Full Length Article

Experimental investigation on sulfur transformation during coal steam gasification with Ca-based absorbent

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A R T I C L E   I N F O

A B S T R A C T

To investigate the effects of temperature, Ca-based absorbent (CaO) and atmosphere on the sulfur transformation characteristics in coal steam gasification, experiments were conducted in a fixed-bed reactor. As temperature increased from 600 °C to 750 °C, H_2S-S (sulfur in H_2S) was elevated by 21.86% and absorbent-S decreased by 7.66%. More gaseous sulfur was captured by organic groups to form organic sulfur in char at higher temperature. CaO promoted the sulfur conversion, and played the role of gaseous sulfur absorbent at the same time, and showed an ability of organic sulfur removal. CaO slowed down the H_2S release by reacting with it to form CaS, resulting in that the peak concentration of H_2S without CaO reached 1026.7 ppm, which decreased to 426.3 ppm with CaO. The increase in Ca/C promoted the sulfur conversion slightly and reduced the sulfate content in char. Compared with inert atmosphere, H_2S-S in the steam atmosphere increased by 35.07%, while absorbent-S decreased by 23.42%. The solid–solid reaction mechanism is more suitable for the sulfate transformation in inert atmosphere, while the gas–solid reaction mechanism is more suitable in steam atmosphere. The sulfur conversion in inert atmosphere was lower, but sulfate had a higher decomposition rate.

1. Introduction

According to the Statistical Review of World Energy 2022 by BP, 160.10 EJ of coal was consumed globally in 2021. Coal is the second most consumed fuel in the world just after oil, of which the consumption accounted for 26.9% of the total global primary energy consumption in 2021. Coal consumption leads to a large amount of CO_2 emissions, aggravating the greenhouse effect. In 2021, 33884.1 million tons of CO_2 was emitted globally [1].

In order to reduce the CO_2 emissions in energy industry, it is necessary to develop carbon capture, utilization, and storage (CCUS) technologies. Chemical looping gasification based on Ca-based absorbent as a CO_2 absorbent (Ca-CLG) is a promising CCUS technology, the principle of which is shown in Fig. 1. Ca-CLG is composed of a gasifier and a combustor. In the process of Ca-CLG, CO_2 can be captured while H_2-rich syngas is produced, achieving efficient coal utilization [2] and concentrated CO_2 collection at the same time [3].

Ca-CLG is in the early stage of development at present, and there are still many problems to be further studied. For example, as shown in Fig. 1, sulfur-containing pollutants will be released, which can cause

acid rain, and is harmful to the environment [4]. In Ca-CLG, sulfur-containing pollutants can also damage the equipment, inactivate the absorbent, and reduce syngas quality [5]. This study mainly focuses on the sulfur-containing pollutants generated in the gasifier. Due to the addition of CaO, the sulfur transformation in Ca-CLG is different from traditional coal gasification, so it is of great significance to study the sulfur transformation characteristics in Ca-CLG.

Sulfur in coal can be mainly divided into organic sulfur and inorganic sulfur. Organic sulfur includes thiophene, sulfone, sulfoxide, etc., and inorganic sulfur includes sulfate, sulfide, pyrite, etc. [6], all of which are transformed into gaseous forms such as H_2S, SO_2, COS, CS_2 in the utilization process [7]. Some scholars have studied the sulfur transformation in coal in pyrolysis [8–10]. Guan et al. [11] and Zhang et al. [12] carried out a co-pyrolysis experiment of coal and Ca-based absorbent and found that $Ca(OH)_2$ and CaO had a favorable effect on sulfur-containing gas capture. The sulfur content in tar decreased, and the content of sulfate and sulfide in char increased, while part of the Ca-based absorbent was converted to CaS [13]. These studies can help to understand sulfur transformation in the gasification process.

Compared with pyrolysis, there is only H_2S but no COS detected
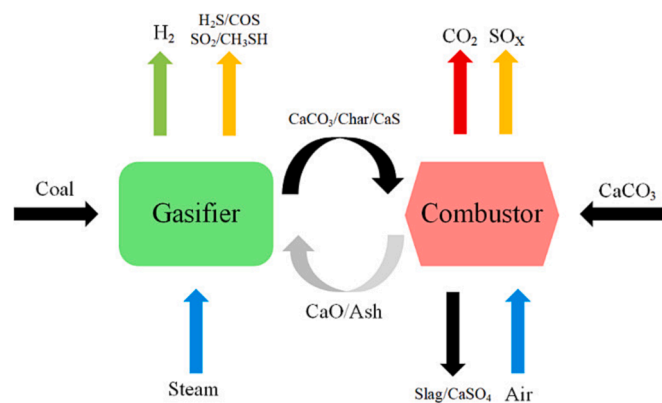

Fig. 1. The principle of Ca-CLG.

during coal gasification [14]. Zhang et al. [15] used FactSage to simulate the thermodynamic equilibrium of gasification and found a similar conclusion, and the generation of H_2S was closely related to the content of Ca and Fe compounds in coal.

Ca-based absorbent also affects the sulfur transformation in coal gasification. Zhang et al. [16] studied the sulfur release of limestone and medium-sulfur coal in the oxygen-enriched steam gasification process in a fluidized bed and found that the addition of limestone reduced sulfur release, the proportion of inorganic sulfur in gas increased, and most of the sulfur in char was thiophene. Zhang et al. [17,18] also discussed the effects of temperature, atmosphere, O/C, and H_2O/C (mole ratio) on sulfur transformation in coal gasification, and found that temperature was positively correlated with sulfur release rate. The yield of H_2S was the highest among gaseous sulfur, and the yield of H_2 was the main factor affecting the mole ratio of H_2S and COS. Han et al. [19] compared the yields of H_2 and H_2S release in gasification and obtained a result that at 1203 K and with a 1:4 mol ratio of CaO/C addition, the contents of H_2 and H_2S in gas were 77.41% and 0.28%, respectively.

Although all the studies above focused on the sulfur transformation in coal, they are not totally suitable to predict sulfur transformation in Ca-CLG in some aspects. Firstly, since the absorbent used in Ca-CLG is limestone (main component CaO), the gasification temperature cannot be too high (over 800 °C), otherwise $CaCO_3$ will decompose [20] and lose the ability of capturing CO_2. The experimental temperatures of the above studies are all relatively high, mostly at around 900 °C, some even over 1000 °C.

Secondly, the gasification atmosphere of Ca-CLG is steam, but that of the above studies are either CO_2, air, or oxygen-rich steam, which are different from Ca-CLG.

Finally, in the study of sulfur transformation in Ca-CLG, not only gaseous sulfur needs to be concerned, but also the changes of sulfur in char and absorbent should be taken into consideration, since there is a combustion process after gasification, and the above studies are not comprehensive enough. To have a further understanding, more work needs to be done.

In this study, a typical medium-sulfur coal is selected as raw material, and a series of gasification experiments under different operating conditions are carried out to investigate the effects of temperature, Ca-based absorbent and atmosphere on sulfur transformation, and sulfur content in gas, char and absorbent are determined. The release characteristics of sulfur-containing gas and the changes in sulfur forms in char are studied. Meanwhile, the transformation of sulfur forms in coal is also experimentally investigated. This work provides a reference for the sulfur-containing pollutants emissions control problems in the application of Ca-CLG.

2. Experimental

2.1. Materials

Run Bei (RB) coal, which is a medium-sulfur coal, was used in this work, ground and sieved to a particle size range of 0.18–0.25 mm, of which ultimate analysis and proximate analysis are listed in Table 1. Before experiments, the coal samples were dried at 105 °C for 24 h to remove moisture.

Industrial CaO was selected as CO_2 absorbent, the composition of which is shown in Table 2. CaO was calcined under a N_2 atmosphere at 850 °C for 2 h to ensure that the $CaCO_3$ and $Ca(OH)_2$ were decomposed into CaO completely, and then sieved to a particle size less than 0.075 mm for an easy differentiation from the coal samples.

2.2. Apparatus and procedure

The experiments were carried out in a fixed-bed reactor as shown in Fig. 2.

2.2.1. Apparatus

The system consists of a steam generation unit, a heating unit, and a gas condensation and analysis unit from left to right in Fig. 2. Steam generation unit consists of deionized water, a peristaltic pump, a gas mass flow controller and a steam generator. Deionized water enters the steam generator through the peristaltic pump and steam is carried by Ar into the reactor.

In the heating unit, resistance wires are used to provide heat, thermocouples are used to measure the temperature of the heating zone. The highest temperature in the reactor is up to 1473 K while the highest heating rate is 25 K/min.

The generated gas enters the gas analysis devices, GC1 and GC2, after passing through the cold trap.

