Journal of the Energy Institute 89 (2016) 264–270

Contents lists available at ScienceDirect

Journal of the Energy Institute

journal homepage: http://www.journals.elsevier.com/journal-of-the-energy-institute

Sulfur behavior during coal combustion in oxy-fuel circulating fluidized bed condition by using TG-FTIR

Luning Tian [a, b], Wei Yang [a], Zhenhui Chen [a], Xianhua Wang [a, *], Haiping Yang [a], Hanping Chen [a]

[a] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, 430074, PR China
[b] Wuhan Optics Valley Environmental Protection Technology Co., Ltd., Wuhan, 430074, PR China

ARTICLE INFO

Article history:
Received 23 July 2013
Accepted 8 September 2014
Available online 28 January 2015

Keywords:
Coal
Pyrolysis
Combustion
Oxy-fuel atmosphere
Sulfur behavior
TG-FTIR

ABSTRACT

The sulfur behaviors of coal pyrolysis and combustion in air and oxy-fuel circulating fluidized bed (CFB) conditions showed that during coal pyrolysis, a significant increase of weight loss and CO emission were presented in CO_2 atmosphere at temperature above 900 K, then the increase of CO emission promoted the transformation of H_2S and other sulfur compounds to COS, and led more SO_2 emission by reduction of $CaSO_4$. The main sulfur-containing gas changed from H_2S in N_2 atmosphere to COS in CO_2 atmosphere. In oxy-fuel combustion, less SO_2, more H_2S and COS released compared with those in air combustion, the SO_2 became the main sulfur-containing gas. With the O_2 concentration increasing, more SO_2, COS and H_2S released at lower temperature by faster burning. As the particle size and heating rate increasing, the SO_2 and H_2S emission increased, and the COS emission decreased. Finally the comprehensive characteristics of sulfur behavior were proposed.

1. Introduction

The oxy-fuel combustion as the most promising clean coal utilization technology, has been investigated extensively on pulverized boiler [1–7]. But now, the CFB boiler is increasingly perceived as the best choice for oxy-fuel combustion because it can control the combustion temperature through fly ash circulating besides recycled flue gas, and then easily realizes the coal combustion under high O_2 concentration. Moreover, it also inherits the CFB boiler advantages, such as widely adaptable of fuel, capture sulfur in situ, and lower NO_x emission. So a considerable number researches on oxy-fuel CFB combustion are now in progress [8–11].

Due to the different gas properties of N_2 and CO_2, the sulfur evolution exhibits some different behaviors in oxy-fuel combustion compared with conventional air combustion. The less emission of SO_2 is recognized in oxy-fuel combustion, and the results are mainly attributed to the lower combustion temperature caused by the high heat capacity of CO_2, or the improvement of self-capturing sulfur ability of ash or the promotion of the sulfur transformed to other sulfur-containing gases. Kiga et al. [1] suggested that more sulfur was retained in ash because of the lower combustion temperature and the enhanced self-capturing sulfur ability of ash. Croiset and Thambimuthu [2] found that the most sulfur released in SO_2 form, and the conversion reach up to 91% in conventional combustion, but it dropped to 75% in once-through O_2/CO_2 combustion and 64% in recycle flue gas combustion because part of sulfur was retained in the ash or some SO_2 was oxidized to SO_3. The similar result of less SO_2 emission in oxy-fuel combustion was also reported in the literatures [5–7]. However, some different conclusions were obtained in previous studies. Liu et al. [4] reported that the SO_2 emission was almost independent of combustion media. Zheng and Furimsky [3] also predicted that the combustion atmosphere had no influence on SO_2 formation by FACT simulation. Duan et al. [8] revealed that more SO_2 released in O_2/CO_2 atmosphere, which might be attributed to the activated $C/S/CO_2$ reaction.

In addition, the pyrolysis as an important initial stage and a key link for the sulfur evolution in coal combustion, was extensively attended and studied in air condition [12–14]. But up to now, there are less studies on coal pyrolysis in oxy-fuel condition, especially for oxy-fuel CFB

---

* Corresponding author. Tel.: +86 (27) 87542417 8211; fax: +86 (27) 87545526.
E-mail addresses: tianluning@126.com (L. Tian), weiyang_4105@yeah.net (W. Yang), chenzh4414@gmail.com (Z. Chen), wxhwhhy@sina.com (X. Wang), yhping2002@163.com (H. Yang), hp.chen@163.com (H. Chen).

http://dx.doi.org/10.1016/j.joei.2015.01.020
1743-9671/

combustion. Duan et al. [8], Rathnam et al. [15], and Naredi and Pisupati [16] all investigated the coal pyrolysis in oxy-fuel condition recently, but they were more interested in pyrolysis characteristics than evaluations of gaseous pollutions. So it necessitated an investigation of coal pyrolysis for deeper insight into the sulfur evolution in oxy-fuel CFB condition. Hence, in this paper, the sulfur behaviors of coal pyrolysis and combustion were investigated using thermogravimetry analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR) in the typical oxy-fuel CFB combustion conditions. Additional combustion experiments with variant particle sizes and heating rates were carried out in order to obtain their effects on sulfur behavior.

