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Sulfur Transformation in the Process of Circulating Fluidized Bed Combustion Combined with Coal Pyrolysis

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The transformation of sulfur was experimentally investigated in a polygeneration process that integrated coal combustion and pyrolysis. High-sulfur Yanzhou coal was pyrolyzed together with circulating ash in a fixed bed. The circulating ash not only fixed some of gaseous sulfur but also decreased the sulfur remained in char compared with coal pyrolysis alone. This unexpected decrease of sulfur in char was due to the rapidly absorption of active sulfur by circulating ash, which effectively inhibited the reactions between active sulfur and organic matrix or mineral matters in coal. The amount of sulfur fixed in ash was increased by raising the pyrolysis temperature and decreasing the ash particle size, while only part of it was secondly released during combustion. The desulfurization burden of circulating fluidized bed boiler was reduced by about 34% in the polygeneration process when pyrolysis and combustion temperatures were 650 and 950 °C, respectively.

1. Introduction

A polygeneration process, which coupled circulating fluidized bed (CFB) combustion with coal pyrolysis, is a more efficient and clean way for coal conversion. Figure 1 shows the principle illustration of polygeneration process. In this process, high-temperature ash from CFB boiler is introduced to the pyrolyzer as solid heat carrier to provide heat for coal pyrolysis, getting gas and tar. The char produced in the pyrolyzer is returned to CFB boiler at the pyrolysis temperature to generate electricity and provide heat. Thus gas, tar, electricity, and heat can be obtained simultaneously in the coupled process. Compared with the individual CFB boiler combustion, the valuable hydrocarbon of coal is first produced before combustion and the utilization efficiency of coal is improved. Moreover, the process has high thermal efficiency for the fully use of sensible heat of hot ash and char.[1] Owing to the attractive application prospect of polygeneration process, plenty of work has been carried out in this field, and they can be mainly grouped in two classes. One is to solve the key technological barriers of polygeneration process such as hot ash allocation,[2] mixing of hot ash and coal,[3,4] and
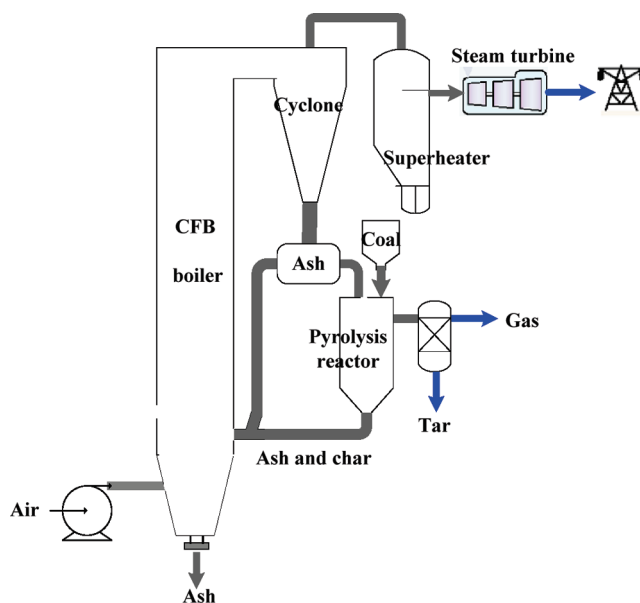

Figure 1. Principle illustration of the polygeneration process.

pyrolysis gas cleanup,[5] and the other is the investigation on effects of operation conditions in coal pyrolysis by solid heat carrier.[6–9] Up to now, most of them are still studied in the laboratory and few researchers are carrying out the pilot development of polygeneration process.[10] With the development of polygeneration process, the sulfur transformation of the process will become an important issue; however, it is

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(1) Liang, P.; Wang, Z. F.; Bi, J. C. *Fuel Process. Technol.* **2007**, *88*, 23–28.

(2) Wang, Z. F.; Liang, P.; Dong, Z. B.; Bi, J. C. *J. N. Univ. China* (*Nat. Sci. Ed.*) **2006**, *24*, 324–327 (in Chinese).

(3) Hu, G. X.; Gong, X. W.; Huang, H.; Fan, H. J.; Wang, Z. *Chem. Eng. Process.* **2008**, *47*, 1777–1785.

(4) Wang, Z. F.; Liang, P.; Dong, Z. B.; Bi, J. C. *Coal Convers.* **2005**, *28*, 48–51 (in Chinese).

