Influence of O₂/C molar ratio and coal feeding rate on sulfur release during CFB gasification

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Abstract. The release behavior of sulfur during coal gasification was studied in a bench-scale self-heated circulating fluidized bed gasifier. With the increase of the O2/C molar ratio, gasification temperature increases, which promotes sulfur release rate and the formation of H2S. The conversion reaction between H2S and COS is far from equilibrium and the yield of COS is excessive. Under the same molar ratio of O2/C, the increase of coal feeding rate can elevate the gasification temperature, promote the release of sulfur and the transformation of gaseous sulfur to H2S.

1. Introduction

Coal is the most abundant fossil fuel reserves in China. The emergence of clean coal technology navigates the direction for the further development of coal utilization. Coal gasification technology, especially circulating fluidized bed gasification technology, is one of the promising technologies. However, the impurities in coal gas reduces the quality of coal gas, and gaseous sulfur is one of the common pollutants, which will pollute the environment and corrode the equipment downstream[1, 2]. Therefore, reducing the yield of gaseous sulfur is necessary, while clearing the release behavior of gaseous sulfur is primary. But few researches published are about sulfur release in the process of fluidized bed gasification, and fewer experimental results published are based on the self-heated circulating fluidized bed experimental platform, which is closed to the commercial circulating fluidized bed.

The influences of the molar ratio of O₂/C and the coal feeding rate on sulfur release behaviors are investigated during the fluidized bed gasification. The experiments were carried out in a lab-scale self-heated circulating fluidized bed. The yields of gaseous sulfur were determined by gas chromatography. The purpose of this paper is to provide suggestions for the optimization of operating parameter, and reduce the cost of pollutant treatment.

2 Experimental Section

2.1 Experimental platform

Fig. 1 shows a schematic diagram of the self-heated circulating fluidized bed experimental platform used in this study. The whole system can be divided into four subsystems: gasifier, coal feeding system, air supply system and auxiliary system. The riser of the CFB gasifier is 6400 mm in height, and the diameters of the three segments are 130mm, 150mm and 180mm, respectively. The riser is connected with a cyclone and a loop seal to form a circulating route. A screw feeder was used to feed coal into the riser, and the coal feeding port is 800mm higher than the blast cap. An air compressor was used to supply air, while O₂ is supplied by cylinders, and the flow rates of gasification agents are controlled by mass flow controllers individually. Temperature measuring ports are placed along the height of the riser, and the temperature measuring points in dense phase region is 215mm higher than the blast cap. The components of gaseous sulfur were quantitatively analyzed by gas chromatograph with an FPD detector (GC9790 PLUS).
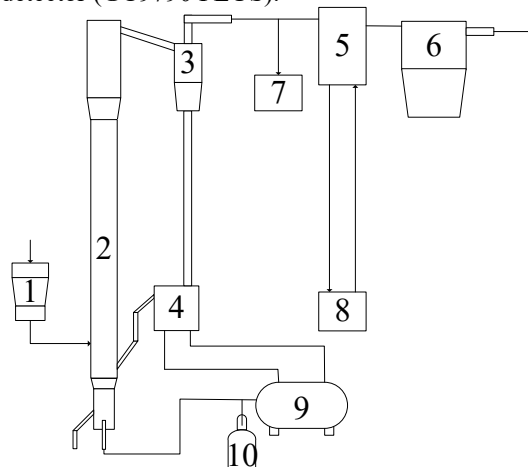
1 coal screw feeder; 2 riser; 3cyclone; 4 loop seal; 5 water cooler; 6 bag filter; 7 gas analyzer; 8 water tank; 9 air compressor; 10 cylinder

Fig. 1 Schematic diagram of the experimental platform

2.2 Experimental materials

The coal from the Shaanxi province of China, called shenmu coal (SM coal) was used in this experiment, with the particle size of 0-1mm. The proximate analyses and the ultimate analyses of SM coal were analyzed according to the Chinese standard, and the results were listed in Table 1.

Table 1 Proximate analyses and ultimate analyses of SM coal

Proximate analysis /wt.%			
M_{ar}	FC_{ar}	V_{ar}	A_{ar}
3.7	54.47	34.15	7.68
Ultimate analysis/ %			
C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}
72.45	4.61	10.23	1.03	0.3

2.3 Data processing

Sulfur release rate can be calculated using sulfur balance, which can be calculated according to the following formula:

$$Sg = \frac{Wc \times S_t - S_{solid}}{Wc \times S_t} \qquad (1)$$

where S_{solid} represents the sulfur in residue, W_C represents the coal feeding rate (kg/h). The yield of certain gaseous sulfur can be calculated according to the following formula:

$$Yield = \frac{S_c}{S_t} \times 100\% \qquad (2)$$

where S_c represents sulfur content of a certain gaseous sulfur (mol/g$_{coal}$).

