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Study on molding semi-coke used for flue-gas desulphurization

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ABSTRACT

This paper investigated the preparation process of molding semi-coke and its application in flue-gas desulphurization. Factors affecting the desulphurization capability of molding semi-coke were studied, including gas temperature, space velocity, O_2 content and H_2O content in flue-gas. Results show that the molding semi-coke would have a better activity if calcined under nitrogen atmosphere with steam and 2% oxygen at 700 °C for 2 h. The optimal operating conditions are as follows: temperature 60–80 °C, space velocity 600 h^{-1}, oxygen content 5% and H_2O content 8%.

1. Introduction

The total discharge of SO_2 in China reached an unprecedented number – 25.49 million tons in 2005 [1]. China issued a work plan on energy conservation and pollutant discharge reduction that pledged the country would reduce its discharge of sulphur dioxide from 25.49 million tons in 2005 to 22.95 million tons in 2010. Although policies had been made to reduce the discharge of SO_2, the number was also as high as 23.20 million tons in 2009. Such large amount of SO_2 has caused many serious problems, such as acid rain, which has done a lot of damages toward the environment. Therefore, further treatment on waste gases seems urgently important. Flue-gas desulphurization (FGD) is currently most widely used technology around the world in reducing SO_2 content of emission hence the occurrence of acid rain, which contributes a lot to the preservation of natural environment [2–4].

Semi-coke is a product of coal pyrolysis at a relatively low temperature (600–700 °C). As a material rich in micro-pores, it performs excellently in adsorption. Also, the large quantity of oxygen-containing functional groups on its surface makes it easy to be modified and used as a kind of adsorbent or catalyst. Based on these features, further research revealed that either active carbon or semi-coke has good desulphurization performance and can be regenerated by water washing method [5–7]. The most widely accepted desulphurization mechanism of carbonaceous catalyst in the presence of O_2 and H_2O can be described as follows [8]:

(1) SO_2, O_2 and H_2O are adsorbed onto the surface of carbonaceous catalyst;
(2) SO_2^* is oxidized to SO_3^* by O_2^*;
(3) SO_3^* turns into $H_2SO_4^*$ in the presence of H_2O;
(4) $H_2SO_4^*$ leaves the surface and unfetters the active sites.

(The mark * denotes the adsorbed state of molecules.)

Most previous researches on desulphurization used irregular semi-coke granule or powder as catalyst whose catalyst bed can induce channeling or short-circuit and change retention time of flue-gas hence reduce the reaction efficiency [9]. Since the pressure drop of catalyst bed is small for the sake of better operation cost and practical conditions in industrial application, too small a particle size of semi-coke is inappropriate. This study attempted to produce molding catalyst on the basis of waste semi-coke, eliminate the disadvantages caused by irregular catalysts, and find out the optimum preparation method as well as proper operating conditions.

2. Materials and methods

2.1. Preparation of molding semi-coke catalyst

Zhalainuoer lignite semi-coke was used as raw material. Table 1 shows the ultimate and proximate analysis of the semi-coke. BET surface area and pore volume were obtained by means of N_2 adsorption isotherms measured at 77 K using an ASAP2010 volumetric adsorption analyzer (Micromeritics Norcross). BET surface area and pore volume are 49.187 m^2/g and 0.0351 cm^3/g, respectively.

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Table 1
The ultimate and proximate analysis of the semi-coke.

Ultimate analysis/%				Proximate analysis/%		
C	H	O	N	Moisture	Ash	Volatile
68.33	4.82	26.28	0.58	7.8	7.19	17.28