(5) Liang, P.; Qu, X.; Bi, J. C. *J. Fuel Chem. Technol.* **2008**, *36*, 401–405 (in Chinese).

(6) Fang, M. X.; Luo, Z. Y.; Li, X. T.; Wang, Q. H.; Ni, M. J.; Cen, K. F. *Energy* **1998**, *23*, 203–212.

(7) Wang, J. G.; Lu, X. S.; Yao, J. Z.; Lin, W. G.; Cui, L. J. *Ind. Eng. Chem. Res.* **2005**, *44*, 463–470.

(8) Liang, P.; Wang, Z. F.; Bi, J. C. *Fuel* **2008**, *87*, 435–442.

(9) Xiong, R.; Dong, L.; Yu, J.; Zhang, X. F.; Jin, L.; Xu, G. W. *Fuel Process. Technol.* **2010**, *91*, 810–817.

(10) Qu, X.; Zhang, R.; Bi, J. C.; Gong, X. K.; Wang, N. R. *Chem. Ind. Eng. Process* **2008**, *27*, 386–390 (in Chinese).

Table 1. Proximate and Ultimate and Sulfur Forms Analysis of Coal[a]

proximate analysis (w_{ad} %)			ultimate analysis (w_{ad} %)						
						St			
M	A	V	C	H	N	Sp	Ss	So	O (diff)
3.75	9.90	38.70	68.37	5.68	1.56	1.42	0.99	1.48	6.85

[a] M, moisture; A, ash; V, volatile matter; ad, air dry; St, total sulfur; Sp, pyritic sulfur; Ss, sulfate sulfur; So, organic sulfur.
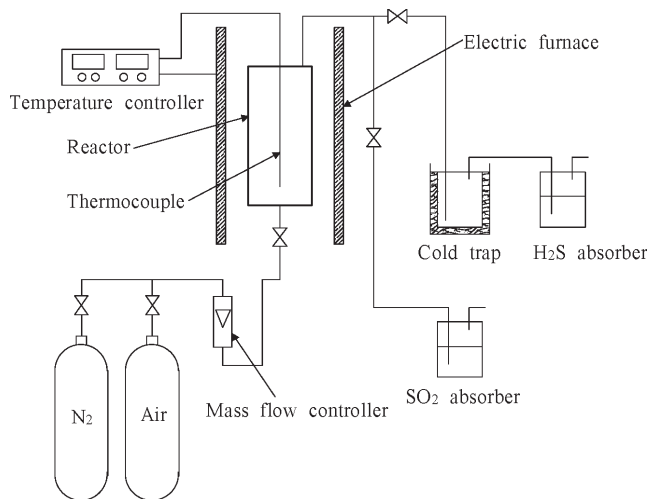
Table 2. Composition of Circulating Ash

Composition Analysis (wt %)									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_5
47.09	36.08	4.35	4.09	2.94	1.35	2.22	0.45	0.42	0.39

scarcely reported in the published literatures. A better understanding of sulfur transformation in the polygeneration process is essential for effective and economic sulfur removal.

Pyritic and organic sulfur are the two major forms of sulfur in coal. In pyrolysis, pyrite is decomposed into sulfide and sulfur. The nascent sulfur is very active, and it captures hydrogen from coal to form H_2S that moves to gas or may react with coal organic matrix to form organic sulfur that remains in char or tar[11,12] or is fixed by mineral matters in coal to form sulfide that remains in char.[13,14] The behavior of organic sulfur depends mainly on the functional group of organic sulfur in coal.[15−17] In the polygeneration process, coal is first pyrolyzed before combustion by hot ash from CFB boiler, and some compounds of sulfur such as H_2S, COS, SO_2, SO_3 in pyrolysis gas will be fixed in ash, which has been approved in our previous work.[18] Then the ash is fed back into boiler furnace together with char, and the second transfer of sulfur fixed in ash may occur in the boiler. As for the oxidation of sulfur fixed in ash during combustion, some studies have been performed, and many useful results have been obtained.[19−21] Nevertheless, a more complete understanding of the behavior of coal sulfur in the polygeneration process is still required, which will provide a theoretic foundation in designing the capacity of desulfurization equipment and determining the amount of adsorbent need.