2. Experimental

A sample of Huangling bituminous coal was used in this study, and the coal was crushed and sieved to obtain the particle size ranges of $\leq$154, 224–300 and 450–600 μm. The ultimate, proximate and sulfur forms analyses of coal sample are listed in Table 1.

Experiments were carried out on the TG-FTIR (TGA: NETZSCH STA409C, FTIR: Bruker EQUINOX55). In each experiment, the thin layer of sample (10 ± 0.01 mg) laid out in the aluminum oxide crucible of the TGA, was heated from room temperature to 1273 K with a certain heating rate in desired atmosphere. The gases of N_2, O_2 and CO_2 were supplied by gas cylinders, and the flow rate of the gas was controlled with the mass flow controller. The total flow rate was kept at 100 ml min^{-1}. The heating rate was set to 10, 30 and 50 K min^{-1}. The pyrolysis experiments were performed at the heating rate of 30 K min^{-1} in N_2 and CO_2 atmospheres, and the combustion experiments were carried out in the mixed gases of $O_2/CO_2 = 10/90$, 20/80, 30/70, 40/60, 60/40 and $O_2/N_2 = 20/80$.

The gaseous products from TGA were purged to FTIR promptly through the connection tube, which was maintained at 453 K in order to prevent the condensation of gases. The spectra of the FTIR were collected at a resolution of 8 cm^{-1}, and the range of IR absorption band was 4000–600 cm^{-1}. In the present work, the gas emission characteristics were analyzed by plotting the absorbance versus temperature at the IR wavenumber based on the Beer–Lambert law. The IR wavenumber of CO, SO_2, COS and H_2S are 2177, 1374, 2042 and 1263 cm^{-1}.

3. Results and discussion

3.1. Sulfur behavior during coal pyrolysis in N_2 and CO_2 atmospheres

The pyrolysis is an important initial stage for sulfur evolution during coal combustion, its behavior will differentiate in volatile components and char yield between N_2 and CO_2 atmospheres. The TG curves and CO profiles during coal pyrolysis in these 2 atm are presented in Fig. 1. As shown, the TG curve of coal pyrolysis in N_2 atmosphere agrees well with that in CO_2 atmosphere before 900 K, which indicates that the CO_2 as an inert atmosphere, has no effect on coal pyrolysis at lower temperature. This is in good agreement with the findings in the literatures [15,16]. With the temperature increasing, a major difference is showed in the TG curves between coal pyrolysis in N_2 and CO_2 atmospheres, the weight loss rate displays an obvious increase in CO_2 atmosphere over 900 K due to the intensive char-CO_2 gasification reaction at higher temperature. Therefore, the ultimately weight loss of coal pyrolysis in N_2 atmosphere (24.79%) is almost equal to the sum of its proximate volatile and moisture (22.20 + 2.45%), while it increases to 38.76% in CO_2 atmosphere. The char-CO_2 gasification reaction also can be confirmed with the FTIR result of CO emission. As seen, the CO emission curve shows an obviously increase after 900 K in CO_2 atmosphere. Duan et al. [8] and Rathnam et al. [15] both reported the similar phenomenon, but they found the char-CO_2 gasification reaction began at about 780 and 1030 K in CO_2 atmosphere respectively. Multiple factors can cause the difference in temperature conditions of char-CO_2 gasification, such as the coal properties (char reactivity, minerals deposited in coal) [15] and experimental conditions (particle size, heating rate) [17,18].