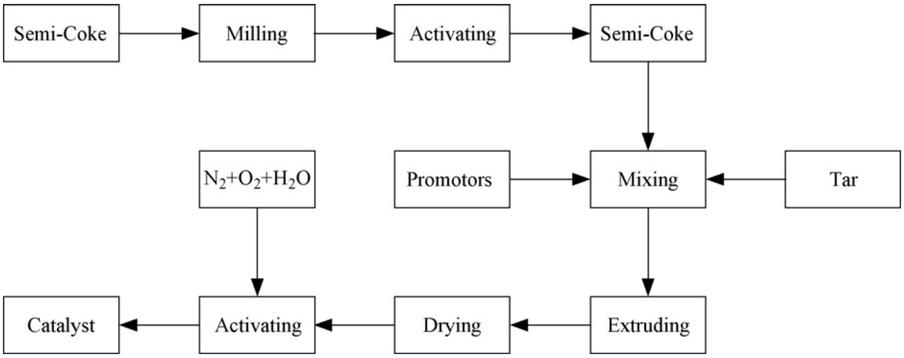

Fig. 1. The preparation process of semi-coke.

Fig. 1 shows the preparation process of molding semi-coke catalyst. Semi-coke was first milled and sieved to obtain granules of about 100 meshes. Secondly, to modify the pore structure and surface chemical property, it was pre-activated by HNO_3. Thirdly, the semi-coke was washed to neutrality with distilled water and dried in an air oven at 110 °C for 4 h. Fourthly, activated semi-coke mixed uniformly with promoters and tars at a certain mass ratio. Fifthly, the mixture was extruded by molding device and dried in an air oven at 110 °C for 4 h again. Finally, the product went through the calcination under N_2 atmosphere with the existence of water and oxygen at 700 °C.

2.2. Activity evaluation of molding semi-coke catalyst

The desulphurization activity was evaluated in fixed-bed equipment (shown in Fig. 2), which consists of three main parts: feeding system, reacting system (φ14 mm × 320 mm) and analyzing system. The composition of gas mixture was similar to flue-gas, containing SO_2, O_2, H_2O and N_2 (balance), flowed through the fixed-bed. H_2O was introduced into the gas stream by administering N_2 and O_2 through a water bath and its content was regulated through the temperature of the bath and confirmed by the amount consumed. The gas velocity was controlled by mass flowmeter. The concentration of SO_2 at the inlet and outlet was measured by iodimetry. The size of molding semi-coke catalyst used in the experiment was φ3 mm × 5 mm and its volume was 5 ml. The operating temperature ranged from 60 to 120 °C and space velocity varied from 450 to 1200 h^{-1}.

The parameters to evaluate the desulphurization activity were SO_2 conversion, breakthrough time and sulphur capacity. SO_2 conversion (η) was calculated through Eq. (1):

$$\eta = \frac{C_i - C_o}{C_i} \times 100\% \qquad (1)$$

C_i – inlet SO_2 concentration; C_o – outlet SO_2 concentration.

Breakthrough time of this experiment was the reaction time when SO_2 conversion decreased from 100 to 80%. Sulphur capacity (Sc%) was calculated through Eq. (2):

$$\text{Sc\%} = \frac{M_{\text{Absorbed SO}_2}}{M_{\text{Catalyst}}} \times 100 \qquad (2)$$

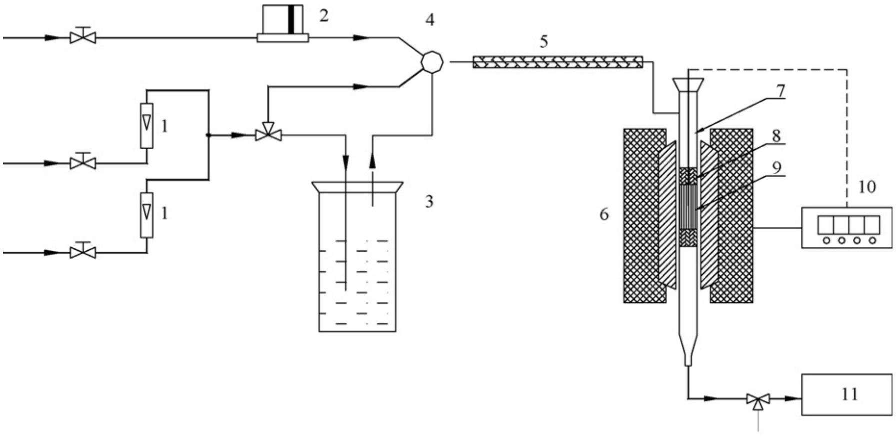

Fig. 2. Schematic diagram of the fixed-bed equipment. (1) Rotor flowmeter, (2) mass flowmeter, (3) humidity reactor, (4) blender, (5) pre-heater, (6) furnace, (7) reactor, (8) silica wool, (9) catalyst, (10) program temperature controller, and (11) sampling.

