

EFFECT OF Fe_2O_3 ON SULFUR TRANSFORMATION DURING COAL PYROLYSIS IN A FLUIDIZED BED REACTOR

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Abstract - XLT lignite with a particle size of 0.9-2mm was pyrolyzed in a fluidized bed reactor with the addition of 10% Fe_2O_3 to study the effect of Fe_2O_3 on sulfur behavior during coal pyrolysis. The results showed that Fe_2O_3 could significantly reduce H_2S release at whole pyrolysis temperatures, and the possible reason was that H_2S was fixed by Fe_2O_3 . The effect of Fe_2O_3 on COS depended on temperatures. Fe_2O_3 even could slightly promote COS at 500°C. Fe_2O_3 could enhance organic sulfur decomposition, which was an important source for COS. With elevating temperatures further, Fe_2O_3 could reduce COS, which was due to the fixation of COS by Fe_2O_3 . Fe_2O_3 also could reduce CH_3SH release, which was mainly ascribed to the enhancement of CH_3SH decomposition due to Fe_2O_3 . The sulfur in the tar was also decreased by the presence of Fe_2O_3 , and the possible reason was that Fe_2O_3 had a catalytic effect on tar sulfur decomposition.

Key words: Fe_2O_3 , Sulfur, Fluidized bed reactor, Coal pyrolysis

1. Introduction

Coal was rich in China and it was the main energy resource. However, the main utilization of the coal was direct combustion, which not only wasted a lot of hydrogen-rich volatile matter, but also caused serious pollution. The volatile matter might be rich in some coals, and this part could be extracted for other uses, such as producing domestic gas, gasoline and diesel oil. Based on this, the coal staged conversion poly-generation process which coupled fluidized bed pyrolysis and circulating fluidized bed combustion was proposed by Zhejiang University, illustrated in Fig.1 [1-5]. In this process, the coal was firstly sent to fluidized bed pyrolyzer to undergo pyrolysis, obtaining pyrolyzed gas, tar and char. The heat for the pyrolysis was provided by high temperature circulating ash, which was collected in the cyclone and sent to the fluidized bed pyrolyzer via recycle devices. The volatile matter, i.e. pyrolyzed gas and tar, was separated from the fine particles in the cyclone. The tar was separated and collected during cooling process and tar capture devices. The tar chiefly comprised of aliphatic hydrocarbon, phenols, and aromatics, could be used to extract high-value chemicals or be upgraded to liquid fuels. The gas is split into two parts: one was sent back into the pyrolyzer to fluidize the bed material, and the other part could not only be used as domestic gas and gaseous fuel, but also used as chemical materials fuel after further clean-up. The char, together with circulating ash, was sent to circulating fluidized bed pyrolyzer for combustion to generate heat and electricity. Up to now, a lot of 1 MW pilot-scale experiments were carried out. 12MW coal staged conversion polygeneration process was designed and established in Huainan, Anhui province. In addition, 300 MW plant was transformed to coal staged conversion process plant, with a capacity of 40t/h coal for the pyrolyzer. Operating results show that coal staged conversion system runs continuously and steadily, realizing poly-generation of heat, electricity, gas and tar from coal in one system. The technical and economic performances of coal staged conversion polygeneration plant were analyzed and compared with those of the conventional CFB power plant based on the evaluation of energy and exergy efficiency, showing that poly-generation plant had higher energy, exergy efficiency and more profitable, compared with CFB power plant.

The coal staged conversion process was also a promising technology to reduce SO₂ emissions. Part sulfur was converted to pyrolyzed gas and tar during pyrolysis, mainly in H₂S form, therefore, SO₂ emission was less compared with direct combustion. It was easier for H₂S removal from pyrolyzed gas than SO₂ removal from flue gas. Therefore, it could reduce cost for sulfur removal for coal staged conversion process compared with direct combustion. What was more, figuring out the sulfur behavior of the gas and tar was also important. It has strict standard for H₂S in the pyrolyzed gas and tar. High H₂S content was not allowed for domestic gas due to safety and for chemical raw materials, for H₂S could lead to the deactivation of its catalyst. So it was of great necessity to figure out the sulfur transformation in the coal staged conversion process.