3. Test Results and Discussions

3.1 The effect of the O₂/C molar ratio

According to Fig. 2, with the increase of O₂/C molar ratio, the bottom temperature of gasifier increases, and the sulfur release rate increases, the yields of H₂S, COS and CS₂ are all increased. The absorption rate of organic gaseous sulfur (such as COS,CS₂) by conventional metal oxide desulfurizer is far lower than that of H₂S[3], thus the relative proportion of H₂S in gaseous sulfur can be used to evaluate the difficulty of further desulfurization. The higher the content of H₂S, the lower the investment and operation cost of downstream desulfurization process. According to Fig. 2 b), the dominate organic gaseous sulfur is COS, which can transform to H₂S, thus the content of H₂S in gaseous sulfur has the same trend with the molar ratio of H₂S/COS. According to Fig. 3, with the increase of O₂/C, the molar ratio of H₂/CO decreases, while that of H₂S/COS increases.
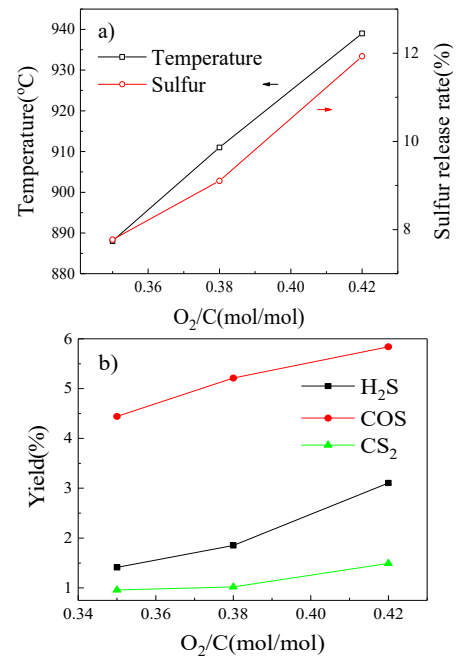

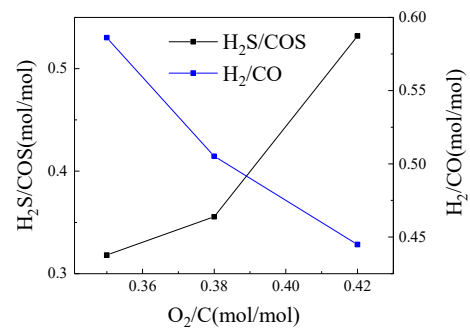**Fig. 2** The trend of temperature and released sulfur with O₂/C

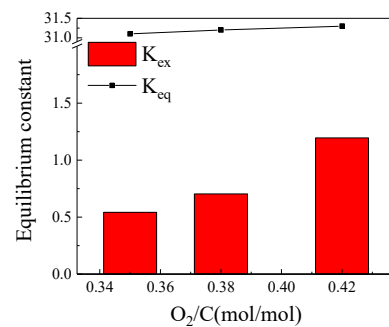**Fig. 3** The trend of H₂S/COS and H₂/CO with O₂/C

Fig. 4 The trend of reaction equilibrium constant

In the process of coal gasification, the sulfur with poor thermal stability will decompose at lower temperature, but the decomposed sulfur will not be completely released to the gas phase, part of which will be captured by char to form more stable organic sulfur. Therefore, the increase of O₂ promotes the destruction of organics in coal and promotes the release of sulfur. Besides, the increase of O₂ promoted the reaction of carbon and oxygen, and promoted the formation of CO. Similarly, the increase of O₂ will promote the decomposition of organics, thus increasing the release of hydrogen radicals, which will be consumed by O₂ simultaneously. Thus H₂/CO decreased

with the increase of O_2/C. H_2S is formed by the combination of H and - HS, while the formation of COS is related to CO[4]. Therefore, the conversion reaction between H_2S and COS is related to the molar ratio of H_2/CO, and the conversion reaction between H_2S and COS is shown as (R1), thus the decrease of H_2/CO will inhibit the formation of H_2S and promote the formation of COS. Besides, reaction (R1) is an exothermic reaction, increasing temperature can promote the transformation of H_2S to COS. However, the molar ratio of H_2S/COS increases with that of O_2/C, which is contrary to the prediction above. The reaction (R1)is far from equilibrium by comparing the reaction equilibrium constant and standard equilibrium constant under different ratio of O_2/C, as shown in Fig. 4, and the yield of COS is excessive at the end of gasification reaction. At the beginning of gasification, coal is fed to the bottom of gasifier, and the oxidation zone is existed at the bottom of gasifier. Moreover, COS and SO_2 is the dominate gaseous sulfur under oxidative atmosphere[5]. Therefore, it can be inferred that sulfur in coal will release in the forms of COS and SO_2 at the bottom of gasifier, while COS and SO_2 will be reduced at the upper of gasifier. However, the conversion reaction (R1) can not reach equilibrium due to the limited reaction duration. Therefore, the yield of CO and H_2 can change the equilibrium state of the conversion reaction (R1), but the effect on the composition of gaseous sulfur can be ignored. Similarly, the effect of temperature on the reaction equilibrium can also be ignored. But simultaneously, increasing temperature can increase the rate of reaction, and thus accelerating the formation of H_2S. Therefore, increasing the molar ratio of O_2/C can improve the molar ratio of H_2S/COS, due to the limited reaction duration.