Table 2
Surface chemical and physical properties of semi-coke samples.

Sample	Basicity/mmol/g	Acidity/mmol/g	Total/mmol/g	Net basicity/mmol/g	Surface area/m^2/g
ZR	0.1065	0.0424	0.1489	0.0646	49.187
ZH	0.0266	0.1993	0.2259	Null	157.36
ZH700	0.7258	0.2315	0.9573	0.4943	314.22
ZHDO700	1.0663	0.2386	1.3049	0.8277	449.33

3. Results and discussion

3.1. Effect of calcination conditions

Fig. 3 shows the variation of breakthrough time of catalysts activated through different calcination methods. ZH700 denotes the catalysts activated at 700 °C with pure N_2 as protection while ZHDO700 denotes those activated at 700 °C with N_2 as protection including moisture and 2% oxygen. The operating conditions were: temperature 80 °C, space velocity 1200 h^{-1}, SO_2 concentration 2200 ppm, O_2 content 5% and water content 8%. The results showed that ZHDO700, whose breakthrough time prolonged 36.4%, had a better desulphurization performance than ZH700. The total content of surface sites of acid nature and basic nature was also estimated through a neutralization technique in order to inspect the change of surface functional groups. ZR stands for raw semi-coke and ZH stands for those activated by HNO_3. The results shown in Table 2 indicated that the net basicity of samples greatly increased after calcination at 700 °C, thus the surface of semi-coke appeared alkaline. Calcination is able to rearrange the functional groups on the surface of semi-coke, and make acid functional groups decompose to alkaline functional groups which are more propitious for SO_2 removal. Table 2 also shows that the surface area increased after calcination treatment, which might primarily result from the reaction between carbon and water vapor, generating CO or CO_2, during which additional pores were formed. Besides, water vapor helps to remove easily soluble impurities and ash hence renew many previously occupied adsorption sites.

3.2. Effect of reaction temperature

Figs. 4 and 5, respectively show how sulphur capacity and breakthrough time vary with operating temperatures. Other operating conditions were: space velocity 1200 h^{-1}, SO_2 concentration 2200 ppm, O_2 content 5% and water content 8%. According to the results, the breakthrough time and sulphur capacity of 60 and 80 °C had no distinct difference. Further increasing temperature to 100 or 120 °C, however, led to a sharp decline on both sulphur capacity and breakthrough time. Therefore, the operating temperature would better be restricted in the range of 60–80 °C. According to the mechanism of desulphurization on carbonaceous catalyst [8], a reasonable explanation might be concluded that lower temperature is favorable for the physical adsorption of flue-gas molecules onto the surface of semi-coke, which is the first

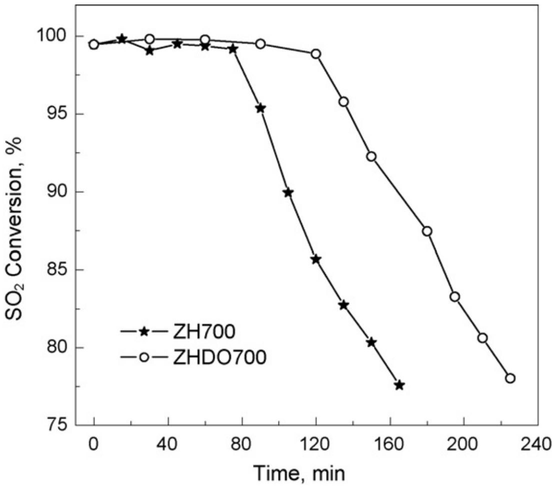

Fig. 3. Breakthrough curve of catalyst activated by different calcination methods.