This work is an attempt to simulate the polygeneration process and investigate the behavior of coal sulfur in the process. Coal sample was first pyrolyzed together with ash (coming from CFB boiler) in a fixed bed, and the effects of pyrolysis temperature and ash particle size on the behavior of sulfur in coal were investigated. The pyrolyzed solids (char and ash) were combusted to determine the secondary transfer of sulfur fixed in ash.

(11) Attar, A. *Fuel* **1978**, *57*, 201–212.
(12) Gryglewicz, G.; Wilk, P.; Yperman, J.; Franco, D. V.; Maes, I. I.; Mullens, J.; Poucke, L. C. V. *Fuel* **1996**, *75*, 1499–1504.
(13) Cypres, R.; Furfari, S. *Fuel* **1982**, *61*, 453–459.
(14) Liu, Q. R.; Hu, H. Q.; Zhou, Q.; Zhu, S. W.; Chen, G. H. *Fuel Process. Technol.* **2004**, *85*, 863–871.
(15) Ismail, K.; Mitchell, S. C.; Brown, S. D.; Snape, C. E. *Energy Fuels* **1995**, *9*, 707–716.
(16) Miura, K.; Mae, K.; Shimida, M.; Minami, H. *Energy Fuels* **2001**, *15*, 629–636.
(17) Gryglewicz, G. *Fuel Process. Technol.* **1996**, *46*, 217–226.
(18) Liang, P.; Wang, Z. F.; Bi, J. C. *J. Fuel Chem. Technol.* **2006**, *34*, 542–546 (in Chinese).
(19) Javad, A.; Rehmat, A.; Banerjee, D. D. *Ind. Eng. Chem. Res.* **1991**, *30*, 1990–1994.
(20) Qiu, K. R.; Lindqvist, O.; Mattisson, T. *Fuel* **1999**, *78*, 225–231.
(21) Wu, S. J.; Uddin, M. A.; Nagamine, S.; Sasaoka, E. *Fuel* **2004**, *83*, 671–677.

Figure 2. Schematic diagram of the experimental setup.

2. Experimental Section

2.1. Samples. The coal sample chosen for this investigation was Yanzhou coal of China. Table 1 shows the proximate, ultimate, and sulfur forms analysis of the coal. The coal was ground to 1.0−2.0 mm (mean diameter 1.5 mm) prior to experiments. The solid heat carrier used in the test was the ash which was fetched from a 75 t/h CFB boiler. The particle size of ash was < 0.2 mm (mean diameter 0.15 mm), and its composition was analyzed by an X-ray fluorescence spectrometer (XRF), as shown in Table 2.

2.2. Apparatus and Procedure. Research on coal pyrolysis with solid heat carrier has been performed using a fixed bed reactor. A schematic diagram of the experimental setup is shown in Figure 2. In each run, about 10 g of coal and a certain amount of ash were mixed uniformly and loaded into the reactor. Initially, the reactor was flushed with N_2 at a flow rate of 300 mL/min for 20 min. Then it was heated by an electric furnace from room temperature to the desired pyrolysis temperature at a heating rate of 30 °C/min. Tar and water were captured by a cold trap. The effluent gas from the trap was collected in a gas bag after hydrogen sulfur was absorbed. After each experiment, tar was separated from water by centrifugation and weighed. The pyrolyzed solids (char and ash) were collected and weighed, and then char and ash were separated by sieving.

To define the sulfur transfer in pyrolyzed solids during combustion, the combustion experiments of ash and char were carried out in the fixed bed reactor. In the tests, about 5 g of ash sample (or 2 g char sample) was combusted with a 400 mL/min air flow and a temperature program of increasing from room temperature to 850−950 °C at 30 °C/min and holding for 20 min. The gas product was discharged after sulfur dioxide was absorbed with 0.1 mol/L I_2 solution.

2.3. Analysis Methods. Hydrogen sulfide in gas was absorbed with a [Zn (CH₃COO) ₂ + NaCH₃COO] solution as zinc sulfide, which was determined by titration. The sulfur content of tar was measured by an elemental analyzer. The total sulfur content of char and ash was analyzed by the Eschka method (ASTM D 3177). The Gladfelter and Dickerhoof method[22] was used in the analysis of the forms of sulfur in char. Sulfate sulfur of char was extracted with 5 M hot hydrochloric acid and measured gravimetrically. Then the residue was extracted with 2 M hot nitric acid, and the concentration of iron in the extracted solution was analyzed using spectrophotometer to determine pyritic sulfur. Organic sulfur was analyzed with the Eschka method by measuring the sulfur content of the residue washed by hot nitric acid. Sulfide sulfur was calculated by difference.