Although a lot of studies had been done for sulfur behavior in the traditional pyrolysis process [6, 7], the sulfur behavior in the pyrolysis process of the coal staged conversion process was not well understood, because it was clearly distinguished from traditional pyrolysis. The most obvious characteristics were the interaction of the coal and circulating ash. The heat for the pyrolysis was provided by the circulating ash, so the pyrolysis was not only abundance in coal, but also abundance in coal ash. The coal ash might affect the pyrolysis behavior during coal pyrolysis. Some research was also done about this. Qu Xuan et al. [6] study the effect of coal ash in a fixed bed reactor, finding that the coal ash could not only reduce gaseous sulfur and tar sulfur, but also could reduce sulfur content retained in the char. Jia Xin et al. [5] studied the sulfur behaviors of coal along with high CaSO₄ content, showed that the presence of coal ash could reduce H₂S release at low pyrolysis temperatures, but could promote H₂S release at high pyrolysis temperatures. The investigation of Liang et al.[8] in a moving bed pyrolyzer demonstrated that the increase of the temperature of the HCPs (hot heat carrier particles) and the HCPs-to-coal blending ratio can increase the pyrolyzed gas yield. Ran et al. [7] investigated the topping gasification and observed that the ash of CFB boiler as the bed materials obviously decreased the gas yield and tar yield. Due to the complex components of the ash, the effect of coal ash on pyrolysis behavior could not be clearly determined. Therefore, it could predict the pyrolysis behavior along with coal ash by obtaining the main components and the effect of the main components on the pyrolysis behavior. Fe₂O₃ was one of the main components in the coal ash. As the first step, the effect of Fe₂O₃ on sulfur behavior was studied. It was well recognized that Fe₂O₃ as H₂S remover could fix H₂S, but the study was mainly focused on the reactions between Fe₂O₃ and pure pyrolyzed gas, the study of sulfur transformation of the pyrolysis of the mixture of coal and Fe₂O₃ in the fluidized bed reactor was little reported. Therefore, the aim of this paper was to study the effect of Fe₂O₃ on sulfur behavior during pyrolysis in a fluidized bed reactor.

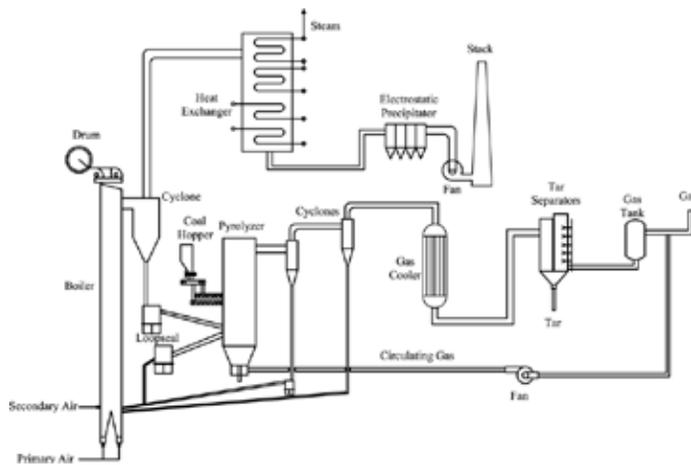


Fig.1. The principle of the coal staged conversion process

2. Experimental

2.1 Samples

A lignite from Xiaolongtan (XLT), Yunnan Province, China was used in this study, and the proximate, ultimate analyses and different forms of sulfur was listed in Table.1. The component of the ash was summarized in Table. 2. The coal was ground and sieved with diameter sizes ranging from 0.9 to 2 mm. The coal sample was heated in an oven at a temperature of 105 °C for 12 h and stored in a drier for use.