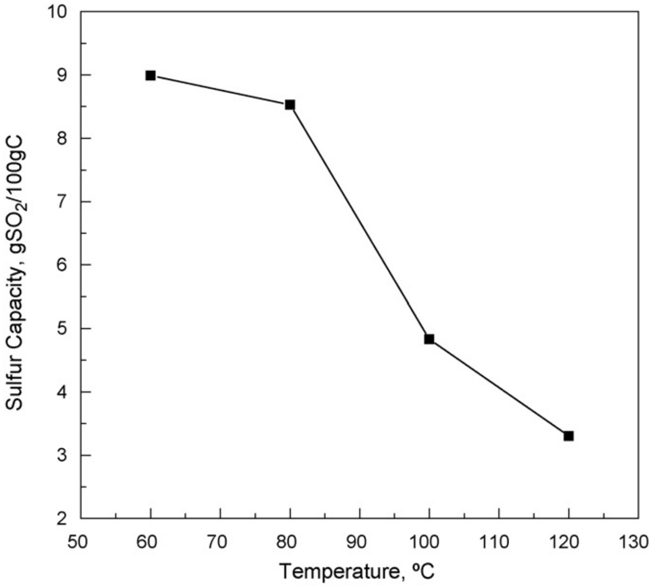

Fig. 4. Effect of reaction temperature on sulphur capacity.

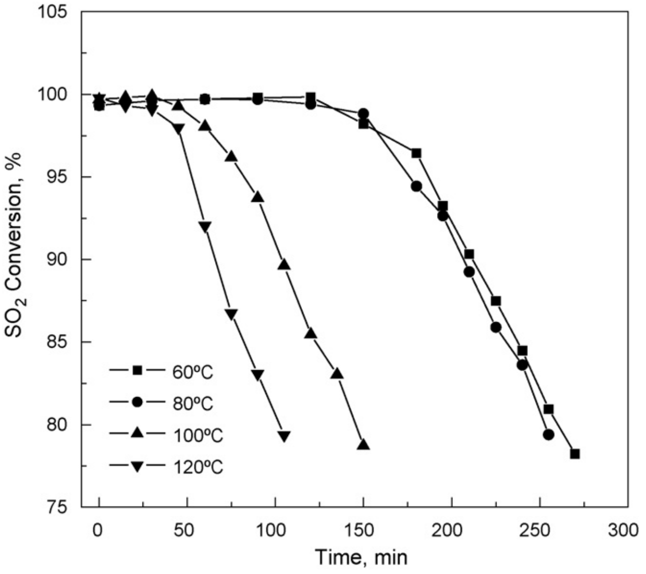

Fig. 5. Breakthrough curve of different temperatures.

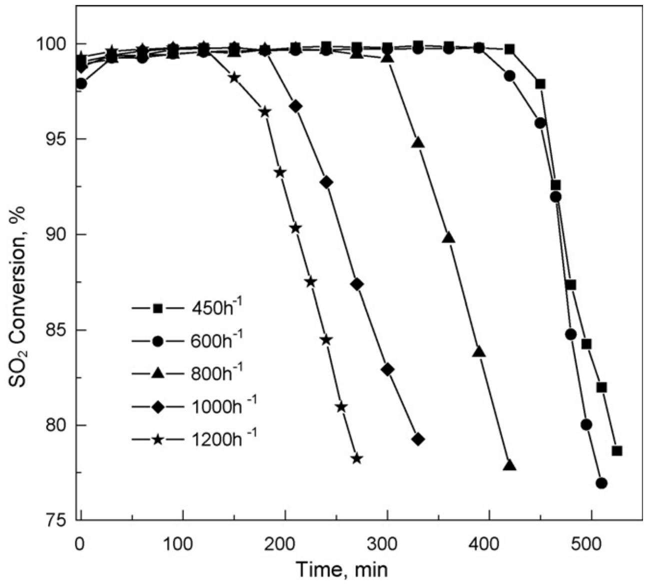

Fig. 6. Breakthrough curve of different space velocities.

step during the SO_2 removal process, while higher temperature enhances the desorption of gas molecules hence decreases the number of adsorbed gas molecules and then limits the catalytic oxidation of SO_2. The reported results of literatures [8,10–12] also reveal that the desulphurization activity of all kinds of carbonaceous catalysts almost goes through a similar process – first increases then decreases – with the increasing of operation temperature; thus, an optimum temperature is always obtainable. But this paper got an optimum temperature falling into the range of 60–80 °C which is lower than Lisovskii's [11] 110–120 °C or Liu's 90 °C [13], probably due to different raw materials or modification methods.