2.2.2. Procedure

The main steps of this experiment are as follows: (i) mix 0.6 g RB coal and different proportion of absorbent evenly, put them inside a quartz boat and push them to the center of the heating zone; (ii) before each experiment, seal the reactor and continuously purge it with Ar (1 L/min) for 30 min to evacuate the air in reactor; (iii) switch the Ar flow rate to 100 mL/min, turn on the peristaltic pump and steam generator and begin heating at a rate of 20 K/min to the desired temperature at the same time, (iv) hold the temperature for 200 min, (v) generated gas entered the online sulfur-containing gas analyzer (GC1) after condensation, and then was collected with a gas bag, (vi) after each experiment, stop heating and turn off the steam generator, maintain the Ar flow rate at 100 mL/min until the reactor cooled down, and collect the mixture of char and absorbent, which were separated by sieve later and stored separately for subsequent analyses. Each experiment was repeated three times, and the results were averaged.

To investigate the effects of temperature, Ca-based absorbent and atmosphere on the sulfur transformation in the gasification process, nine groups of experiments were carried out, of which operating conditions are shown in Table 3.

Groups 1 to 4 were set to investigate the effect of temperature on sulfur transformation, groups 2 and 5 to 8 were set to investigate the effect of Ca-based absorbent, groups 2 and 9 were set to compare the

Table 1
Ultimate analysis, proximate analysis of RB coal (ad, wt%).

Proximate analysis				Ultimate analysis				
M	A	V	FC	C	H	N	O*	S
1.23	11.09	38.66	49.02	67.19	4.16	1.21	13.11	2.01

*: by difference, O = 100-M-A-C-H-N-S; M, moisture; A, ash; V, volatile; FC, fixed carbon.

Table 2
Composition of industrial CaO (wt%).

Compound	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Others*
Content	1.09	0.40	0.10	97.81	0.24	0.36

*: By difference.

differences of sulfur transformation in different atmospheres with Ca-based absorbent. The amount of CaO added was determined according to the calcium to carbon mole ratio (Ca/C), for example, when Ca/C is 1, it means that the mole ratio of Ca content in absorbent to the C content in coal is 1.

2.3. Analysis

The concentration of various sulfur-containing gases in gas was analyzed online by GC1, the composition of the gas in gas bag was analyzed offline by GC2 (7890A, Agilent), the sulfur content in char and absorbent was determined by Kulun sulfur tester (CLS-2, Jiang Fen), the content of carbon in char was determined using elemental analyzer, the sulfur forms in char were analyzed by X-ray photoelectron spectroscopy (XPS), and the components of CaO were characterized by X-ray diffraction (XRD).

GC1 (GCS-80, Hui Fen) equipped with a flame photometric detector (FPD) was used to analyze the concentration of H$_2$S, COS, CH$_3$SH, SO$_2$. Before experiment, the GCs were calibrated using a series of different concentrations of gases to ensure accuracy and reproducibility.

XRD was used to identify the mineral matter of the absorbent, using a PANalytical X'Pert'3 Powder X-ray diffractometer at a scan speed of 2°/min. XPS measurements were performed by Thermo Scientific K-Alpha, using a standard Al Kα (hν = 1486.6 eV) X-Ray source. All the binding energies were referenced to C1s of adventitious carbon at 284.8 eV.

3. Results and discussion

3.1. The effect of temperature on sulfur transformation

3.1.1. The effect of temperature on sulfur distribution in gasification products

Fig. 3(a) shows the sulfur distribution in different products after gasification at different reaction temperatures when Ca/C was 1.5. There were three main transformation directions of sulfur in coal: captured by CaO (absorbent-S), residual in char (char-S), and transformed into gaseous forms. Char-S stands for the mass of sulfur in char as a percentage of the total sulfur in coal. All the data in Fig. 3(a) has been converted to elemental sulfur content and normalized, and the normalization standard is sulfur content in ultimate analysis.

In this experiment, the gaseous sulfur was mainly H$_2$S, and the other forms were not detected or the concentrations were too low to be detected. Zhang et al. [18] reported that almost no other gaseous sulfur was detected except H$_2$S and COS, and the yield of COS (3%) was much lower than H$_2$S. And the yield of COS was due to the existence of O$_2$ in their experiment, which is different from the pure steam (plus Ar) gasification in this work. As shown in Fig. 3(a), the sulfur transformation was sensitive to temperature. When the temperature increased, the sulfur in coal tended to be transformed more into the gaseous form, H$_2$S-S, but char-S decreased. H$_2$S-S at 750 °C was even about 1.55 times as much as that at 600 °C. There are two reasons: on the one hand, higher temperature promoted the sulfur conversion directly; on the other hand, the reactions between steam and carbon (Eqs. (8)-(9)) are endothermic, which were enhanced at higher temperatures, the chemical bonds between carbon and sulfur were broken, and as a result, more sulfur participated in the reactions, therefore sulfur conversion was promoted indirectly [21].

To verify the second explanation above, carbon conversion rate C% and sulfur conversion rate S% were calculated as follows:

Table 3
Operating conditions for each group.

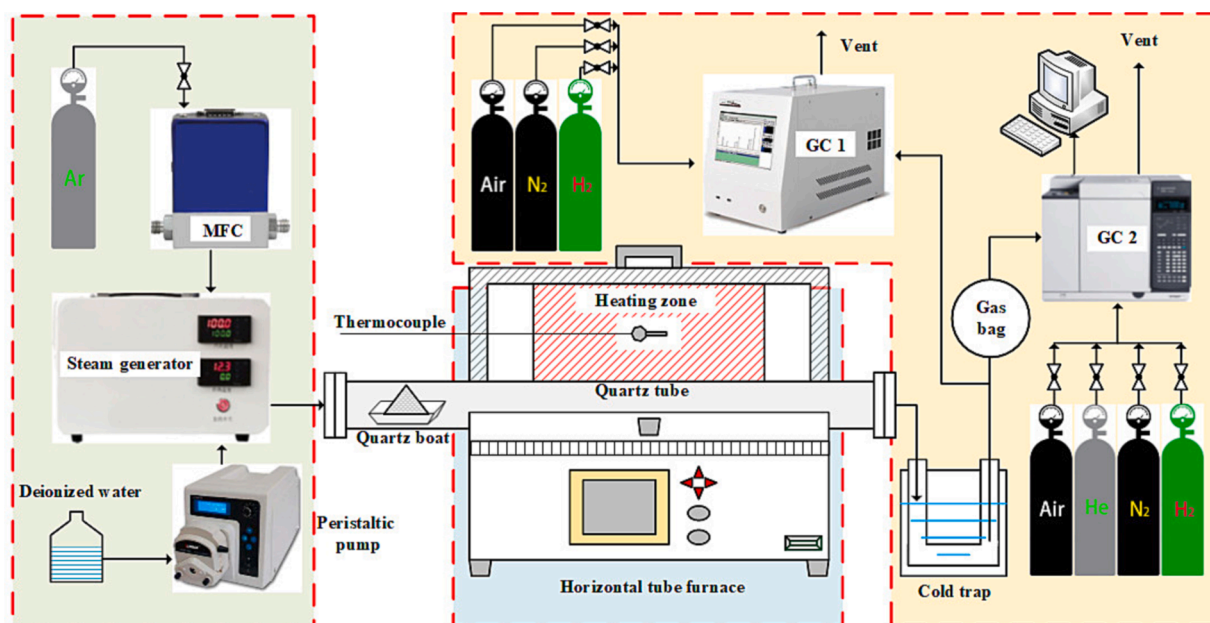| Group	Temperature/°C	Ca/C (mole ratio)	Atmosphere
1	600	1.5	Steam
2	650	1.5	Steam
3	700	1.5	Steam
4	750	1.5	Steam
5	650	0	Steam
6	650	0.5	Steam
7	650	1	Steam
8	650	1.25	Steam
9	650	1.5	Ar

