H<sub>2</sub>S at low temperatures, but promote H<sub>2</sub>S at high temperatures.
- The coal ash could enhance COS evolution at high temperature.
- The release of H<sub>2</sub>S and COS seemed to be less affected by the ash which was prepared under 1000 °C than that under 800 °C and 900 °C.
- The evolution of H<sub>2</sub>S and COS under pyrolyzed atmosphere followed the same general trend with that under N<sub>2</sub> atmosphere.

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## ABSTRACT

The Xiaolongtan coal with different blend ratios (ash/coal) of ash was pyrolyzed in a fixed bed reactor to study sulfur transformation during the pyrolysis of the mixture of coal and coal ash. The addition of coal ash inhibited H<sub>2</sub>S evolution at low temperatures, and this was because H<sub>2</sub>S was captured by Fe<sub>2</sub>O<sub>3</sub> of the coal ash. However, the coal ash promoted H<sub>2</sub>S evolution at high temperatures, which should be due to the reaction  $4\text{H}_2 + \text{CaSO}_4 \rightarrow \text{CaO} + 3\text{H}_2\text{O} + \text{H}_2\text{S}$ . More COS was evolved with the addition of coal ash at 700–800 °C, and the possible reason was that COS could be produced through the reactions  $4\text{CO} + \text{CaSO}_4 \rightarrow \text{CaO} + 3\text{CO}_2 + \text{COS}$  and  $2\text{C} + \text{CaSO}_4 \rightarrow \text{CaO} + \text{CO}_2 + \text{COS}$ . The addition of coal ash reduced tar sulfur. The effects of the conditions (temperature of ash preparation and atmosphere) on the sulfur containing gas were also discussed. The evolution of H<sub>2</sub>S and COS were less affected by the ash prepared under 1000 °C than that under 800 °C and 900 °C. The possible reason was that the reactions among the volatile matters and coal ash were unfavorable due to the sintering of the ash under 1000 °C. The effect of coal ash on H<sub>2</sub>S and COS under simulated pyrolyzed gas atmosphere was similar to that under N<sub>2</sub> atmosphere, but higher H<sub>2</sub>S and COS yields were obtained under simulated pyrolyzed gas atmosphere.

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## 1. Introduction

Presently, the emission of SO<sub>2</sub> from coal combustion is one of the main pollution sources, so desulfurization technology has received many researchers' considerable attentions. The coal staged conversion process is one of the most promising technologies to realize high desulfurization efficiency [1,2] and the principle is shown in the previous study [3]. In the pyrolysis process of coal staged conversion process, some sulfur existed in the coal is converted to sulfur containing gas and tar sulfur, which is mainly in H<sub>2</sub>S form. The rest sulfur which existed in the char is converted to SO<sub>2</sub> in the combustion process. Compared with the removal SO<sub>2</sub> from the flue gas, it is much easier to remove H<sub>2</sub>S from the coal gas.

What's more, valuable products, like sulfur and sulfuric acid, can be obtained in the process of H<sub>2</sub>S removal.

Due to the promising application of the coal staged conversion process in sulfur removal, the study on the sulfur transformation especially in the coal pyrolysis is of great necessity. Although sulfur transformation during traditional pyrolysis has been well investigated, the sulfur transformation in the coal staged conversion process is not well understood. Because sulfur transformation in the coal staged conversion process is clearly distinguished from the traditional coal pyrolysis process and the most striking feature of the sulfur transformation in the coal staged process is the interaction of the coal and abundant circulating ash. Much high temperature circulating ash is needed to satisfy the pyrolysis temperature, and the ratio of coal ash to coal in the pyrolyzer ranges from 1 to 5. Sulfur transformation during the pyrolysis of the mixture of coal and coal ash is not well understood. The existence of circulating ash may have a great influence on the sulfur transformation during

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the pyrolysis and the sulfur of the coal ash (CaSO<sub>4</sub>) also can be transformed to other forms of sulfur in this process, which was rarely reported in published literatures. Therefore, this paper aims to give a comprehensive investigation of sulfur transformation during the pyrolysis of the mixture of coal and coal ash.

## 2. Experimental

### 2.1. Samples

The coal used in this study is Xiaolongtan (XLT) lignite. It was crushed and sieved to provide the raw coal sample with a particle size range less than 0.15 mm. The proximate analysis, ultimate analysis and sulfur forms are summarized in Table 1. The coal ash was prepared according to the following procedures: the raw coal with the size of less than 0.15 mm was heated at 10 °C/min from room temperature to the desired temperatures (800, 900, 1000 °C) and held for 2 h in a muffle furnace. The ash constituents of different ashes are summarized in Table 2. The coal ash, unless otherwise stated, was referred to as that obtained at 900 °C without desulfurizer. The XRD results of the coal ash are presented in Fig. 1. It could be seen that the ash was mainly made up of SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, CaSO<sub>4</sub>, etc. Different blend ratios of ash/coal were prepared by mechanically mixing and the blend ratios (ash/coal) by weight used in this study were 0, 1, 3 and 5. It was referred to as raw coal without coal ash when the blend ratio was 0.