3.3. *Effect of space velocity*

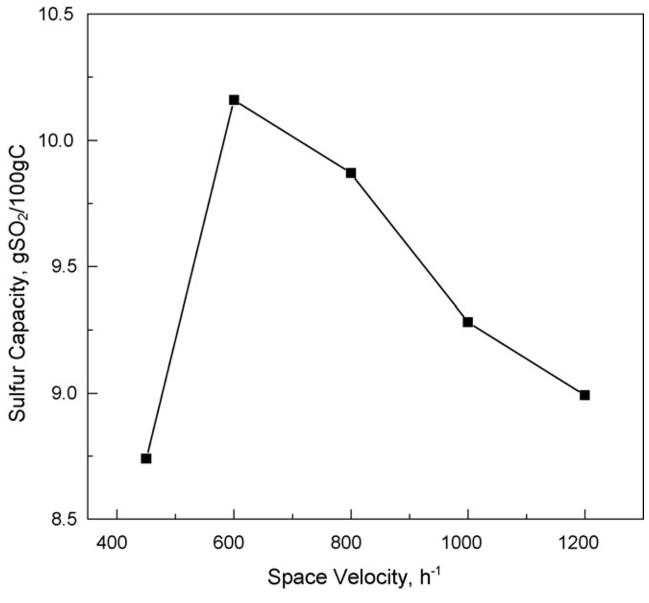

Fig. 7. Effect of space velocity on sulphur capacity.

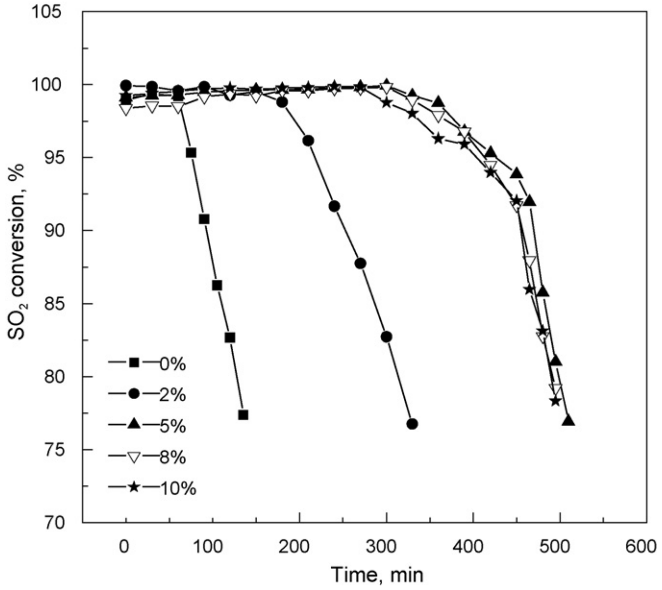

Fig. 8. Breakthrough curve on different O_2 contents.