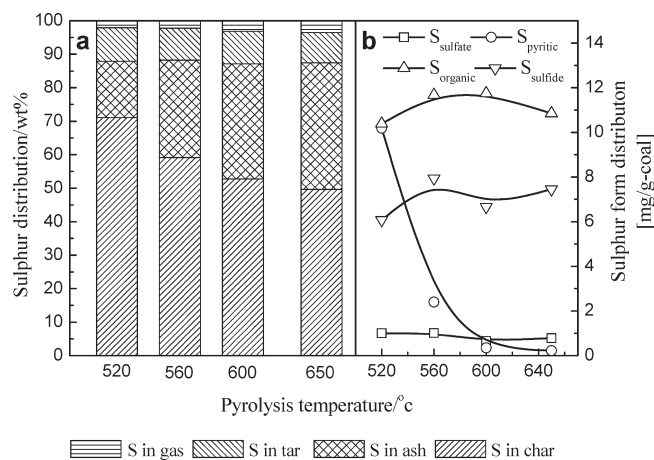(22) Gladfelter, W. L.; Dickerhoof, D. W. *Fuel* **1976**, *55*, 355–359.

Figure 3. Effect of pyrolysis temperature on sulfur distribution of pyrolysis products and sulfur form distribution of char (conditions: the ratio of ash to coal of 2:1, coal diameter of 1.0−2.0 mm, ash diameter of <0.2 mm).

Sulfur dioxide released during combustion was determined by iodimetry.

X-ray diffraction (XRD) analyses were applied to pyrolyzed solids (char and ash) to identify their key mineral matter compounds. A Bruker D8 advance power X-ray diffractometer (50 kV at 40 mA) using Ni-filtered Cu Kα radiation was used. Each sample was scanned in steps of 2θ within in the scattering range of 0−70°.

3. Results and Discussion

3.1. Effect of Pyrolysis Temperature. During coal pyrolysis by CFB ash, both the variation of the ratio of ash to coal and ash temperature will change the pyrolysis temperature. The effect of temperature on sulfur distribution in pyrolysis products is shown in Figure 3a. Circulating ash displayed significant action of sulfur retention. With the increase of pyrolysis temperature, most of sulfur released during coal pyrolysis was captured by ash. When the pyrolysis temperature was 650 °C, about 75% of sulfur released in pyrolysis was fixed in ash. Figure 3b shows the effect of pyrolysis temperature on the forms of sulfur in char. Pyritic sulfur showed a pronounced decrease with increasing pyrolysis temperature from 520 to 650 °C. Meanwhile some sulfide was formed. The sulfate sulfur of char was almost constant at the same temperature range. The content of organic sulfur tended to increase with temperature up to 600 °C, then decreased when temperature was further increased to 650 °C. Sulfur remaining in char was mainly organic sulfur and sulfide sulfur at the optimum pyrolysis temperature range (600−650 °C) which was obtained in our previous work.[1]

The above results have shown that ash can fix some of volatile sulfur-containing compounds that released in pyrolysis. In order to further clear the effect of ash on the release of sulfur in coal pyrolysis by CFB ash, Yanzhou coal was pyrolyzed at 620 °C using quartz sand (inert carrier) and CFB ash as heat carrier, respectively. Figure 4 shows the sulfur distribution in pyrolysis products at different heat carriers. Compared with quartz sand as heat carrier, not only sulfur in gas and tar was decreased but also sulfur remaining in char was reduced when coal was pyrolyzed by ash.

During coal pyrolysis with quartz sand, some of gaseous sulfur released from coal was moved to char again by reacting with coal organic matter to form new C−S bonds or was
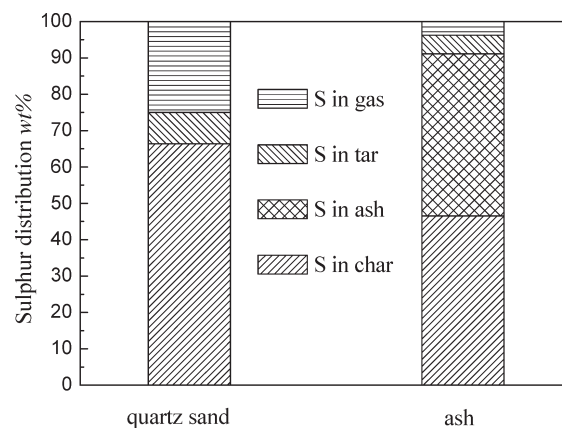

Figure 4. Effect of heat carrier on sulfur distribution of pyrolysis products (conditions: pyrolysis temperature of 620 °C, the ratio of ash to coal of 3:1, coal diameter of 1.0−2.0 mm, ash diameter of <0.2 mm).