### 2.2. Apparatus and procedure

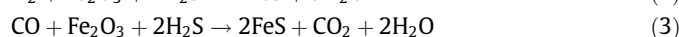
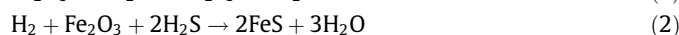
The pyrolysis was performed in a normal horizontal tube furnace and the schematic flow diagram of experimental unit is shown in previous study [3]. During each experiment, 4 g coal with a certain ratio of coal ash was placed in the constant temperature zone of the reactor at room temperature. Prior to every experiment, 200 ml/min N<sub>2</sub> as carrier gas was introduced to purge the system for 40 min, and then the samples were heated at 20 °C/min from room temperature to the desired temperatures (500, 600, 700 and 800 °C) and held for 30 min to ensure full pyrolysis. The gas was collected in a gas bag from T–50 to T+50 respectively during each experiment (T = 350, 450, 550, 650 and 750 °C), and the average concentration of the gas collected from T–50 to T+50 was measured by gas chromatography equipped with flame photometric detector. The volume of the gas was measured by a gasmeter. The amount of H<sub>2</sub>S was used to represent H<sub>2</sub>S release from T–50 to T+50. The amount of H<sub>2</sub>S was determined: T<sub>H<sub>2</sub>S</sub> = C<sub>H<sub>2</sub>S</sub>·V, where T<sub>H<sub>2</sub>S</sub> was total H<sub>2</sub>S amount, C<sub>H<sub>2</sub>S</sub> was the average concentration of H<sub>2</sub>S and V was the volume of the gas collected from T–50 to T+50. The liquid products were captured by a thimble filter in a tar trap cooled by a bath of ice/ethanol, and the cold trap and connection line were washed with acetone. The sulfur content of tar was determined by SN analyzer (KY-3000SN) that could be used to determine sulfur content and nitrogen content of liquid samples. It was emphasized that the different forms of sulfur for char were not determined here mainly due to much high content of ash. For example, the ash content was more than 90% when the blend ratio was 5. The determination of different sulfur forms according to GB was greatly influenced by the much high

content of ash and could not achieve satisfactory results. XRD analysis the ash was performed by using a PANalytical X'Pert PRO X-ray diffractometer with a Cu Ka radiation source. Surface morphologies of the ash were obtained from SEM measurement, which was conducted on a field emission scanning electronic microscope equipped with an energy dispersive X-ray spectroscopy.

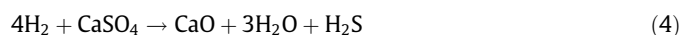
## 3. Results and discussion

### 3.1. Evolution of sulfur containing gases

Fig. 2 shows H<sub>2</sub>S evolution during the pyrolysis of the mixture of coal and coal ash. It could be seen that the addition of coal ash reduced the H<sub>2</sub>S release below 600 °C. The investigation of Qu et al. [1] indicated that gaseous sulfur was fixed by the circulating ash, which was in line with the results obtained in this study. It was well recognized that Fe<sub>2</sub>O<sub>3</sub> was very effective in capturing H<sub>2</sub>S through Eqs. (1)–(3) [4] and Fe<sub>2</sub>O<sub>3</sub> had been used as a desulfurizer in industry. The Fe<sub>2</sub>O<sub>3</sub> content is high in the coal ash according to the XRD results (Fig. 1), thus it was not surprising that the evolution of H<sub>2</sub>S was greatly inhibited by the presence of coal ash.



However, it should be noted that the presence of coal ash could promote H<sub>2</sub>S evolution above 600 °C. This phenomenon was especially pronounced at 750 °C. The result was interesting that Fe<sub>2</sub>O<sub>3</sub> was also very effective in capturing H<sub>2</sub>S even at 800 °C, whereas the fact was H<sub>2</sub>S was greatly increased with the coal ash. This suggested that there must have been other reasons which could greatly promote H<sub>2</sub>S evolution at high temperatures and the increase of H<sub>2</sub>S due to this promotion was more than counterbalanced by the decrease of H<sub>2</sub>S due to Fe<sub>2</sub>O<sub>3</sub>. H<sub>2</sub>S might be formed through the side reaction between H<sub>2</sub> and CaSO<sub>4</sub> of the ash (Eq. (4)) [5,6], which might be the main reason for the increase of H<sub>2</sub>S. To confirm this, 20 g pure coal ash was heated at 20 °C/min to 800 °C under 200 ml/min simulated pyrolyzed gas. The simulated pyrolyzed gas was made up of 25% CO, 25% CO<sub>2</sub>, 25% H<sub>2</sub> and 25% CH<sub>4</sub> by volume, which could represent the typical pyrolyzed gas. It was interesting to find that a large amount of H<sub>2</sub>S was produced in this case. The amount of H<sub>2</sub>S evolved at 750 °C was 4.181 mg, while the increase of H<sub>2</sub>S due to the addition of coal ash was only 3.34 mg. Therefore, it could be believed that the reaction of Eq. (4) might be a reasonable explanation for the increasing H<sub>2</sub>S concentration at high temperatures.



To prove the mechanism of the effect of coal ash addition on H<sub>2</sub>S evolution further, pure Fe<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> were added for pyrolysis respectively. Fig. 3 compares H<sub>2</sub>S evolution with the addition of ash, Fe<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub>. It was found that both coal ash and Fe<sub>2</sub>O<sub>3</sub> could reduce H<sub>2</sub>S evolution. This further suggested that the decrease of H<sub>2</sub>S by the presence of coal ash at low temperatures was mainly due to Fe<sub>2</sub>O<sub>3</sub> of the ash. At high temperature, both CaSO<sub>4</sub> and coal ash could promote H<sub>2</sub>S evolution at high

**Table 1**  
Main characteristics of XLT coal.

	Proximate analysis (wt%, ad)			Ultimate analysis (wt%, ad)				Sulfur forms (wt%, ad)			
	M	V	A	C	H	N	O*	St	Ss	Sp	So*
XLT	2.68	44.02	18.19	48.72	4.64	1.24	22.02	2.51	0.83	0.32	1.36

M, moisture; V, volatile, A, ash; St, total sulfur; Sp, pyritic sulfur; Ss, sulfate sulfur; and So, organic sulfur, O\*, So\*, by difference. O\* = 100-M-A-C-H-N-S, So\* = St-Ss-Sp.

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