The space velocity of simulated flue-gas was studied. The sulphur capacity curve and breakthrough curve were shown in Figs. 6 and 7, respectively. Other operating conditions were: temperature 60 °C, SO_2 concentration 2200 ppm, O_2 content 5% and water content 8%. Space velocity was selected between 450 and 1200 h^{-1}. Fig. 6 displays that lower space velocity, such as 450 and 600 h^{-1}, resulted in longer breakthrough time. As space velocity went up from 600 to 1200 h^{-1}, breakthrough time dropped down continuously, which could be attributed to the fact that the retention time diminishing with the increase of space velocity. Fig. 7 indicates that sulphur capacity reached the highest point – 10.16 g SO_2/100 g C when the space velocity was 600 h^{-1}. The desulphurization reaction can be divided into four steps [8]: adsorption of gas molecules, diffusion, oxidation reaction and desorption of productions. At lower space velocity (below 600 h^{-1}), the diffusion of flue-gas is probably the control step of desulphurization. But if space velocity is too low, a stagnant layer is to be formed on the external surface of semi-coke, which can block some pores and prevent more gas molecules from adsorbing onto the active sites of the surface of semi-coke catalyst, thus the oxidation reaction cannot occur sufficiently. That is why sulphur capacity was lower at 450 h^{-1}. On the other hand, space velocity above 600 h^{-1} also decreases sulphur capacity for too short retention time does not allow sufficient adsorption of flue-gas onto the surface of semi-coke and effective reaction.

3.4. *Effect of O_2 content*

Figs. 8 and 9 show how desulphurization performance is influenced by the content of O_2. Other operating conditions were: temperature 60 °C, SO_2 concentration 2200 ppm, space velocity 600 h^{-1} and water content 8%. When the content of O_2 raised from zero to 5%, the breakthrough time and sulphur capacity both presented a surge; however, they descended slightly when the content of O_2 continued to increase from 5 to 10%. This phenomenon could be accounted for through the dual roles of O_2 in this process. The desulphurization would totally rely on the physical adsorption of SO_2 without the existence of O_2. Once O_2 is introduced into flue-gas, the adsorbed SO_2 would be oxidized catalytically by adsorbed O_2 over the surface of semi-coke, in which case the desulphurization performance would get enormous enhancement. However, O_2 is not able to change the adsorbed SO_2 into SO_3 if not got adsorbed – that is, this transformation could occur nowhere but

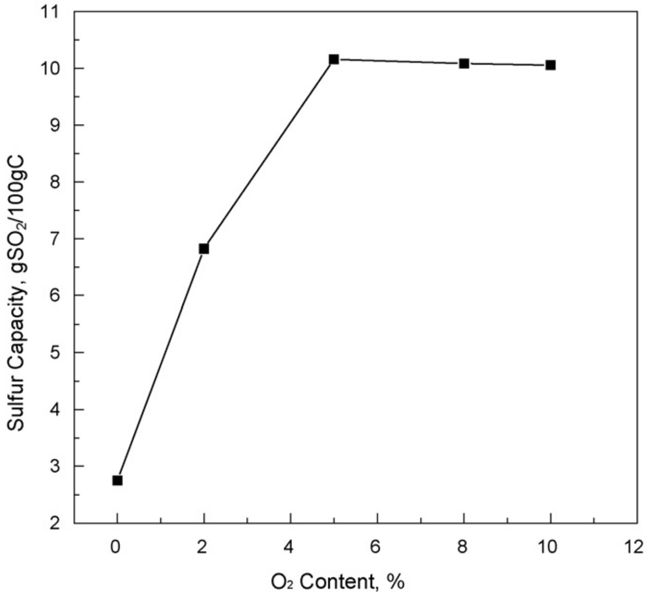

Fig. 9. Effect of O_2 content on sulphur capacity.

the surface of semi-coke. Therefore, an excessive amount of O_2 has little to do with the improvement of desulphurization performance. On the contrary, too many O_2 molecules will occupy limited active sites on the surface of semi-coke, which prevents the adsorption of SO_2 and H_2O molecules, resulting in the decrease of sulphur capacity. In this case, O_2 plays a competitive role with SO_2 and H_2O. Consequently, the optimum O_2 content was 5% in this experiment.