3.2 The effect of coal feeding rate

According to Fig. 5 ,at the same molar ratio of O_2/C, with the increase of coal feeding rate and the flow rate of gasification agent, the sulfur release rate and the temperature increases, and the yields of H_2S, COS and CS_2 are also increased. According to Fig. 6, with the increase of coal feeding rate, the molar ratio of H_2/CO decreases, while that of H_2S/COS increases.
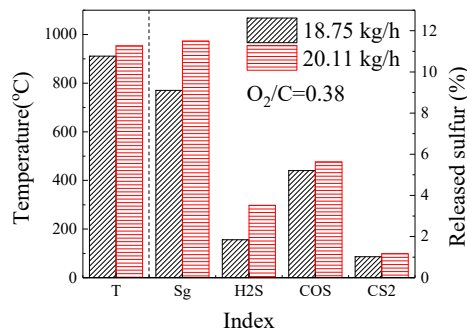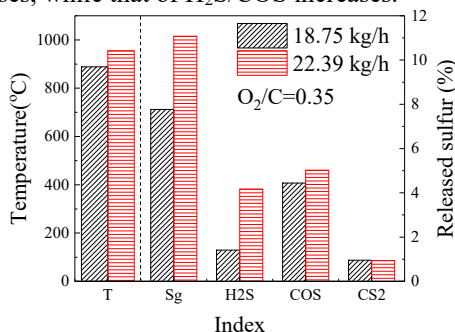

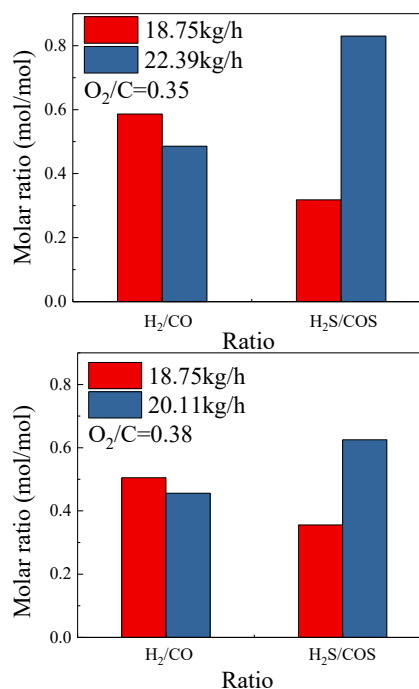**Fig. 5** Comparison of various indexes under different coal feeding rate

Fig. 6 Comparison of various molar ratio under different coal feeding rate

Under the same molar ratio of O_2/C, the heat dissipation capacity of self-heated gasifier changes little, and the increase of coal feeding rate reduces the proportion of heat loss. Therefore, the increase of coal feeding rate will lead to the increase of temperature and the promotion of CO yield and H_2 yield. Moreover, the molar ratio of H_2/CO decreases with the increase of coal feeding rate, indicating the equilibrium of the conversion reaction (R1) moves towards the direction of COS formation. However, the molar ratio of H_2S/COS increases with the coal feeding rate, which indicating the equilibrium shift of the conversion reaction (R1) has little effect on the composition of gaseous sulfur. The inference above proves that when the conversion reaction is far from equilibrium, the coal gas component has little effect on the conversion of H_2S and COS, while the increase of temperature accelerates the formation of H_2S.

$$COS + H_2 \rightleftharpoons CO + H_2S \qquad (R1)$$
$$C + CO_2 \rightarrow 2CO \qquad (R2)$$
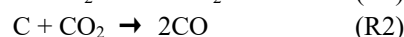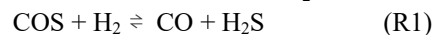
4 Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) In the process of SM coal gasification, the sulfur in coal is mainly released in the form of H_2S, COS and CS_2.

(2) With the increase of O_2/C molar ratio, both of the sulfur release rate and the gasification temperature increase. The conversion reaction between H_2S and COS is far from equilibrium, thus the increase of gasification temperature accelerates the conversion reaction and promotes the formation of H_2S.

(3) Under the same O_2/C molar ratio, increasing the coal feeding rate increases the gasification temperature, promote the release of sulfur and the formation of H_2S.

Acknowledgements

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