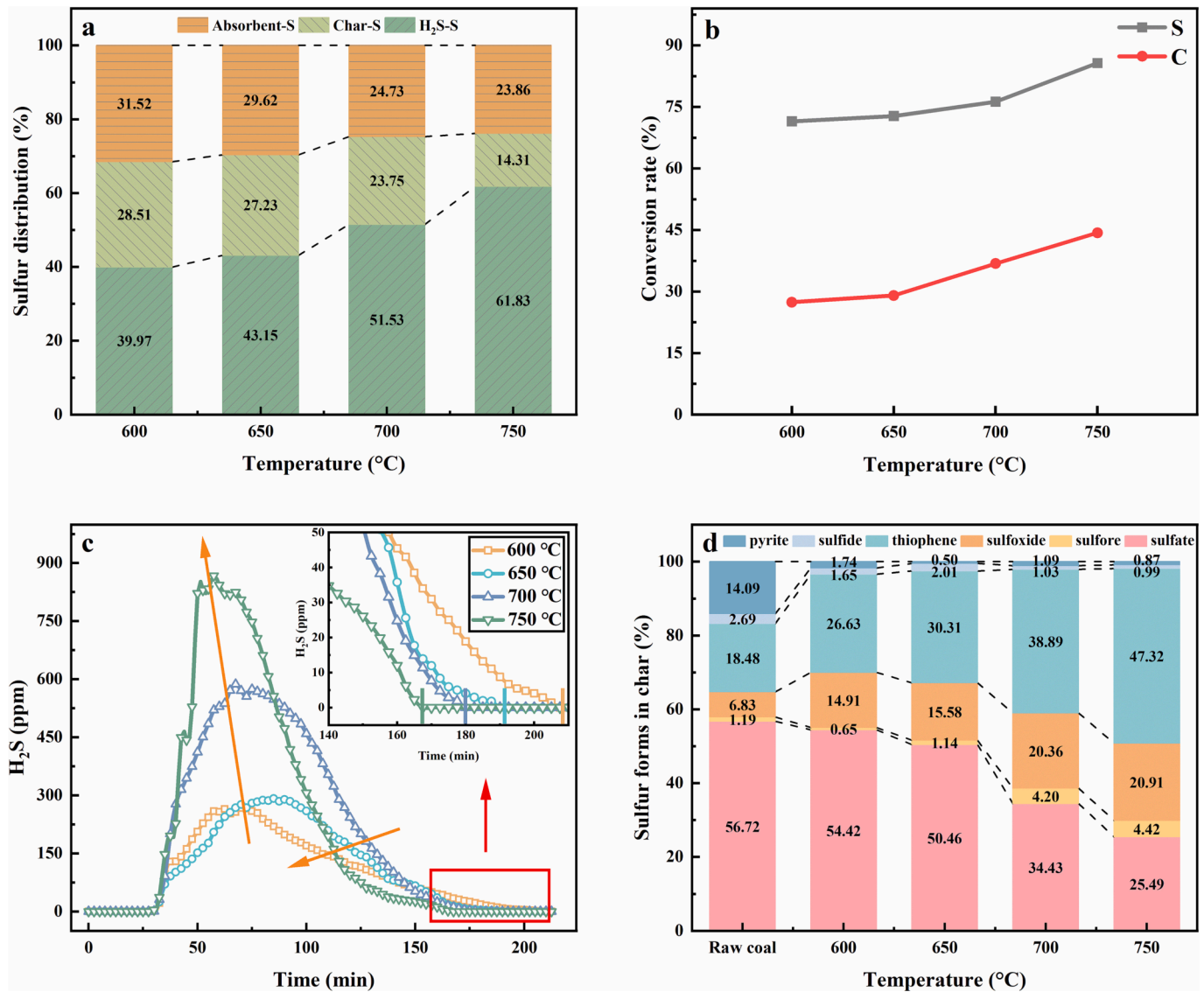**Fig. 2.** Schematic diagram of the fixed-bed reactor system.

Fig. 3. (a) sulfur distribution in products at different temperatures; (b) carbon and sulfur conversion rate at different temperatures; (c) release characteristics of H_2S at different temperatures; (d) sulfur forms in char at different temperatures.

$$C\% = \frac{C_{coal} - C_{char}}{C_{coal}} \qquad (1)$$

where, C_{coal} and C_{char} respectively represented the content of carbon in coal and char.

$$S\% = \frac{S_{coal} - S_{char}}{S_{coal}} \qquad (2)$$

where, S_{coal} and S_{char} respectively represented the content of sulfur in coal and char. And Fig. 3(b) shows the results. It can be seen that C% and S% increased simultaneously with increasing temperature, which can be a proof. The conversion rates of carbon and sulfur in coal were raised from 22% to 33% and from 22% to 28% when temperature increased in a previous research [16], which showed the same tendency.

It's noticed that in Fig. 3(a) the increase of H_2S-S was more than the decrease of char-S, which indicated that part of the absorbent-S was released as temperature rose.

$$H_2S + CaO \rightarrow CaS + H_2O \qquad (3)$$

This is because that Eq. (3) is an exothermic reaction [22], inhibited when temperature rises, thus the efficiency of CaO of sulfur-containing

gases fixation decreased. On the other hand, CaS can be hydrolyzed under steam atmosphere to generate H_2S as follows:

$$CaS + H_2O \rightarrow CaO + H_2S \qquad (4)$$

which is an exothermic reaction [22], promoted when temperature rises. The above two factors together lead absorbent-S to show a decreasing trend.

In summary, the sulfur transformation from coal to gas in the form of H_2S was promoted when gasification temperature rose.

3.1.2. The effect of temperature on the release of gaseous sulfur

It's of great importance to understand the release characteristics of gaseous sulfur when studying sulfur transformation in gasification. Therefore, in this work, the release of gaseous sulfur (H_2S) at different temperatures during the whole experiment was monitored and Fig. 3(c) shows the release curve with time.

As can be seen, the time when H_2S was first detected was relatively constant, at about 30 min. Considering the delay of GC 1, it was corresponded to about 550 °C. The generation of H_2S was attributed to the decomposition of unstable organic components and pyrite in coal at this moment [23]. Each curve tended to be taller and narrower overall with

temperature increasing, meaning that the time to reach the peak concentration of H_2S release was getting shorter, about 10 min earlier at 750 °C than at 600 °C, and the time that the reaction lasted was getting shorter as well, about 40 min less at 750 °C than at 600 °C, indicating an acceleration of reaction. At the same time, the peak concentration of H_2S release became higher, reaching a maximum of about 900 ppm at 750 °C, while it was only less than 300 ppm at 600 °C, indicating that the reaction was enhanced, from another perspective. This can also explain the decrease in absorbent-S with temperature increasing in Fig. 3(a): a large amount of H_2S was released in a short time that could not be captured by absorbent in time.

In summary, not only the sulfur transformation was promoted, but the speed and intensity of the reactions were promoted with temperature increasing.

3.1.3. The effect of temperature on the sulfur forms in char

For a further understanding of sulfur transformation in gasification, the content of sulfur forms in char at different temperatures were determined through XPS analysis, shown in Fig. 3(d). The "pyrite", for example, means the mass of pyrite sulfur in char as a percentage of the total sulfur in char.

Sulfur exists in coal mainly in the form of sulfate, sulfone, sulfoxide, thiophene, sulfide and pyrite [24], of which binding energies in XPS analysis are usually considered to be 169.5 ± 0.5 eV, 168.0 ± 0.5 eV, 166.0 ± 0.5 eV, 164.1 ± 0.2 eV, 163.3 ± 0.4 eV and 162.5 ± 0.3 eV respectively [25–29]. Sulfate is the main sulfur form in RB coal, accounting for 56.72%, followed by thiophene and pyrite in this experiment.

As shown in Fig. 3(d), the pyrite was almost completely decomposed through Eqs. (5)-(6) as the temperature increased. These two reactions can take place at about 500 °C and 590 °C [30]. Pyrite decomposition was the main source of H_2S in the early stage of gasification.

$$FeS_2 + 2H \rightarrow H_2S + FeS \qquad (5)$$

$$3FeS_2 + 4H_2O \rightarrow 4H_2S + Fe_3O_4 + S_2 \qquad (6)$$

Organic sulfur (including thiophene, sulfoxide, and sulfone) in char gradually increased, among which thiophene showed the largest increase, followed by sulfoxide, because inorganic sulfur was captured by organic groups in coal in the process and transformed into organic sulfur [31,32]. Zhang et al. [16] reported that at 900 °C, the thiophene content in char after gasification was about 55%, while that in raw coal was only 20%. This is similar to the results in Fig. 3(d).

Sulfate continued to decrease in the opposite. The sulfate in coal is mainly $CaSO_4$ [33], and pure $CaSO_4$ is only decomposed at above 1300 °C [34]. Therefore, it is presumed that some factors can reduce the decomposition temperature of $CaSO_4$ in this experiment. The following experiments listed in Table 4 were conducted using pure $CaSO_4$ (particle size below 0.075 mm) and RB coal as raw materials to verify this and to investigate the sulfate conversion in coal during gasification.

Groups 1 and 2 were designed to exclude the possibility that pure $CaSO_4$ would be decomposed at low temperatures and that CaO would react with $CaSO_4$ or have a catalytic effect on $CaSO_4$ decomposition. Group 3 was a control group for coal gasification. Groups 4 to 6 were set to investigate the effect of temperature on the $CaSO_4$ decomposition in

Table 4
Operating conditions for each group.

Group	Reactants (mass ratio)	Temperature/°C	Atmosphere
1	$CaSO_4$	650/700/750	Steam
2	$CaSO_4$ + CaO (1:1)	650/700/750	Steam
3	Coal	650	Steam
4	$CaSO_4$ + Coal (1:1)	650	Steam
5	$CaSO_4$ + Coal (1:1)	700	Steam
6	$CaSO_4$ + Coal (1:1)	750	Steam
7	$CaSO_4$ + Coal (1:1)	700	Ar

gasification; group 7 was set to investigate the effect of atmosphere. After each experiment was over, char and $CaSO_4$ were separated by sieve. The H_2S concentration was monitored online, and the H_2S release curves of each group are shown in Fig. 4(a).