3.5. *Effect of H_2O content*

The effect of H_2O content on desulphurization activity was studied and the results were plotted in Figs. 10 and 11, respectively. As is shown, the desulphurization activity was quite poor when no water existed in flue-gas. As H_2O content was augmented, the desulphurization activity of semi-coke rose up obviously and achieved the acme – breakthrough time was 510 min and sulphur capacity was 10.16 g SO_2/100 g C – when H_2O content was up to 8%. But further increase of water content, such as elevating to 12%, would cause a lower desulphurization activity. According to the mechanism of SO_2 removal on carbon materials [11,14,15], H_2O in feed stream plays an indispensable role in desulphurization by taking part in the formation of H_2SO_4. Since water forms a thin membrane on the surface of semi-coke in which SO_2 is easily dissolved and immediately interacts with H_2O molecules ($SO_2 + H_2O \rightarrow HSO_3^- + H^+$), what diffuses into the pores of semi-coke across the water membrane and reacts with the adsorbed O_2 in the pores is HSO_3^- instead of SO_2 ($HSO_3^- + O_2^* \rightarrow HSO_4^-$). In short, H_2O plays a cooperative role in the adsorption of SO_2 and O_2, which boosts the desulphurization activity apparently. If the water content exceeds 8%, however, the water membrane would become too thick that a large quantity of H_2O molecules would prevent the adsorption of SO_2 and O_2. Besides, H_2O molecules of exorbitant number are to take up more limited adsorption sites, which inhibit the adsorption of SO_2 and O_2 molecules. In this case, H_2O plays a competitive role in the adsorption of SO_2 and O_2, which leads to lower desulphurization activity.

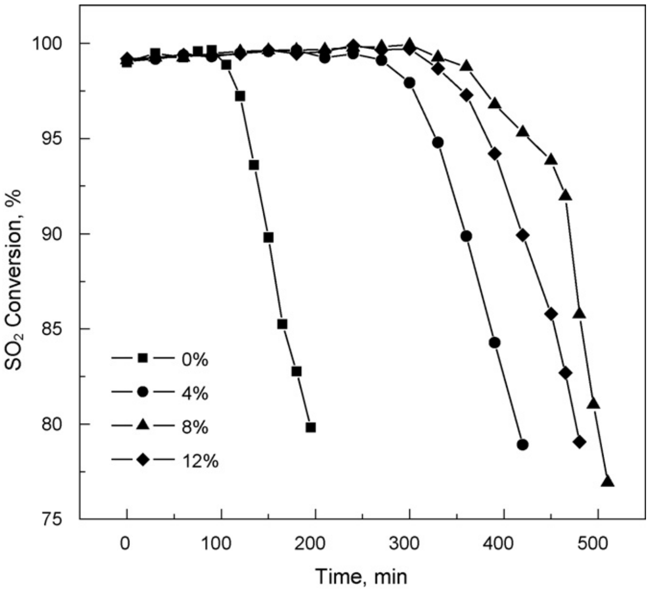

Fig. 10. Breakthrough curve of different H_2O contents.

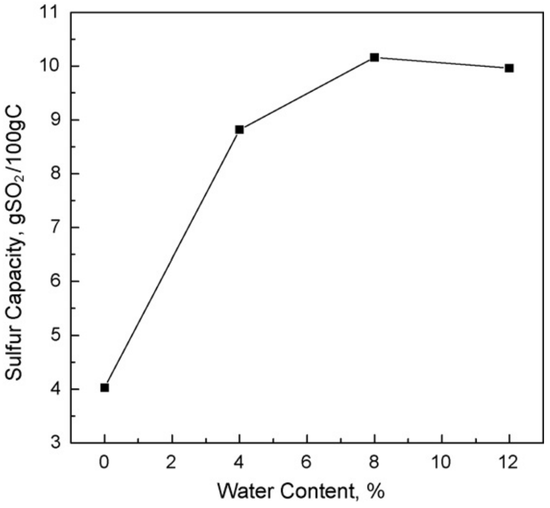

Fig. 11. Effect of H_2O content on sulphur capacity.

4. Conclusions

(1) Activated semi-coke was extruded then calcined under N_2 protection with the existence of water and oxygen at 700 °C (ZHDO700). It showed higher desulphurization activity than that treated without water and oxygen (ZH700).
(2) The optimal desulphurization operating conditions were: temperature 60–80 °C, space velocity 600 h^{-1}, oxygen content 5% and H_2O content 8%. The sulphur capacity of this operating condition is 10.16 g SO_2/100 g C.

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