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.

Table. 2: Analysis of ash compositions in raw coals (wt%)

Compound	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Others ^a
XLT	33.47	8.09	12.04	19.11	3.42	0.76	0.16	20.01	2.94

^a by difference

2.2 Apparatus and operation conditions

The experiments were carried out in a lab-scale bubbling fluidized bed reactor and it was illustrated in Fig.2. The reactor, with an inner diameter of 30mm and a height of 700mm, was made of stainless steel. The reactor was electrically heated and the temperature was measured by 3 thermocouples. The bed materials chosen in this study were silica sand with a particle size ranging from 0.16mm to 0.3mm. N₂ was used as fluidizing gas to provide an inert pyrolysis atmosphere, which was introduced through the bottom of the reactor and regulated by a mass controller. The superficial gas volume at operating temperatures was 4 L/min, the gas volume for N₂ used in this work was fixed at 6 L/min, which was 1.5 times the superficial gas volume. The fluidized bed reactor was heated to the desire temperatures and the temperatures were set to 500, 600, 700 and 800°C, 190g silica sand was sent to the reactor through the top of the reactor firstly and then 2g Fe₂O₃ was also introduced through the top of the reactor. 20g coal was fed to fluidized bed reactor through a screw. The discharged gas from the pyrolyzer passed through four pipe condensers and two thimble filters, which was placed in a low temperature water tank where the temperature could reach -40°C. In this process, the pyrolyzed tar and water was separated and collected. Tar-water mixture was recovered by acetone washing of the connection line and the trap. Sulfur concentration of the acetone lotion was measured by SN analyzer, and the total sulfur content in the tar was calculated as follows:

$$\text{Sulfur content in tar} = C_s * W;$$

Where C_s represented the sulfur concentration of acetone lotion, and W represented the weight of acetone lotion.

The pyrolyzed gas was collected in a gas bag, and the sulfur concentration of the gas was measured by a gas chromatograph (Agilent 7890A) equipped with FPD detector. Since the N₂ generated or consumed could be negligible compared with the carrier gas (N₂), N₂ tracing method was used for the calculation of gases yields:

$$V = \frac{V_{N_2}}{C_{N_2}},$$

where V_{N₂} represented the total volume of carrier gas (N₂) introduced to this system during the whole

experiment, C_{N₂} represented the concentration of N₂.

After each run, the residual was taken out from the bottom of the fluidized bed reactor. The char could be separated from the silica sands by sieve and then weighted. The total sulfur content of coal and the char was analyzed through coulometry. The different forms of the coal were analyzed according to GB/T 215-2003. The Gladfelter and Dickerhoof method [9] was used to analyze the forms of sulfur in char.

The determination of H₂S, COS, CH₃SH and tar sulfur was expressed as follows:

$$\text{Release (H}_2\text{S, COS, CH}_3\text{SH, tar sulfur)} = \frac{S_{\text{H}_2\text{S}} + S_{\text{COS}} + S_{\text{CH}_3\text{SH}} + S_{\text{tar sulfur}}}{S_{\text{coal}} W_{\text{coal}}}$$

The total sulfur release was expressed as follows:

$$\text{Total sulfur release} = \frac{S_{\text{H}_2\text{S}} + S_{\text{COS}} + S_{\text{CH}_3\text{SH}} + S_{\text{tar sulfur}}}{S_{\text{coal}} W_{\text{coal}}}$$