No H_2S was detected in neither group 1 nor group 2, of which curves were not drawn in Fig. 4(a) therefore. It suggested that $CaSO_4$ could not be decomposed under this condition and that CaO had no catalytic effect. The mixture of $CaSO_4$ and coal produced more H_2S compared with group 3, which was only coal gasification, and the yield of H_2S increased substantially with the temperature increasing. H_2S-S was even much more than all the sulfur in coal at 750 °C. Moreover, all the groups except group 6 stopped releasing H_2S by 150 min, while a lot of H_2S was still detected in group 6 after 250 min. All the results above can verify the decrease in the $CaSO_4$ decomposition temperature.

The sulfur forms in char of group 4 in Table 3 and group 6 in Table 4 were determined and then compared to get a better understanding of $CaSO_4$ evolution, as shown in Fig. 4(b). The H_2S released in group 6 was the most, which is more suitable for comparison. And to keep the temperature consistent, which influenced the $CaSO_4$ composition a lot, group 4 in Table 3 was chosen as a control group.

Compared with group 4, the thiophene content in char of group 6 increased substantially, because the latter group produced more H_2S and more H_2S was captured by organic groups to form thiophene. The sulfate content decreased instead, which might be related to the long reaction time of group 6.
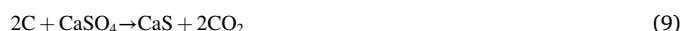
XRD measurements of pure $CaSO_4$ and the $CaSO_4$ of group 6 after reaction were carried out to investigate the transformation of $CaSO_4$ better. As shown in Fig. 5, the signal intensity of $CaSO_4$ decreased and that of CaS enhanced after the reaction, indicating that $CaSO_4$ was partially converted to CaS. The signal intensity of CaO and $Ca(OH)_2$ also enhanced, which was attributed to Eq. (4), generating H_2S and CaO from CaS, and then part of the CaO was converted to $Ca(OH)_2$ under steam atmosphere.

After 250 min of the reaction, the steam supply to group 6 was stopped but the temperature was still held. It was found that H_2S was stopped releasing, indicating that steam did promote the decomposition of $CaSO_4$. To figure out what made the $CaSO_4$ decomposed, all the gas produced in 5 min was collected with sample bags every 50 min, as marked on the curve of group 6 in Fig. 4(a), and then analyzed by GC2. The results are listed in Table 5.

It can be seen from Table 4 that the main component was H_2 and CO_2 along with a small amount of CO, among which H_2 and CO are highly reductive and can react with $CaSO_4$ to produce H_2S through the following reactions [17,35]:

$$4H_2 + CaSO_4 \rightarrow CaO + 3H_2O + H_2S \qquad (7)$$

$$4CO + CaSO_4 \rightarrow CaS + 4CO_2 \qquad (8)$$

In addition, some studies [35,36] have reported that carbon in coal caused $CaSO_4$ to decompose at relatively low temperatures:

$$2C + CaSO_4 \rightarrow CaS + 2CO_2 \qquad (9)$$

$$C + 2CaSO_4 \rightarrow 2CaO + 2SO_2 + CO_2 \qquad (10)$$

$$2C + CaSO_4 \rightarrow CaO + CO_2 + COS \qquad (11)$$

Besides, it has been reported [41] that some inherent alkaline minerals in coal can slightly exacerbate the decomposition $CaSO_4$. There are various alkaline minerals in coal, like Fe_2O_3, which can also catalyze the decomposition of $CaSO_4$. On the other hand, these alkaline minerals catalyze the gasification as well because they can provide higher surface area as a porous support.

As mentioned above, CaS will be hydrolyze to produce H_2S in the presence of steam through Eq. (4). The above two reasons led to the decomposition of $CaSO_4$ and the production of a large amount of H_2S as well as the appearance of CaS in $CaSO_4$ after the experiment.
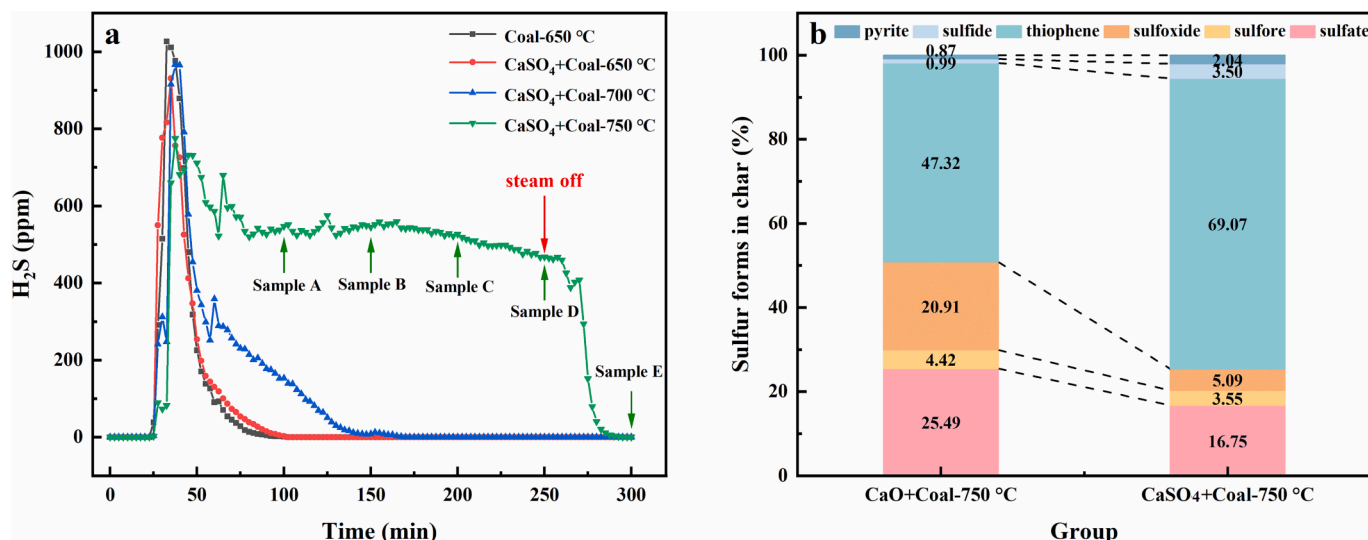
Fig. 4. (a) H_2S release characteristics of the groups in Table 4; (b) comparison of sulfur forms in char of group 4-Table 3 and group 6-Table 4.
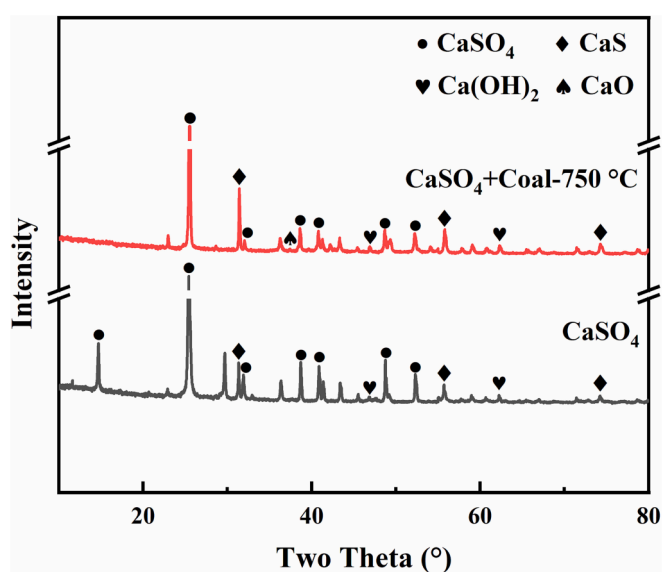

Fig. 5. XRD analysis of pure $CaSO_4$ and the $CaSO_4$ from group 6-Table 4.

Table 5
Components of gas sample A to E.

Sample	CO	CO_2	CH_4	H_2
A	0.506%	1.482%	0.084%	3.145%
B	0.582%	1.592%	0.067%	2.972%
C	0.472%	1.305%	0.047%	2.432%
D	0.419%	1.147%	0.040%	2.167%
E	0	0	0	0

In summary, the sulfate in coal was converted to H_2S, and the increase in temperature promoted this conversion in gasification.

3.2. The effect of Ca/C on sulfur transformation

3.2.1. The effect of Ca/C on the sulfur distribution in gasification products

Fig. 6(a) shows the sulfur distribution after gasification at different Ca/C and the reaction temperatures was 650 °C. "The rest" in Fig. 6(a) contains sulfur in COS and tar. In Fig. 6(a), only the group without CaO addition contains this item, this is because: 1), limited by the scale of the

apparatus, a little coal was used as sample, leading to a low yield of tar; 2), the steam atmosphere provided a large amount of H·, which combined with tar to form smaller molecules, making the tar less; 3), CaO is widely considered to be a high-efficient catalyst to reduce tar. Thus, there was barely no tar collected in the groups with CaO addition for analysis. Due to the above reasons, the sulfur in tar isn't discussed in this work.