Table 3. Analysis of Sulfur Forms in Chars at Different Heat Carriers

	sulfur forms in char (wt %)			
heat carrier	$S_{sulfate}$	$S_{organic}$	S_{pyrite}	$S_{sulfide}$
quartz sand	0.13	2.11	0.04	1.55
ash	0.09	1.71	0.05	1.13

Table 4. Effect of Ash Particle Size on Sulfur Distribution in Pyrolysis Products

sulfur distribution in products (wt %)			ash composition (wt %)		
	ash particle size (mm)			ash particle size (mm)	
	0.20−0.30	0.30−0.60		0.20−0.30	0.30−0.60
sulfur in gas	7.89	16.83	SiO_2	40.01	36.53
sulfur in tar	11.13	12.40	Al_2O_3	44.83	42.07
sulfur in char	50.24	61.93	Fe_2O_3	3.65	5.39
sulfur in ash	30.73	8.84	CaO	4.72	8.04
			MgO	2.69	2.49
			TiO_2	1.09	1.90
			SO_3	1.73	1.97
			K_2O	0.38	0.42
			Na_2O	0.47	0.55
			P_2O_5	0.05	0.15

fixed by mineral matters in coal to form sulfide.[12,14] However, coal particles were uniformly enclosed by ash particles in coal pyrolysis by CFB ash, and sulfur-containing compounds released in pyrolysis were fixed timely by ash, which inhibited the sulfur transfer from gas to char. In order to verify the viewpoint, the forms of sulfur in char at two heat carriers were analyzed, and the results are shown in Table 3. The contents of organic sulfur and sulfide in char, obtained when ash was used as heat carrier, were both lower than quartz sand.

3.2. Effect of Ash Particle Size. The fuel of CFB boiler has a wide size distribution, and the disintegration of coal particles tends to occur during combustion. Therefore, the particle size distribution of circulating ash is also wide. In addition, the variation of cyclone separation efficiency may bring on the change of circulating ash particle size. To investigate the effect of ash particle size on sulfur distribution in pyrolysis products, ash was separated into size fractions using the sieves. The fractions were 0.20−0.30 and 0.30−0.60 mm. Pyrolysis tests were carried out at 600 °C with coal particle size of <0.2 mm,
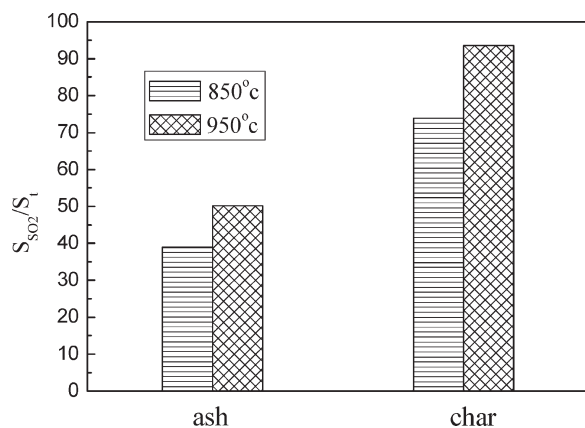
Figure 5. SO$_2$ emission during combustion of char and circulating ash.

and the results are shown in Table 4. Sulfur contents in gas, tar, and char decreased and that in ash increased with a decrease of ash particle size.

It has been known that calcium oxide in ash plays an important role for the fixation of sulfur during pyrolysis.[23] The extent of sulfur capture mainly depends on the amount of adsorbent and the sorbent surface area.[24] The richer the amount of adsorbent, the larger is the sorbent surface area and the greater is the extent of sulfur capture. As can be seen from Table 4, the larger ash particle has higher calcium oxide content, while it has lower sulfur-capturing capacity. The reason for this phenomenon is possibly that the calcium content of ash measured by XRF is the total amount of calcium, and it contains aluminosilicate-type glass and crystalline compounds of calcium such as anhydrite, gypsum, calcite, dolomite, and lime.[25,26] The sulfur-capturing capacity of ash is mainly dependent on the free lime content, and there may be higher free lime content in the smaller ash. In addition, the adsorbent has larger surface area in the smaller ash particle, which may contribute to the higher sulfur-capturing capacity.