During coal pyrolysis, the H_2S, COS and SO_2 are the major sulfur-containing gases, and their emission profiles in N_2 and CO_2 atmospheres are shown in Fig. 2. As shown, the change of pyrolysis atmosphere has no influence on sulfur emission at temperature below 900 K, but with the temperature further increasing, some differences appear in H_2S, COS and SO_2 emission during CO_2 pyrolysis, which is consistent to the TG result of coal pyrolysis. As seen from Fig. 2(a), the H_2S mainly releases between 700 and 900 K in the 2 atm. Two channels for the formation of H_2S are possible during coal pyrolysis: (a) the reaction of sulfide with H_2; (b) the reaction of elemental sulfur (S) or sulfur radicals with coal-H (alkyl, hydroaromatic). Here, the unstable organic sulfur (aliphatic thiols, thioether) is first pyrolyzed to form sulfur radicals, and then the sulfur radicals react with coal-H to release H_2S at about 700 K by reaction (1) [19]. Furthermore, a part of FeS_2 quickly react with H_2 to produce H_2S at around 773 K by reaction (2), and the others would be pyrolyzed to form S which then reacts with coal-H to produce H_2S by reaction (3) with a quick rate between 773 and 823 K [12]. So the main peak of H_2S emission appears at about 780–850 K as result of the overlaps of these reactions.

$$R - SH(R - S - R) \rightarrow S\ radicals \xrightarrow{Coal-H} H_2S + unsaturated - HC \tag{1}$$

$$FeS_x + H_2 \rightarrow FeS_{x-1} + H_2S \tag{2}$$

$$FeS_x \rightarrow FeS_{x-1} + S \xrightarrow{Coal-H} H_2S \tag{3}$$

Table 1
Analyses of Huangling bituminous coal.

Ultimate and proximate analysis (wt-%, as air dry basis)									Sulfur forms (wt-%)			
C	H	O	N	S	FC	A	V	M	Pyrite	Sulfate	Organic	Total
50.77	2.75	7.34	0.59	1.87	41.12	34.23	22.20	2.45	0.81	0.20	0.86	1.87

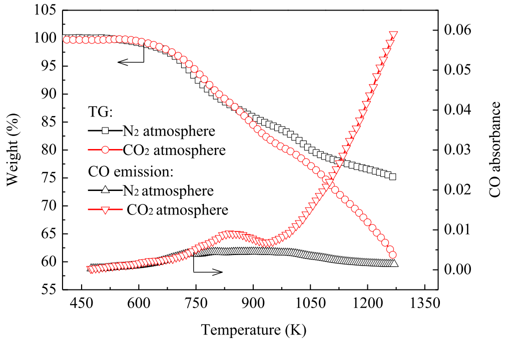

Fig. 1. TG and CO emission profiles of coal pyrolysis.

With the temperature further increasing, some stabile organic sulfur (aromaticthiols, thioether) can be pyrolyzed to release H_2S, and FeS can directly or indirectly produce H_2S via above reactions at the temperature high than 1073 K. So the shoulder peak of H_2S emission is presented at about 1100 K in N_2 atmosphere. However, in CO_2 atmosphere, the H_2S emission is close to zero at about 1100 K, which can be explained by gas phase secondary reaction. The higher concentration CO_2 and CO both can react with H_2S to produce COS at higher temperature by reactions (4) and (5) [20]. Meanwhile, it also causes the increase of COS emission, as shown in Fig. 2(b).

$$H_2S + CO \rightarrow COS + H_2 \tag{4}$$

$$H_2S + CO_2 \rightarrow COS + H_2O \tag{5}$$

Moreover, the another important reason for more COS emission in CO_2 atmosphere is the gas–solid reactions of CO with sulfur compounds via reactions (6) and (7) [13]. While in N_2 atmosphere, the little COS is formed by the reactions of small amount of CO with sulfur compounds. The results indicate that the COS emission is mainly related to CO.

$$CO + FeS_2 \rightarrow FeS + COS \tag{6}$$

$$CO + S(S\ radicals) \rightarrow COS \tag{7}$$

As seen in Fig. 2(c), three emission peaks appear in SO_2 profile in N_2 atmosphere, while an additional emission peak is presented in CO_2 atmosphere after 1000 K. The SO_2 mainly releases from the sulfates decomposition during coal pyrolysis. The decomposition temperature of sulfate in coal is obviously lower than pure sulfate alone. The iron sulfates decompose between 500 and 800 K, and the $CaSO_4$ decomposition starts at about 623 K, but only a small amount of $CaSO_4$ decomposes at low temperature due to its good heat stability. The additional peak of SO_2 emission in CO_2 atmosphere is possibly related to the high CO concentration, which leads to the re-emission of SO_2 caused by the reductive decomposition of $CaSO_4$ with CO via reaction (8). The similar phenomenon was observed by Anthony and Granatstein [21].