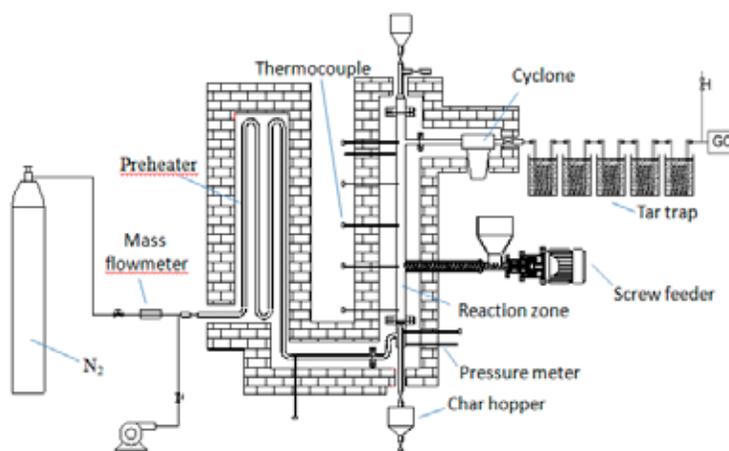


Fig.2. Schematic of experimental apparatus

3. Results and discussions

3.1 Effect of Fe₂O₃ on H₂S release

Fig.3 illustrates the variation of H₂S yield with the temperatures by the both presence and absence of Fe₂O₃. As could be seen, during pyrolysis of raw coal, H₂S yield was significantly increased from 22.51% to 37% when the temperature was increased from 500 °C to 600 °C. During raw coal pyrolysis at low temperatures, a great deal of H₂S was released due to decomposition of pyrite and unstable organic sulfur, such as thiol and thioether [10, 11]. However, the evolution of H₂S was only slightly increased when the pyrolysis temperature was further increased, which was similar with the results in the fixed bed reactor. For example, H₂S release was only slightly increased from 37% to 40.3% with elevating temperature from 600 °C to 800 °C. The reasons were might be as follows: (a). the main forms of sulfur in the char, mainly in the form of FeS_x and stable organic sulfur such as thiophene, was rather stable, so that only a little char sulfur was decomposed even at high temperature. (b) It was well recognized that H₂S was transformed to new organic sulfur through the reactions between organic matrix and H₂S, or sulfide sulfur through the reactions between H₂S and alkaline-earth mineral matter. Therefore, sulfur from coal pyrolysis was fixed in the char due to alkaline-earth mineral matter. (c) High temperature from coal pyrolysis caused the collapse of pore structure, inhabiting further evolution of H₂S[12-14].

H₂S evolution was largely reduced with the presence of 10% Fe₂O₃ at all test temperatures. H₂S was reduced about 8% to 15% when the Fe₂O₃ was added. It was well known that Fe₂O₃ could fix H₂S, thereby reducing H₂S release and Fe₂O₃ had been applied in industry for removing H₂S from coal gas[15]. The fixation of H₂S due to Fe₂O₃ was expressed as reactions 1-3. Therefore, it was easily understood that H₂S release was decreased with the addition of Fe₂O₃. In our previous work, H₂S was largely reduced from 19.12% for raw coal to 7.36% for that with the addition of 5% Fe₂O₃ in a fixed bed reactor, which suggested that about 67% of total H₂S was fixed by Fe₂O₃ at 800°C. However, in this study, H₂S was only slightly reduced from 40.2% for raw coal to 32.16% for that with the addition of 10% Fe₂O₃ in a fluidized bed reactor, which suggested that only a little percent of H₂S was fixed by Fe₂O₃ in a fluidized bed reactor. It meant the effect of Fe₂O₃ on H₂S was rather different for different reactors. The fixation of H₂S by Fe₂O₃ in a fixed bed reactor was remarkably pronounced, compared with that in a fluidized bed reactor. The difference might be due to the extent of the contact of H₂S and Fe₂O₃. The contact of H₂S and Fe₂O₃ was strong in a fixed bed reactor, so that Fe₂O₃ could obviously reduce H₂S release. On the contrary, the contact of Fe₂O₃ and H₂S was rather weak in a fluidized bed, so that H₂S was only a little decreased by Fe₂O₃. This might provide a reasonable explanation for different of H₂S removal due to Fe₂O₃ for different bed reactors.