3.3. Combustion of Char and Circulating Ash. In the polygeneration process, char produced in the pyrolyzer will be fed back into CFB boiler for combustion together with circulating ash. In order to get a fuller understanding of the second transfer of sulfur in pyrolyzed solids, the combustion of char and ash was performed. Figure 5 shows the effect of temperature on SO$_2$ emission during combustion of char and ash. It could be seen that 73.90% of sulfur in char was released when the temperature was 850 °C. With the temperature increased to 950 °C, 93.57% of sulfur in char was released. In contrast, the ratio of releasing sulfur of ash at 850 and 950 °C are only 38.99% and 50.13%, respectively.

The above experimental results (Figure 3b) have shown that sulfur remaining in char was mainly organic sulfur and sulfide when the pyrolysis temperature was 650 °C. During combustion, organic sulfur will be oxidized to SO$_2$, and the following reactions might occur in the oxidation
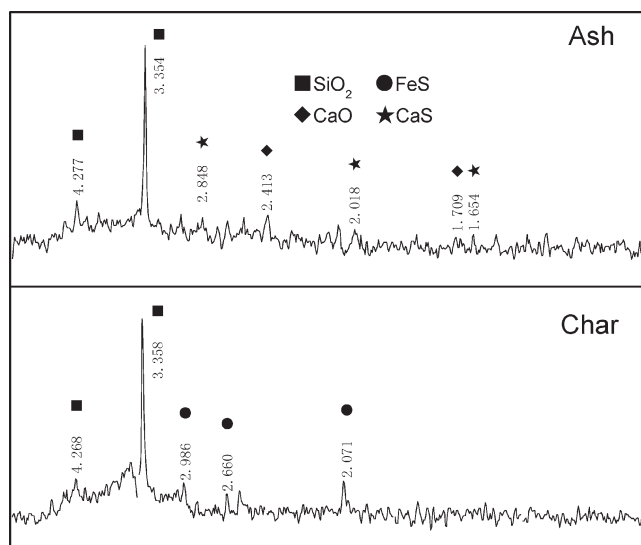

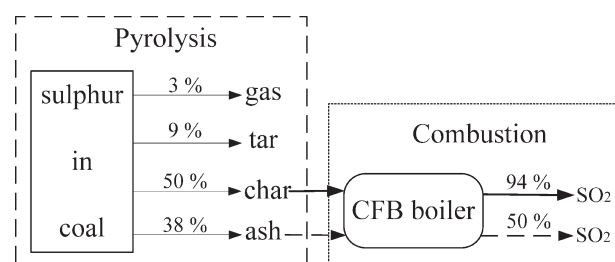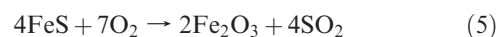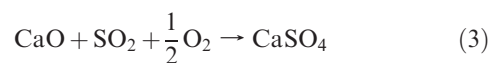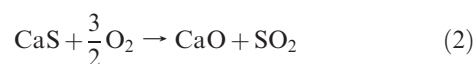**Figure 6.** XRD results of ash and char after pyrolysis.

Figure 7. Sulfur transfer in the polygeneration process (pyrolysis temperature of 650 °C; combustion temperature of 950 °C).

of sulfide:[20]

$$CaS + 2O_2 \rightarrow CaSO_4 \tag{1}$$

$$CaS + \frac{3}{2}O_2 \rightarrow CaO + SO_2 \tag{2}$$

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \tag{3}$$

$$CaS + 3CaSO_4 \rightarrow 4CaSO_4 + 4SO_2 \tag{4}$$

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2 \tag{5}$$

Previous investigations into the oxidation of CaS showed that the product tended to be CaSO$_4$ at lower temperature (<850 °C), while it was inclined to be CaO or both CaO and CaSO$_4$ accompanying the evolution of SO$_2$ at higher temperature.[27] However, FeS would be oxidized to Fe$_2$O$_3$ and SO$_2$ through reaction 5.[28] When the pyrolyzed solids (char and char) were combusted at 950 °C, 93.57% of sulfur in char was released, and only half of sulfur fixed in ash was emitted. Guan et al. also found that the sulfur fixed in the form of CaS in the chars gave out less SO$_2$ than the raw coal added with same additives during combustion.[29] From these results, it is