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \tag{8}$$

The total emission of sulfur-containing gases during coal pyrolysis are estimated with time integral of the gas absorbance, as presented in Fig. 3. The total amounts of COS and SO_2 emission in CO_2 atmosphere are larger than those in N_2 atmosphere, but H_2S emission shows reverse trend. The major contributor to the sulfur-containing gases is H_2S in N_2 atmosphere, and it changes to COS in CO_2 atmosphere. The difference of sulfur evolution between N_2 and CO_2 atmosphere mainly appears at higher temperature due to the intensive char-CO_2 gasification reaction in CO_2 atmosphere.

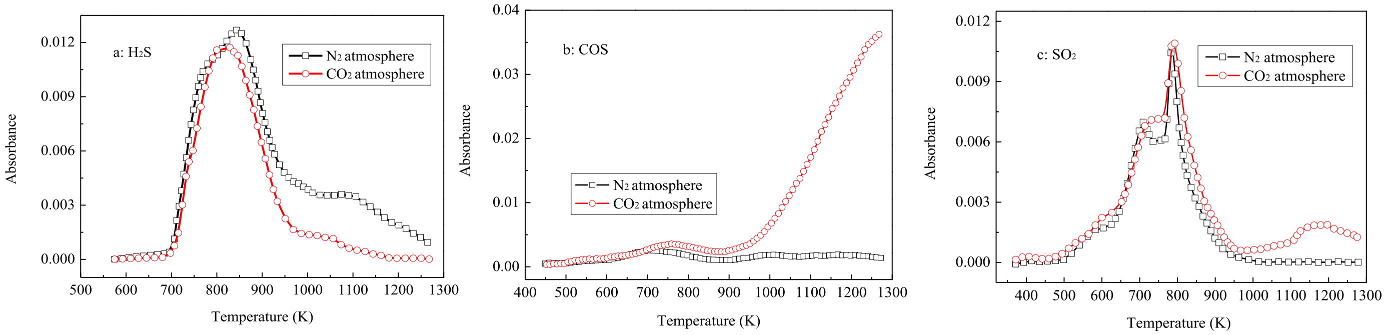

Fig. 2. Profiles of sulfur-containing gases emission during coal pyrolysis.

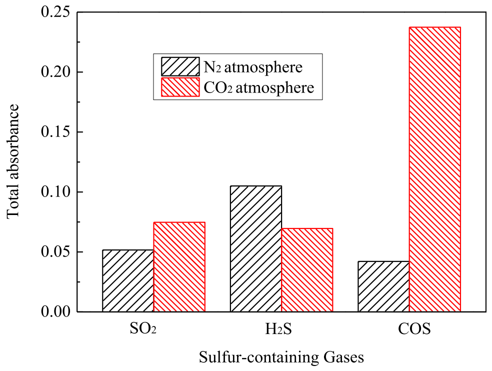

Fig. 3. Total emission profiles of sulfur-containing gases during coal pyrolysis.

3.2. *Sulfur behavior during coal air and oxy-fuel combustion*

The SO_2 emission profiles during coal air and oxy-fuel combustion are shown in Fig. 4(a). The profiles of SO_2 emission show similar trends with two shoulder peaks and one main peak in these two combustion modes. The peaks of sulfur emission at different temperatures are corresponding to different sulfur forms deposited in coal. The three picks successively correspond to the unstable organic, pyrite and some stable organic sulfur at temperature of 650, 700 and higher than 773 K [17,18]. It also can be seen that the main peak value of SO_2 emission in oxy-fuel combustion is lower than that in air combustion. This can be explained by that more sulfur is retained in ash at lower combustion temperature, or transforms to other sulfur-containing gases, which are demonstrated by the ash composition in Table 2, and the COS and H_2S emission in Fig. 4(b, c).

As shown in Fig. 4(b, c), more COS and H_2S release between 700 and 950 K during oxy-fuel combustion compared with those in air combustion, which are caused by more CO formed in oxy-fuel combustion. The presence of high concentration CO improves the COS formation and provides a reducing environment to well suppress the further oxidation of COS and H_2S. However, the forming mechanism of CO is probably different between coal combustion and above pyrolysis experiments. The char-CO_2 gasification reaction which is used to explain more CO formed during coal pyrolysis in CO_2 atmosphere after 900 K, can be ignored at temperature below 900 K because of its low reaction rate. Thus, the more CO emission during coal combustion is considered to be due to the lower diffusivity of oxygen in high CO_2 concentration atmosphere. Wall et al. [6] reported that the oxygen diffusion rate in CO_2 atmosphere is about 0.8 times of that in N_2 atmosphere.