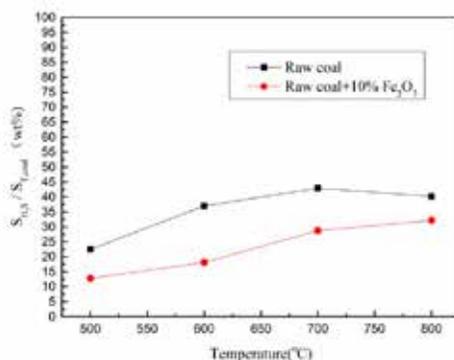
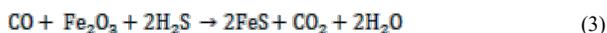
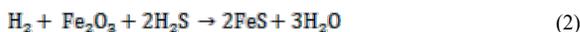
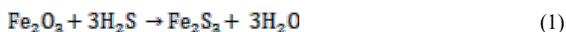


Fig.3. H₂S evolution as a function of pyrolysis temperatures with the presence and absence of Fe₂O₃

3.2 Effect of Fe₂O₃ on COS release

The effect of Fe₂O₃ on COS release at different pyrolysis temperatures were shown in Fig. 4. It was well recognized that there were various routes to form COS during the pyrolysis, including the direct decomposition of some organic sulfur of coal, the reactions of sulfur from decomposition of pyrite and CO or CO₂, as well as the secondary reactions between H₂S and CO or CO₂[16]. The COS evolution was increased constantly with elevating pyrolysis temperature from 500°C to 700°C, however, when the temperature was further increased, little change was detected. Similar study was obtained by others that COS was mainly produced at low temperature[13].

The presence of Fe₂O₃ could inhibit COS evolution above 600°C. On one hand, Fe₂O₃ could reduce H₂S release, thereby reducing COS release through secondary reactions. On the other hand, Fe₂O₃ could directly

capture COS. Based on the two aspects, COS was decreased by the presence of Fe_2O_3 at high temperatures. It should be noted that Fe_2O_3 could slightly increase COS evolution. Fe_2O_3 could promote organic sulfur decomposition, which was an important resource for COS.

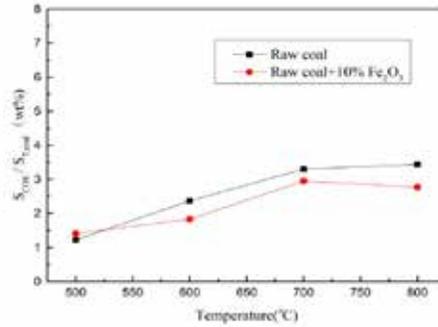


Fig.4. The variation of COS with the pyrolysis temperature by the presence and absence of Fe_2O_3

3.3 Effect of Fe_2O_3 on CH_3SH evolution

Fig.5 showed variation of the CH_3SH evolution as a function of temperatures by the presence and absence of Fe_2O_3 . CH_3SH was decreased monotonously with pyrolysis temperatures, which was consistent with Zhou's study[13]. CH_3SH was mainly produced via the decomposition of organic sulfur in the form as thiols, polysulfides, disulfides, dialkyl sulfides and alkyl-aryl sulfides, etc. Less CH_3SH was released at high temperature[17], which suggested that CH_3SH decomposition was enhanced at high temperatures.

Compared with raw coal, less CH_3SH was produced with the addition of Fe_2O_3 . Fe_2O_3 had two contrary effects on CH_3SH . On one hand, Fe_2O_3 facilitated non-stable organic sulfur decomposition, thereby in favor of CH_3SH formation. On the other hand, Fe_2O_3 also enhanced CH_3SH decomposition. Less CH_3SH by the presence of Fe_2O_3 was released, which showed that the decomposition of CH_3SH due to Fe_2O_3 was more than CH_3SH formation due to Fe_2O_3 .