More gaseous sulfur was released compared to the group without CaO. This is because, on the one hand, CaO promoted the WGSR (Water-Gas Shift Reaction), Eqs. (12)-(17), by absorbing CO_2, resulting in an increase in the carbon conversion rate and thus the sulfur conversion rate increased as well, as shown in Fig. 6(b).

$$C + H_2O \rightarrow CO + H_2 \tag{12}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \tag{13}$$

$$C + 2H_2 \rightarrow CH_4 \tag{14}$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{15}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{16}$$

$$CaO + CO_2 \rightarrow CaCO_3 \tag{17}$$

On the other hand, CaO could not only absorb CO_2, but also played a role of catalyst to catalyze the tar decomposition and facilitate the gasification to generate more gaseous sulfur [9].

The sulfur content in char and gas showed a slight decreasing trend with increasing Ca/C, overall, indicating that the increase of CaO in a certain range could enhance the catalytic effect on the gasification as well as fix more H_2S. It is noticed that there was no obvious difference between the results of group 7 and group 8 in Table 3, indicating that the catalytic effect of CaO had a limit as Ca/C gradually increased. When the Ca/C was 1.5, the sulfur content in char instead increased, due to the excess CaO that instead blocked the contact of coal particles with the atmosphere and then hindered the gasification probably, resulting in a decrease in the sulfur content in gas. Similarly, the above assumption can be proved by calculating the carbon and sulfur conversion rate of each group, as shown in Fig. 6(b).

In summary, CaO played both the role of a catalyst for promoting the sulfur transformation from coal to gaseous state and a desulfurizer for fixing gaseous sulfur, and there was a competitive relationship between these two mechanisms.
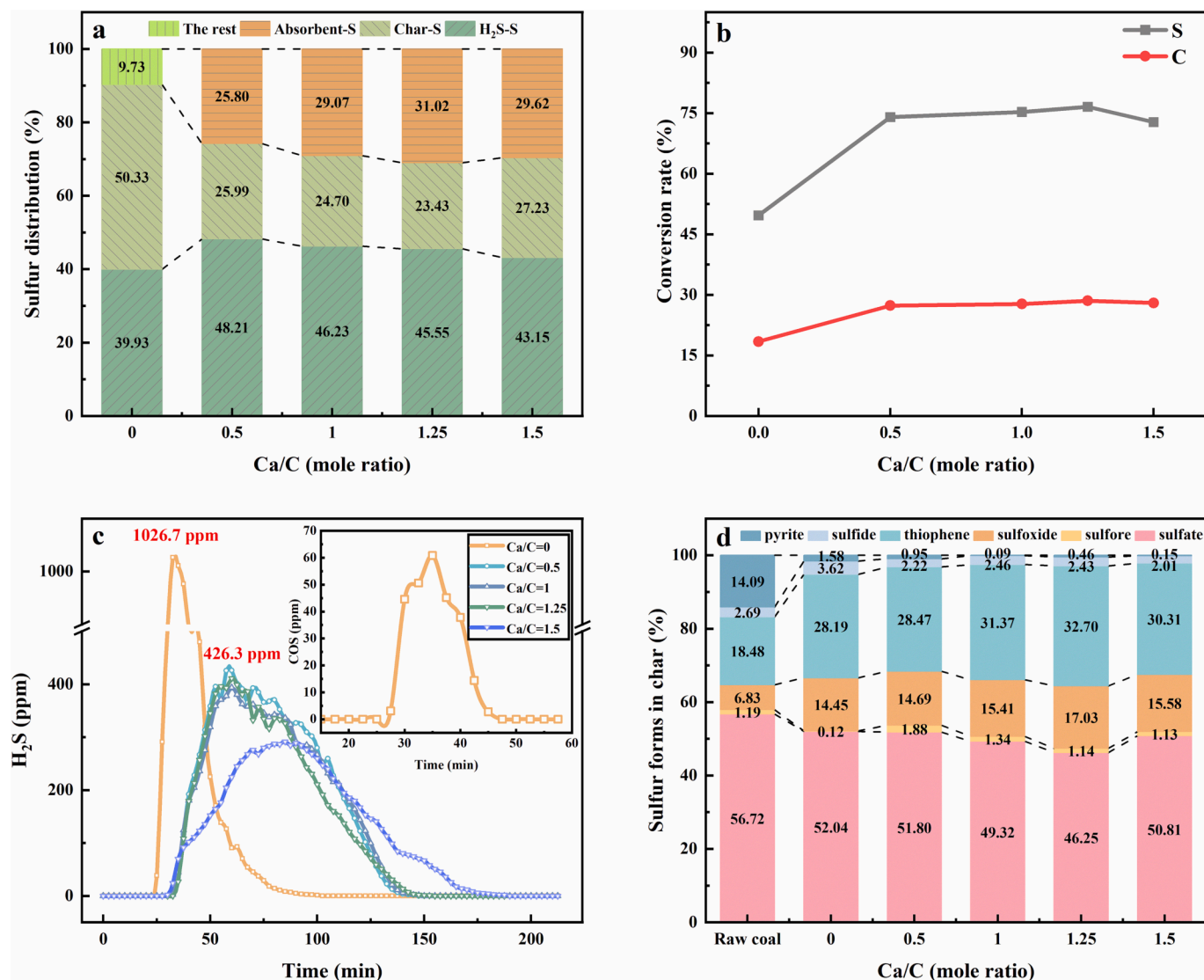
Fig. 6. (a) sulfur distribution at different Ca/C; (b) carbon and sulfur conversion rate at different Ca/C; (c) release characteristics of gaseous sulfur at different Ca/C; (d) sulfur forms in char at different Ca/C.

3.2.2. The effect of Ca/C on the release of gaseous sulfur

Fig. 6(c) shows the gaseous sulfur release curve at different Ca/C with time. The H_2S release characteristics of the group without CaO and the other groups were different in two aspects. On the one hand, when Ca/C was 0, a small amount of COS was detected in the gas, while there was no COS detected in the other groups, indicating that CaO contributed to the removal of organic sulfur.

$$CaO + COS \rightarrow CaS + CO_2 \quad (18)$$

Meanwhile, COS will be hydrolyzed in a steam atmosphere:

$$COS + H_2O \rightarrow H_2S + CO_2 \quad (19)$$

The above two reactions led to the non-detection of COS in the groups with CaO.

On the other hand, the highest H_2S concentration was 426.3 ppm when Ca/C was 0.5 with a long release duration, while that was 1026.7 ppm when Ca/C was 0 with a concentrated release within the early period. And the time H_2S started to be released when Ca/C was 0 was a little earlier than that in the other groups. All the above results indicated that CaO could inhibit the H_2S release. Therefore, CaO did have an advantage in fixing sulfur taking the short reaction time in actual utilization into consideration.

Two CaO samples were collected at 50 min and 150 min in the experiment process when the Ca/C was 1.5 for XRD analysis in order to investigate the H_2S release inhibition mechanism of CaO. The XRD results are shown in Fig. 7(a).

Compared with CaO sampled at 50 min, the signal intensity of Ca$(OH)_2$ in CaO sampled at 150 min was significantly enhanced, the signal of CaO was significantly weakened, and the signal of $CaCO_3$ was also slightly enhanced. CaS appeared after 50 min, but then disappeared after 150 min, so it can be presumed that CaO was involved in this process as an intermediate, slowing down the release of H_2S.

$$CaO + H_2S \rightleftharpoons H_2O + CaS \quad (20)$$

CaO firstly fixed the H_2S into the form of CaS, and as the reaction proceeded, CaS was hydrolyzed in the steam atmosphere to regenerate H_2S. Therefore, the H_2S release curves of the groups with CaO were relatively flat.

In order to verify that the hydrolysis of CaS was possible to occur under this condition, 1 g CaS was placed in the tube furnace and experiments under different conditions were carried out. The H_2S release with time was monitored the same as those previous experiments, and the results are shown in Fig. 7(b).