The total emission profiles of sulfur-containing gases during coal air and oxy-fuel combustion are shown in Fig. 5. The total amount of SO_2 emission in oxy-fuel combustion is lower than that in air combustion, and the opposite trend is displayed in H_2S and COS emission. The SO_2 becomes the main sulfur-containing gas in coal combustion because more H_2S and COS are oxidized to SO_2.

3.3. *The influence of O_2/CO_2 concentration on sulfur behavior during coal combustion*

The SO_2, COS and H_2S emission profiles during coal combustion in different O_2/CO_2 atmospheres are shown in Fig. 6. As seen, with the increasing of O_2 concentration, the main evolving peaks of SO_2, COS and H_2S are more evident with the peak values increase and the peak positions shift to lower temperature zone, the emission times shorten. The increase of O_2 concentration promotes the oxidation of sulfur precursors, but on the other, it also greatly accelerates the formation of sulfur precursors and CO by the faster burning in lower temperature zone, and then the CO can well suppress the further oxidation of COS and H_2S. Consequently, more sulfur is released at lower temperature with the faster burning in higher O_2 concentration.

3.4. *The effect of particle size and heating rate on sulfur behavior*

The total emission profiles of SO_2, COS and H_2S from coal oxy-fuel combustion with different particle sizes and heating rates are shown in Fig. 7. It is known that the large particle coal combustion happens at high temperature zone because the less specific area, larger heat

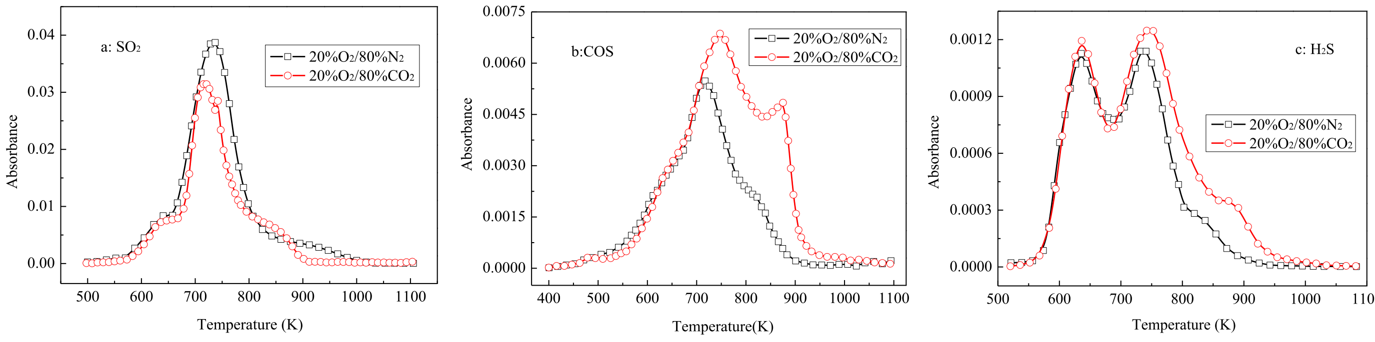

Fig. 4. Profiles of sulfur-containing gases emission during coal air and oxy-fuel combustion.

Table 2
Analysis of ash composition (wt-%).

Atmosphere	C	O	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Ti	others
$20\%O_2/80\%N_2$	10.69	38.71	0.30	9.88	19.29	0.59	2.16	0.81	0.77	9.73	5.87	0.53	0.68
$20\%O_2/80\%CO_2$	11.76	39.61	0.36	8.98	17.56	0.46	4.06	0.63	0.89	9.63	4.97	0.51	0.59

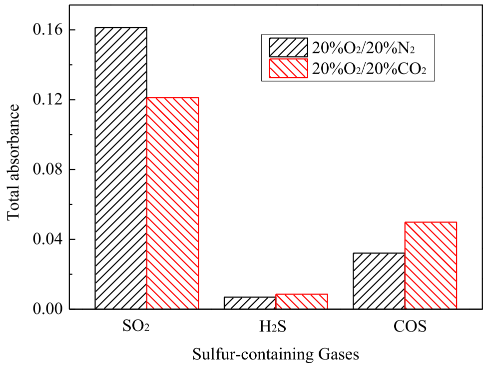

Fig. 5. Total emission profiles of sulfur-containing gases during coal air and oxy-fuel combustion.

and mass diffusion restriction in the interior of particle, and at high heating rate, the coal combustion also shifts to higher temperature zone by the thermal hysteresis. So the increase of particle size and heating rate are beneficial to sulfur evaluation, the SO_2, H_2S and COS emission all shift to higher temperature zone almost without any change in its shape, the SO_2 and H_2S emission increase with the particle size and heating rate, but COS emission shows opposite trend, which is probably caused by the less CO emission.