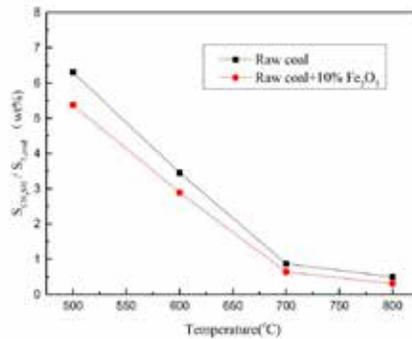


Fig.5. Effect of Fe_2O_3 on CH_3SH evolution

3.4 Effect of Fe₂O₃ on tar sulfur

The variation of tar sulfur both the presence and absence of Fe₂O₃ was illustrated in Fig. 6. It could be seen that tar sulfur was slightly decreased with the addition of Fe₂O₃ under all tested pyrolysis temperature, compared with raw coal pyrolysis. It was well known that Fe₂O₃ had a catalytic effect on tar sulfur decomposition[18]. Besides, Fe₂O₃ could capture HS radical, the formation of tar sulfur was decreased due to the lack of HS radical. Therefore, it was easily understood that Fe₂O₃ could reduce tar sulfur.

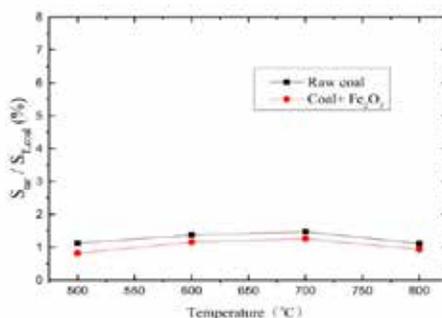


Fig.6. Effect of Fe₂O₃ on tar sulfur

3.5 Effect of Fe₂O₃ on total sulfur release

The total sulfur release was shown in Fig.7 by the presence and absence of Fe₂O₃. The addition of Fe₂O₃ was not in favor of total sulfur release. For example, the total sulfur release was decreased from 48.64% for raw coal to 33.58% when Fe₂O₃ was added at 700°C. The addition of Fe₂O₃ could largely reduce H₂S release, forming FeS_x, which could explain why Fe₂O₃ inhibited total sulfur release.

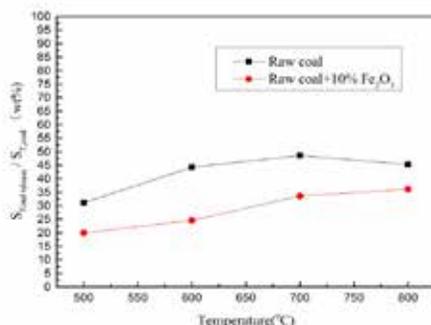


Fig.7. Effect of Fe₂O₃ on total sulfur release

Conclusions

XLT lignite by both the presence and absence of 10% Fe₂O₃ were pyrolyzed in a fluidized bed reactor between 500-800°C to study the effect of Fe₂O₃ on sulfur behavior during pyrolysis. The following conclusions could be draw:

- (1) H₂S could be greatly reduced with the addition of 10% Fe₂O₃ under all tested pyrolysis temperatures, compared with raw coal. Fe₂O₃ could fix H₂S through the reaction, thereby reducing H₂S release.
- (2) Fe₂O₃ could slightly increase COS release at 500°C, however, when the temperature continue to rise, Fe₂O₃ inhibited COS evolution. On one hand, Fe₂O₃ could directly capture COS, on the other hand, Fe₂O₃ could inhibited the formation of COS through secondary reaction due to the lack of H₂S.

- (3) Fe₂O₃ slightly reduced CH₃SH evolution, which suggested that Fe₂O₃ promoted CH₃SH decomposition.
- (4) Fe₂O₃ reduced tar sulfur during pyrolysis, which was because Fe₂O₃ had a catalytic effect on the decomposition of tar sulfur.

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