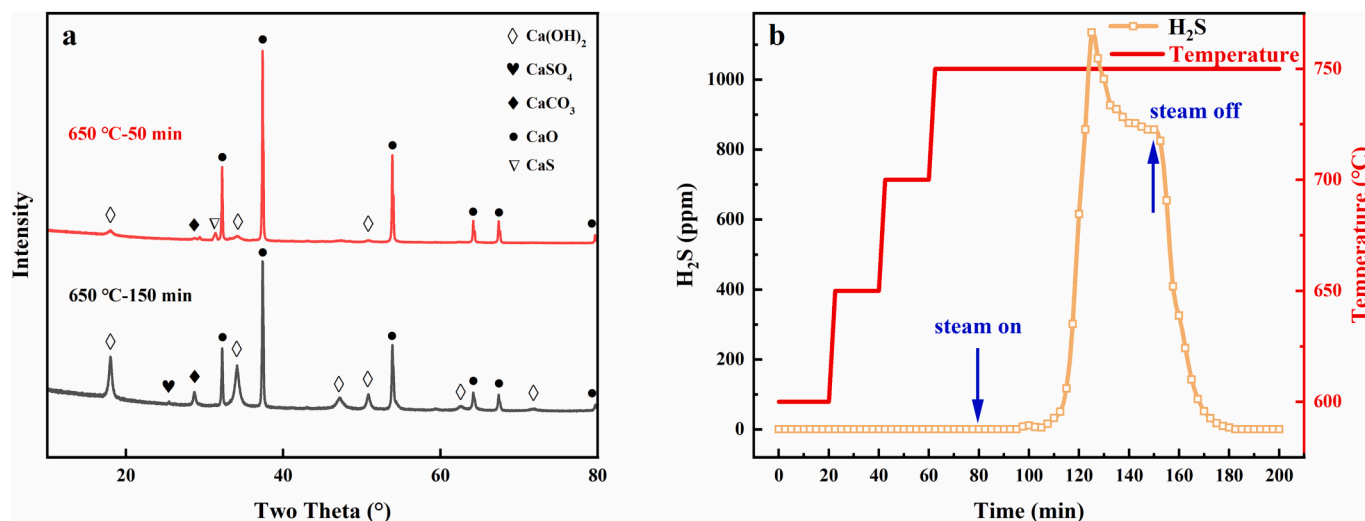CaS pyrolysis experiments were conducted at 600 °C to 750 °C, and

Fig. 7. (a) XRD analysis of the CaO after different reaction time; (b) release characteristics of H_2S during CaS gasification

no H_2S was detected, ruling out the possibility of CaS decomposition in an inert atmosphere. After steam was introduced into the reaction zone at 750 °C, a large amount of H_2S was released. Once the supply of steam was stopped, the H_2S release gradually decreased until there was no H_2S, suggesting that the above assumption was reasonable.

In summary, CaO functioned as a desulfurizer by absorbing H_2S and slowing down the H_2S release.

3.2.3. The effect of Ca/C on the sulfur forms in char

The sulfur forms in char with different CaO addition are shown in Fig. 6(d). As the Ca/C increased, sulfate in char continued to decrease and organic sulfur gradually increased, but the decrease and increase were not significant. The catalytic and reaction-promoting effects of CaO led to an elevated overall sulfur conversion, while more H_2S was produced and then captured by organic groups, so the organic sulfur content increased. Similarly, when the Ca/C reached 1.5, the overall reaction was hindered by the excess CaO.

In general, the effect of Ca/C on the sulfur forms in char was small.

3.3. The effect of atmosphere on sulfur transformation

3.3.1. The effect of atmosphere on the sulfur distribution in gasification products

Fig. 8(a) shows the sulfur distribution in the products in Ar and steam atmosphere. The sulfur fixed by CaO in steam was much less than that in Ar, since steam hindered the sulfur fixation [37]. Only a small amount of H_2S was released in Ar, while a large amount of H_2S was released in steam. This suggested that steam promoted the sulfur conversion into H_2S, because not only did steam not consume the self-contained hydrogen radicals in coal, but it also produced more hydrogen radicals through the gasification reaction with carbon instead, thus promoting the production of H_2S. Due to the insufficient hydrogen radicals in Ar, the sulfur-containing groups could not combine with hydrogen radicals, but part of them combined with each other or with the organic groups to form new organic sulfur, thus detrimental to sulfur removal [38]. The two reasons together led to a low sulfur content in char, but a high sulfur content in gas.

However, the carbon conversion rate was 30.79% in Ar, which was instead higher than 28% in steam atmosphere. This could not be explained by the carbon and sulfur synergistic conversion mechanism. There must be other reasons, which were experimentally investigated in
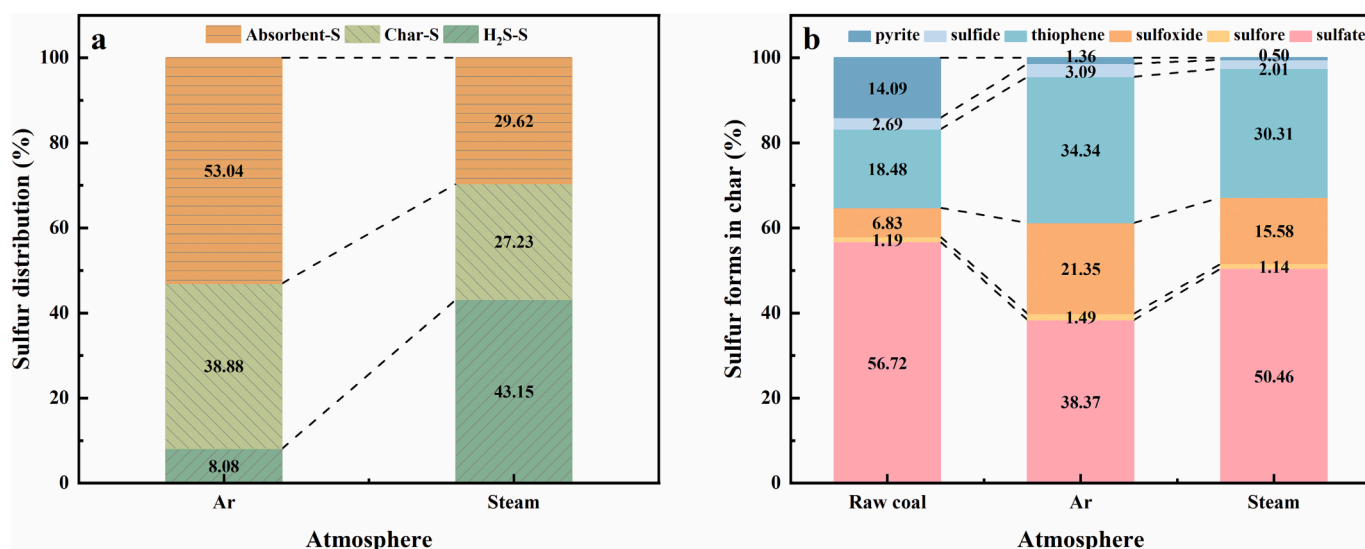

Fig. 8. (a) sulfur distribution in different atmospheres; (b) sulfur forms in char in different atmospheres.

the following section.

3.3.2. The effect of atmosphere on the sulfur forms in char

Group 5 and group 7 in Table 4 were carried out to explain this phenomenon. At the end of the experiment, the remaining $CaSO_4$ was weighed and the $CaSO_4$ decomposition rates of group 7 and group 5 were calculated as 10.33% and 6.67%, respectively. The similar results were reported in a previous work [39], where the decomposition rate of $CaSO_4$ was about 20%, much higher than that of group 5.

For a further investigation, the sulfur forms in char in the two processes were determined, results are shown in Fig. 8(b). Just like the $CaSO_4$ decomposition rates above, the sulfate content in char in Ar atmosphere was lower than that in steam atmosphere.

It has been reported that the carbon in coal as a solid reductant can promote the $CaSO_4$ decomposition [36]. There are two possible reaction mechanisms of carbon and $CaSO_4$, one is the solid–solid reaction mechanism, as Eqs. (9)-(11), and the other one is the gas–solid reaction mechanism, as Eqs. (7)-(8). For the solid–solid reaction mechanism, carbon in coal is directly involved in the $CaSO_4$ decomposition as a solid reductant, while in the gas–solid reaction mechanism, CO and H_2 produced through Eqs. (7)-(8) as gaseous reductants are the main cause of $CaSO_4$ decomposition. The solid–solid reaction mechanism is more suitable in Ar atmosphere, while the gas–solid reaction mechanism is more suitable in steam atmosphere.

However, as the results shown in 3.1.3, there was not high CO content in the gas product, while the H_2 content was high. But the reaction that H_2 took part in was weak at relatively low temperatures [40], so the solid–solid reaction mechanism in Ar atmosphere caused more $CaSO_4$ decomposed, resulting in a slightly higher carbon conversion rate and a lower sulfate content in char than those in steam atmosphere. It also explains the very low yield of H_2S in Ar atmosphere.

Although it is well understood that the solid–solid reactions are more difficult to occur than gas–solid reactions, the small particle size of both $CaSO_4$ and coal used in this experiment and the homogeneous mixing of them provided a condition for the solid–solid reactions to occur. In addition, it has been reported that the mineral fraction exacerbates the occurrence of the solid–solid reactions [41], and the addition of CaO also promoted the reaction of carbon and $CaSO_4$.

In summary, compared to in steam atmosphere, the sulfur conversion was lower in Ar atmosphere, but the sulfate in coal had a higher decomposition rate.

3.4. The transformation paths of sulfur in coal

According to all the results and analysis presented above, the transformation path of sulfur in coal can be described as shown in Fig. 9.