3.5. A scheme on sulfur transformation process during coal oxy-fuel combustion

Finally, the sulfur evolution process during coal combustion in oxy-fuel condition is proposed in Fig. 8. A part of pyrite sulfur can be pyrolyzed to form sulfide and S, and then the S can react with H and CO to produce H_2S and COS, or directly be polymerized to S_n [20]. The other pyrite and the intermediate of sulfide can directly react with H_2, CO and C to form H_2S, COS and CS_2 at different temperature zones, respectively. Moreover, the H_2S can be oxidized to form COS by CO and CO_2, and COS can directly decompose or react with H_2S to produce CS_2. Because the rate of CS_2 formation is much slower at the temperature involved here, the trace amount of CS_2 is not considered in this study. The sulfate sulfur can directly decompose or reduce by CO to produce SO_2. The behavior of organic sulfur is complex, it is general agreement that the organic sulfur pyrolysis to form S radicals firstly, and then the free sulfur radicals transform to various sulfur compounds as the pyrite sulfur [19]. In addition, all sulfur compounds can be oxidized to SO_2 by oxygen in the emission process. More SO_3 emission is considered at the high O_2 concentration atmosphere, but it is not detected by FTIR because almost all SO_3 can be converted into $H_2SO_4(g)$ at the temperature below 473 K [2,22].

Moreover, the mutual transformations among three different sulfur forms were proposed in the literatures [14,19,23]. The nascent and active sulfur from the pyrite or organic sulfur can react with the active site of inorganic matrix or origin matrix to form new sulfate or organic sulfur retained in the char, and the sulfate sulfur can be reacted with organic matrix or inorganic matter to form stable organic sulfur trapped in thiophenic.

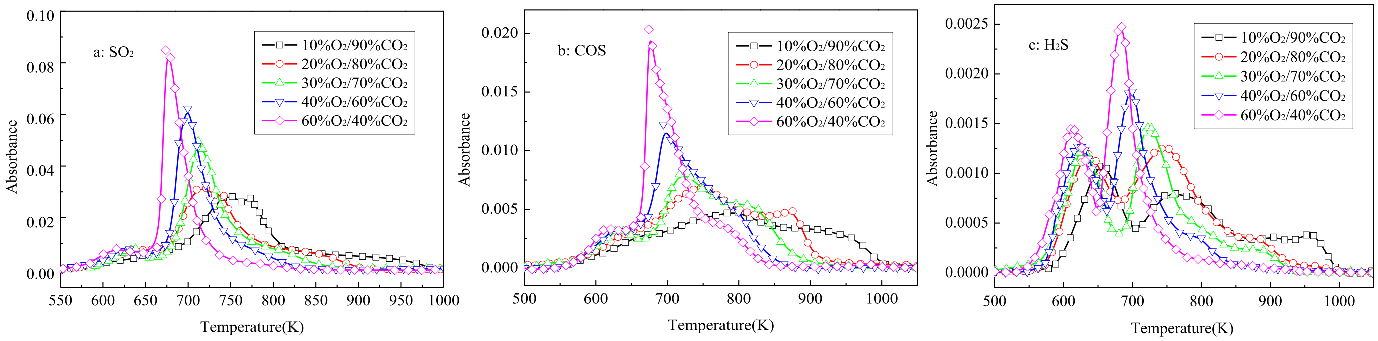

Fig. 6. Profiles of sulfur-containing gases emission during coal combustion in different O_2/CO_2 atmospheres.