(23) Uzun, D.; Ozdogan, S. *Fuel* **2004**, *83*, 1063–1070.
(24) Agnihotri, R.; Chauk, S. S.; Mahuli, S. K.; Fan, L. S. *Chem. Eng. Sci.* **1999**, *54*, 3443–3453.
(25) Vassilev, S. V.; Vassileva, C. G. *Energy Fuels* **2005**, *19*, 1084–1098.
(26) Vassilev, S. V.; Menendez, R.; Alvarez, D.; Somonano, M. D.; Tarazona, M. R. M. *Fuel* **2003**, *82*, 193–1811.

(27) Davies, N. H.; Laughlin, K. M.; Hayhurst, A. N. *Twenty Fifth Symposium* (*International*) *on Combustion*; The Combustion Institute: Pittsburgh, PA, 1994; pp 211–218.
(28) Palmer, A.; Heeney, P.; Furimsky, E. *Fuel Process. Technol.* **1989**, *23*, 75–85.
(29) Guan, R. G.; Li, W.; Li, B. Q. *Fuel* **2003**, *82*, 1961–1966.

inferred that most of sulfide in char is FeS, while sulfur in ash exists mainly in the form of CaS.

X-ray diffraction (XRD) analyses of char and ash after pyrolysis were also performed to further verify the inference, and the results are shown in Figure 6. The XRD spectrum of char had only strong peaks of SiO_2 (4.268, 3.358) and weak peaks of FeS (2.986, 2.660, 2.071), and the main peaks were SiO_2 (4.277, 3.354), CaO (2.413, 1.709), and CaS (2.848, 2.018, 1.654) in the XRD spectrum of ash.

3.4. Analysis of Sulfur Transfer in the Polygeneration Process. Figure 7 shows the transfer of coal sulfur in the polygeneration process when pyrolysis and combustion temperatures are 650 and 950 °C, respectively. During coal pyrolysis by ash, about 5% of sulfur in coal moved into gas, which could be easily treated or recovered because of its higher concentration than flue gas. Sulfur remained in char after pyrolysis was only half of raw coal, and 38% of coal sulfur was fixed in ash. Most of sulfur remained in char was secondly released in the form of SO_2, while the ratio of releasing sulfur fixed in ash was 50% at the same condition. By comparison with individual coal combustion, the reduced desulfurization ($DeSO_x$) burden of CFB boiler in the polygeneration process can be calculated by the following expression:

$$\text{reduced } DeSO_x \text{ burden, wt \%} = S_{gas} + S_{tar} + S_{char}(1 - S_{char,SO_2}) + S_{ash}(1 - S_{ash,SO_2})$$

where S_{gas}, S_{tar}, S_{char}, and S_{ash} represent the percent of coal sulfur converted into gas, tar, char, and ash during coal pyrolysis by circulating ash, respectively. S_{char,SO_2} and S_{ash,SO_2} denote the released ratio of sulfur remained in char and that fixed in ash during combustion. Experimental results

obtained at 650 °C pyrolysis and 950 °C combustion showed that the desulfurization burden of CFB boiler was reduced by about 34% in the polygeneration process.

4. Conclusions

The transformation of sulfur has been studied in a polygeneration process of CFB combustion combined with coal pyrolysis. Circulating ash had significant action of sulfur retention during coal pyrolysis by circulating ash. It could react with some of the volatile sulfur-containing compounds released in pyrolysis and fix them in ash. In addition, ash could also decrease the sulfur remaining in char. By comparison with quartz sand as heat carrier, sulfur remaining in char was decreased from 66.44% to 46.52% when coal was pyrolyzed by ash at 620 °C. Sulfur remaining in char was mainly organic sulfur and sulfide (FeS); about 94% of them were secondly released during combustion at 950 °C. Sulfur fixed in ash existed mainly in the form of sulfide (CaS), and half of it was converted to $CaSO_4$ during combustion. The desulfurization burden of CFB boiler was reduced by about 34% when pyrolysis and combustion temperatures were 650 and 950 °C, respectively. Compared with the individual CFB combustion, not only the utilization efficiency of coal is improved but also the desulfurization burden of boiler is reduced in the polygeneration process.