Almost all pyrite is decomposed thermally when heated, or reacts with steam to form H_2S and a small amount of sulfide residue in char. As the reaction proceeds, this sulfide together with the inherent sulfide in coal is gasified to generate H_2S.

Organic sulfur has three transformation paths: (i) be decomposed thermally to a variety of gaseous sulfur, such as H_2S/COS, COS will be gasified by steam to generate H_2S; (ii) be gasified into H_2S directly; (iii) be combined with inorganic sulfur to generate more stable organic sulfur residue in char, such as thiophene.

Sulfate reacts with the reductive gas generated in gasification, like H_2/CO/methane, to release sulfur. When there is a lack of steam in the atmosphere, sulfate will react with carbon in coal to generate other gaseous sulfur, like COS.

Most of the gaseous sulfur will be fixed by CaO in forms of sulfate and sulfide, part of which will be gasified back to H_2S. A small part of gaseous sulfur will be captured in char in the form of sulfide by the
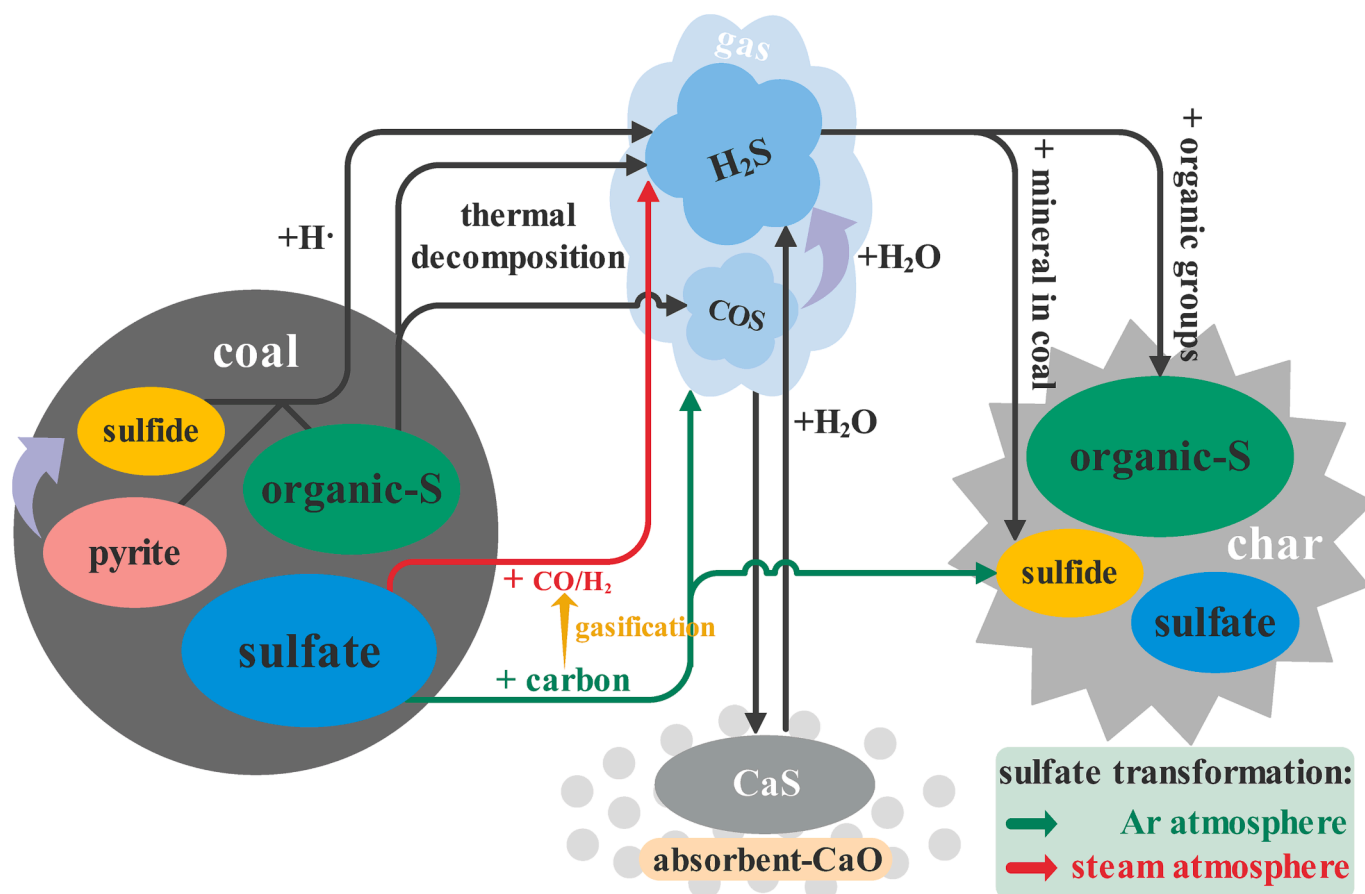

Fig. 9. The transformation paths of sulfur in coal.

inherent alkali metal oxides in coal.

The above processes maintain a dynamic equilibrium finally: part of the sulfur is converted to H_2S, some is fixed in CaO in the form of CaS, and the rest residual in char is mainly in the form of stable organic sulfur.

4. Conclusions

The effects of temperature, Ca/C and atmosphere on the sulfur transformation in coal steam gasification with Ca-based absorbent were investigated in a fixed-bed reactor. The sulfur distribution in gasification products was determined, and the release characteristics of gaseous sulfur was monitored. Finally, the changes of sulfur forms in char under different condition were compared. The results show that:

H_2S is the main gaseous sulfur, and the increase in temperature enhances the conversion of sulfur in coal to H_2S, but inhibits the capacity of sulfur fixation of CaO.

2. Sulfate and organic sulfur in coal transform into gaseous sulfur. Part of the inorganic gaseous sulfur is captured by the organic groups in coal into organic sulfur, like thiophene and sulfoxide, leading to the decrease of sulfate and the increase of organic sulfur in char.

3. CaO functions as a catalyst to enhance the sulfur conversion to gaseous sulfur and a gaseous sulfur absorbent at the same time, and there is a competitive relationship. Meanwhile, CaO shows a removal effect on gaseous organic sulfur. CaO can slow the release of gaseous sulfur by reacting with it to form CaS. The effect of CaO on sulfur forms in char is weak overall.

4. Compared with the inert atmosphere, the steam atmosphere supplies more hydrogen radicals, which promotes the sulfur conversion to H_2S, and hinders the sulfur-fixing effect of CaO at the same time, resulting in the decrease of the sulfur content in char and the increase of that in gas.

5. The solid–solid (carbon-sulfate) reaction mechanism is more suitable for the sulfate conversion in the inert atmosphere, while the gas–solid (CO/H_2-sulfate) reaction mechanism is more suitable in the steam atmosphere, to generate H_2S. The sulfur conversion in the inert atmosphere is lower, but the sulfate in coal has a higher decomposition rate.

CRediT authorship contribution statement

Chengdong Ying: Conceptualization, Data curation, Investigation, Writing – original draft. **Qinhui Wang:** Conceptualization, Writing – review & editing, Funding acquisition. **Yunjin Yang:** Supervision. **Zhimin Huang:** Investigation, Supervision. **Yao Zhu:** Writing – review & editing. **Jianmeng Cen:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] BP, BP Statistical Review of World Energy 2021, in, London, 2021.

[2] Zhu X, Zhang J, Yan J, Shen L. Characteristic Evaluation and Process Simulation of CuFe2O4 as Oxygen Carriers in Coal Chemical Looping Gasification. ACS Omega 2021;6:4783–92. https://doi.org/10.1021/acsomega.0c05691.

[3] Wang Q, Rong N, Fan H, Meng Y, Fang M, Cheng L, et al. Enhanced hydrogen-rich gas production from steam gasification of coal in a pressurized fluidized bed with CaO as a CO2 sorbent. Int J Hydrogen Energy 2014;39:5781–92. https://doi.org/10.1016/j.ijhydene.2014.01.153.

[4] Saikia J, Saikia P, Boruah R, Saikia BK. Ambient air quality and emission characteristics in and around a non-recovery type coke oven using high sulphur coal. Sci Total Environ 2015;530–531:304–13. https://doi.org/10.1016/j.scitotenv.2015.05.109.

[5] Wang Z, Li Q, Lin Z, Whiddon R, Qiu K, Kuang M, et al. Transformation of nitrogen and sulphur impurities during hydrothermal upgrading of low quality coals. Fuel 2016;164:254–61. https://doi.org/10.1016/j.fuel.2015.10.015.

[6] Chou C-L. Sulfur in coals: A review of geochemistry and origins. Int J Coal Geol 2012;100:1–13. https://doi.org/10.1016/j.coal.2012.05.009.

[7] Krishnamoorthy V, Pisupati SV. Fate of Sulfur during Entrained-Flow Gasification of Pittsburgh No. 8 Coal: Influence of Particle Size, Sulfur Forms, and Temperature. Energy Fuel 2016;30:3241–50. https://doi.org/10.1021/acs.energyfuels.5b02691.