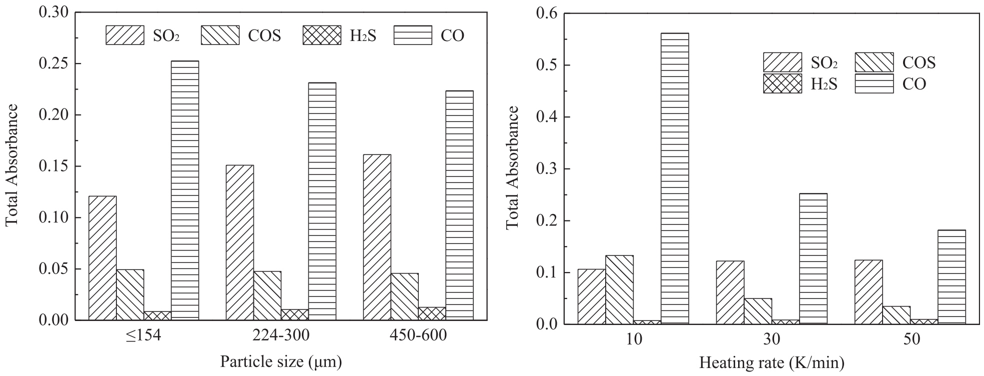

Fig. 7. Total emission profiles of sulfur-containing gases and CO with different particle sizes and heating rates.

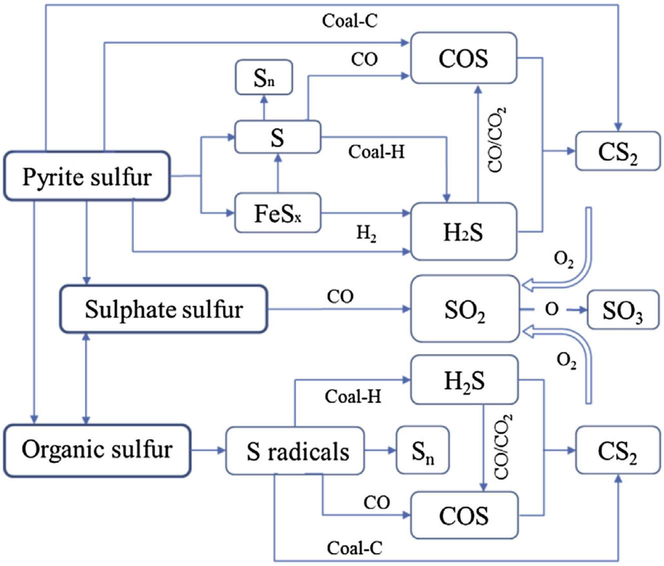

Fig. 8. A schematic of sulfur transformation during coal oxy-fuel combustion.

4. Conclusion

During coal pyrolysis, the weight loss and sulfur evolution profiles are almost identical between in N_2 and CO_2 atmospheres before 900 K, but then the weight loss and CO emission increase obviously due to the char-CO_2 gasification reaction in CO_2 atmosphere, and the increase of CO emission promotes the transformation of H_2S and other sulfur compounds to COS, and leads to more SO_2 emission by reduction of $CaSO_4$, the major contributor to the sulfur-containing gases during coal pyrolysis changes from H_2S in N_2 atmosphere to COS in CO_2 atmosphere. In coal combustion, the less SO_2, more H_2S and COS release in oxy-fuel combustion compared with their in air combustion because more sulfur retains in ash and transforms to H_2S and COS. The SO_2 becomes the main sulfur-containing gas in coal combustion because more H_2S and COS are oxidized to SO_2. With the O_2 concentration increasing, the main peaks of SO_2, COS and H_2S become more evident with the peak values increase and the peak positions shift to lower temperature zone, more SO_2, COS and H_2S release at lower temperature by the faster burning. As the particle size and heating rate increase, the SO_2 and H_2S emission increase, while the COS emission decreases by the less CO emission. Finally the comprehensive characteristics of sulfur behavior during coal combustion were proposed.

Acknowledgments

Financial supports of the National Basic Research Program of China (No. 2013CB228102) and National Natural Science Foundation of China (No. 51376075 and 51276075) are gratefully acknowledged.

References

[1] T. Kiga, S. Takano, N. Kimura, K. Omata, M. Okawa, T. Mori, M. Kato, Characteristics of pulverized-coal combustion in the system of oxygen/recycled flue gas combustion, Energy Convers. Manage. 38 (Suppl.) (1997) S129–S134.
[2] E. Croiset, K.V. Thambimuthu, NO_x and SO_2 emissions from O_2/CO_2 recycle coal combustion, Fuel 80 (14) (2001) 2117–2121.
[3] L. Zheng, E. Furimsky, Assessment of coal combustion in O_2+CO_2 by equilibrium calculations, Fuel Process. Technol. 81 (1) (2003) 23–34.
[4] H. Liu, R. Zailani, B.M. Gibbs, Comparisons of pulverized coal combustion in air and in mixtures of O_2/CO_2, Fuel 84 (7–8) (2005) 833–840.

[5] J.C. Chen, Z.S. Liu, J.S. Huang, Emission characteristics of coal combustion in different O_2/N_2, O_2/CO_2 and O_2/RFG atmosphere, J. Hazard. Mater. 142 (1–2) (2007) 266–271.

[6] T. Wall, Y. Liu, C. Spero, L. Elliott, S. Khare, R. Rathnam, F. Zeenathal, B. Moghtaderi, B. Buhre, C. Sheng, R. Gupta, T. Yamada, K. Makino, J. Yu, An overview on oxyfuel coal combustion-State of the art research and technology development, Chem. Eng. Res. Des. 87 (8) (2009) 1003–1016.

[7] L. Chen, S.Z. Yong, A.F. Ghoniem, Oxy-fuel combustion of pulverized coal: characterization, fundamentals, stabilization and CFD modeling, Prog. Energy Combust. Sci. 38 (2) (2012) 156–214.

[8] L. Duan, C. Zhao, W. Zhou, C. Liang, X. Chen, Sulfur evolution from coal combustion in O_2/CO_2 mixture, J. Anal. Appl. Pyrolysis 86 (2) (2009) 269–273.

[9] T. Czakiert, K. Sztekler, S. Karski, D. Markiewicz, W. Nowak, Oxy-fuel circulating fluidized bed combustion in a small pilot-scale test rig, Fuel Process. Technol. 91 (11) (2010) 1617–1623.

[10] Y. Tan, L. Jia, Y. Wu, E.J. Anthony, Experiences and results on a 0.8 MWth oxy-fuel operation pilot-scale circulating fluidized bed, Appl. Energy 92 (2012) 343–347.

[11] C. Lupiáñez, I. Guedea, I. Bolea, L.I. Díez, L.M. Romeo, Experimental study of SO_2 and NO_x emissions in fluidized bed oxy-fuel combustion, Fuel Process. Technol. 106 (2013) 587–594.

[12] W.H. Calkins, Investigation of organic sulfur-containing structures in coal by flash pyrolysis experiments, Energy Fuels 1 (1) (1987) 59–64.

[13] D. Shao, E.J. Hutchinson, J. Heidbrink, W. Pan, C. Chou, Behavior of sulfur during coal pyrolysis, J. Anal. Appl. Pyrolysis 30 (1) (1994) 91–100.

[14] S. Yani, D. Zhang, An experimental study into pyrite transformation during pyrolysis of Australian lignite samples, Fuel 89 (7) (2010) 1700–1708.

[15] R.K. Rathnam, L.K. Elliott, T.F. Wall, Y. Liu, B. Moghtaderi, Differences in reactivity of pulverised coal in air (O_2/N_2) and oxy-fuel (O_2/CO_2) conditions, Fuel Process. Technol. 90 (6) (2009) 797–802.

[16] P. Naredi, S. Pisupati, Effect of CO_2 during coal pyrolysis and char burnout in oxy-coal combustion, Energy Fuels 25 (6) (2011) 2452–2459.

[17] K. Sugawara, Y. Tozuka, T. Sugawara, Y. Nishiyama, Effect of heating rate and temperature on pyrolysis desulfurization of a bituminous coal, Fuel Process. Technol. 37 (1) (1994) 73–85.

[18] F. García-Labiano, J. Adánez, E. Hampartsoumian, A. Williams, Sulfur release during the devolatilization of large coal particles, Fuel 75 (5) (1996) 585–590.

[19] L. Xu, J. Yang, Y. Li, Z. Liu, Behavior of organic sulfur model compounds in pyrolysis under coal-like environment, Fuel Process. Technol. 85 (8–10) (2004) 1013–1024.

[20] A. Attar, Chemistry, thermodynamics and kinetics of reactions of sulphur in coal-gas reactions: a review, Fuel 57 (4) (1978) 201–212.

[21] E.J. Anthony, D.L. Granatstein, Sulfation phenomena in fluidized bed combustion systems, Prog. Energy Combust. Sci. 27 (2) (2001) 215–236.

[22] D. Fleig, E. Vainio, K. Andersson, A. Brink, F. Johnsson, M. Hupa, Evaluation of SO_3 measurement techniques in air and oxy-fuel combustion, Energy Fuels 26 (9) (2012) 5537–5549.

[23] J. Yperman, D. Franco, J. Mullens, L.C. Van Poucke, G. Gryglewicz, S. Jasienko, Determination of sulfur groups in pyrolysed low-rank coal by atmospheric-pressure t.p.r, Fuel 74 (9) (1995) 1261–1266.