[8] Hu H, Zhou Q, Zhu S, Meyer B, Krzack S, Chen G. Product distribution and sulfur behavior in coal pyrolysis. Fuel Process Technol 2004;85:849–61. https://doi.org/10.1016/j.fuproc.2003.11.030.

[9] Khan MR. Prediction of sulphur distribution in products during low temperature coal pyrolysis and gasification. Fuel 1989;68:1439–49. https://doi.org/10.1016/0016-2361(89)90043-4.

[10] Czaplicki A, Smołka W. Sulfur distribution within coal pyrolysis products. Fuel Process Technol 1998;55:1–11. https://doi.org/10.1016/S0378-3820(97)00052-0.

[11] Guan R, Li W, Li B. Effects of Ca-based additives on desulfurization during coal pyrolysis. Fuel 2003;82:1961–6. https://doi.org/10.1016/s0016-2361(03)00188-1.

[12] Zhang Y, Liang P, Jiao T, Wu J, Zhang H. Effect of foreign minerals on sulfur transformation in the step conversion of coal pyrolysis and combustion. J Anal Appl Pyrol 2017;127:240–5. https://doi.org/10.1016/j.jaap.2017.07.028.

[13] Shi T, Guo H, Liu Y, Wang L, Lei Y, Hao H, et al. DFT combined with XANES to investigate the sulfur fixation mechanisms of H2S on different CaO surfaces. Fuel 2022;327. https://doi.org/10.1016/j.fuel.2022.125204.

[14] Zhao LH, Chu XJ, Cheng SJ. Sulfur Transfers from Pyrolysis and Gasification of Coal. Adv Mat Res 2012;512–515:2526–30. https://doi.org/10.4028/www.scientific.net/AMR.512-515.2526.

[15] T. Zhang, Q. Guo, Q. Liang, G. Yu, The Generation Properties of Sulfur Compounds During Coal Gasification by Thermodynamic Equilibrium Simulation, Proceedings of the Chinese Society of Electrical Engineering, 31 (2011) 32-39.

[16] Xian S, Fan Y, Zhang H, Chai Z, Zhu Z. Effects of temperature and limestone on sulfur release behaviors during fluidized bed gasification. J Energy Inst 2020;93:2074–83. https://doi.org/10.1016/j.joei.2020.05.003.

[17] Xian S, Zhang H, Chai Z, Jiang D, Zhu Z. Release Behavior of Sulfur during Fluidized Bed Gasification. J Therm Sci 2021. https://doi.org/10.1007/s11630-021-1476-6.

[18] Xian S, Zhang H, Fan Y, Chai Z, Zhu Z. Effects of the ratio of O2/C and H2O/C on sulfur release behaviors during fluidized bed gasification. Fuel 2021;297. https://doi.org/10.1016/j.fuel.2021.120751.

[19] Han LJ, Li D, Li CS. Batch analysis of H2-rich gas production by coal gasification using CaO as sorbent. Energy Sources Part A 2016;38:243–50. https://doi.org/10.1080/15567036.2012.761296.

[20] Rong N, Wang Q, Fang M, Cheng L, Luo Z, Cen K. Steam Hydration Reactivation of CaO-Based Sorbent in Cyclic Carbonation/Calcination for CO2 Capture. Energy Fuel 2013;27:5332–40. https://doi.org/10.1021/ef4007214.

[21] Liu F, Li B, Li W, Bai Z, Yperman J. Py-MS Study of Sulfur Behavior during Pyrolysis of High-sulfur Coals under Different Atmospheres. Fuel Process Technol 2010;91:1486–90. https://doi.org/10.1016/j.fuproc.2010.05.025.

[22] Davies NH, Dennis JS, Hayhurst AN. Reaction between calcium oxide and hydrogen sulphide and also its modelling for a fluidised bed coal gasifier. J Energy Inst 2007;80:65–72. https://doi.org/10.1179/174602207x187186.

[23] Maa PS, Randall Lewis C, Hamrin CE. Sulphur transformation and removal for Western Kentucky coals. Fuel 1975;54:62–9. https://doi.org/10.1016/0016-2361(75)90030-7.

[24] H. Fan, X. Cao, L.I.J.T.P.G. Ning, STUDY ON EDUCTION BEHAVIOR OF DIFFERENT SHAPE SULFUR CONTENT IN COAL UNDER HIGH TEMPERATURE, (2004).

[25] Liu Y, Che D, Xu T. X-Ray Photoelectron Spectroscopy Determination of the Forms of Sulfur in Coal and Its Chars. J Xi'an Jiaotong Univ 2004;38:101–4.

[26] Urban NR, Ernst K, Bernasconi S. Addition of sulfur to organic matter during early diagenesis of lake sediments. Geochim Cosmochim Acta 1999;63:837–53. https://doi.org/10.1016/s0016-7037(98)00306-8.

[27] Calkins WH. Investigation of organic sulfur-containing structures in coal by flash pyrolysis experiments. Energy Fuel 1987;1:59–64. https://doi.org/10.1021/ef00001a011.

[28] Casanovas J, Ricart JM, Illas F, Jimenez-Mateos JM. The interpretation of X-ray photoelectron spectra of pyrolized S-containing carbonaceous materials. Fuel 1997;76:1347–52. https://doi.org/10.1016/s0016-2361(97)00153-1.

[29] Chen P. Application of XPS in study forms of organic sulfur in macerals of Yanzhou coal 1997;25:238–41.

[30] Shao DK, Hutchinson EJ, Heidbrink J, Pan WP, Chou CL. BEHAVIOR OF SULFUR DURING COAL PYROLYSIS. J Anal Appl Pyrol 1994;30:91–100. https://doi.org/10.1016/0165-2370(94)00807-8.

[31] Attar A. Chemistry, thermodynamics and kinetics of reactions of sulphur in coal-gas reactions: A review. Fuel 1978;57:201–12. https://doi.org/10.1016/0016-2361(78)90117-5.

[32] Du J, Yu J, Qiao L, Reina TR, Sun L. The reaction mechanism and sulfur evolution during vulcanized nature rubber pyrolysis in the atmosphere of H2O: A ReaxFF molecular dynamics study. Polym Degrad Stab 2022;203. https://doi.org/10.1016/j.polymdegradstab.2022.110064.

[33] Jia X, Wang Q, Cen K, Cheng L. Sulfur transformation during the pyrolysis of coal mixed with coal ash in a fixed bed reactor. Fuel 2016;177:260–7. https://doi.org/10.1016/j.fuel.2016.03.013.

[34] Yan Z, Wang Z, Liu H, Tu Y, Yang W, Zeng H, et al. Decomposition and solid reactions of calcium sulfate doped with SiO2, Fe2O3 and Al2O3. J Anal Appl Pyrol 2015;113:491–8. https://doi.org/10.1016/j.jaap.2015.03.019.

[35] Zhang J, Zhu M, Jones I, Onyeka Okoye C, Zhang Z, Gao J, et al. Transformation and fate of sulphur during steam gasification of a spent tyre pyrolysis char. Fuel 2022.;321. https://doi.org/10.1016/j.fuel.2022.124091.

[36] Jia X, Wang Q, Han L, Cheng L, Fang M, Luo Z, et al. Sulfur transformation during the pyrolysis of coal with the addition of CaSO4 in a fixed-bed reactor. J Anal Appl Pyrol 2017;124:319–26. https://doi.org/10.1016/j.jaap.2017.01.016.

[37] Husmann M, Kienberger T, Zuber C, Jong Wd, Hochenauer C. Application of CaO Sorbent for the Implementation and Characterization of an in Situ Desulfurization Steam-Blown Bubbling Fluidized-Bed Test Rig for Biomass Gasification. Ind Eng Chem Res 2015;54:5759–68. https://doi.org/10.1021/acs.iecr.5b00593.

[38] Xu L, Yang J, Li Y, Liu Z. Desulfurization behavior of yanzhou coal through pyrolysis (I) sulfur transfer during pyrolysis. J Chem Ind Eng 2003;54:1430–5.

[39] Jia X, Wang Q, Cen K, Chen L. An experimental study of CaSO 4 decomposition during coal pyrolysis. Fuel 2016;163:157–65. https://doi.org/10.1016/j.fuel.2015.09.054.

[40] Tian H, Guo Q, Yue X, Liu Y. Investigation into sulfur release in reductive decomposition of calcium sulfate oxygen carrier by hydrogen and carbon monoxide. Fuel Process Technol 2010;91:1640–9. https://doi.org/10.1016/j.fuproc.2010.06.013.

[41] Jia X, Wang Q, Cheng L, Han L, Ye C, Fang M, et al. Sulfur Behavior of Coal and Ash during Coal Pyrolysis Combined with Combustion. Energy Fuel 2016;30:9589–95. https://doi.org/10.1021/acs.energyfuels.6b01619.