Effects of Modified Pyrolysis Tar on Gas Desulphurization Performance

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ABSTRACT: *The paper introduced effects of modified pyrolysis tar on flue gas desulfurization. This experiment selected the pyrolysis tar as the raw material, researched the effects on desulfurization performance under different modification solution, concentration, solid liquid ratio of pyrolysis tar and modified solution, calcination temperature and calcination time by 16 group orthogonal experiments. The results showed that: (1) The significance of five factors impact on the modified pyrolysis tar desulfurization performance in order was: types of the modified solution > modification solution concentration > calcination time > solid-liquid ratio > calcination temperature. (2) The modified effects of nitric acid and phosphoric acid were better. (3) The higher nitrate concentration, the better modified effect of pyrolysis tar. (4) The rate of desulfurization increased mainly associated with acidic groups on the surface of the pyrolysis tar, desulfurization performance get better along with the acidic groups increasing.*

KEY WORDS: *Flue gas desulfurization, Sulfur dioxide, Modified pyrolysis tar, Boehm titration.*

INTRODUCTION

Sulfur dioxide is an essential product in the process of coal burning; its emissions not only caused serious environmental pollution, but had crisis on people's health. Therefore, effective management and control of sulfur dioxide becomes crucial [1]. Most of the porous materials have the disadvantage of high cost, bad chemical stability and low efficiency, so it is difficult to achieve effective control for sulfur dioxide [2-4]. The pyrolytic tar is the carbon material, which can adsorb SO_2 with micro porous structure and functional groups [5,6], so the modified pyrolysis tar was selected as a new trend for removal of sulfur dioxide. Firstly, using method of oxidation to modify the deactivated pyrolysis tar, then through the backflow, drying and calcination to prepare a kind of high desulfurization efficiency adsorbent. The desulfurization performance was studied with the different modification solution, concentration, and solid-liquid ratio to pyrolysis tar and modification solution, calcination temperature, and calcination time and analyzes the mechanism [7-8].

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Table 1: Orthogonal experiment of modified pyrolysis tar.

sample	modified solution type	concentration	S/L	temperature(°C)	time(h)
1	HNO_3	10%	1:1	200	1
2	HNO_3	15%	1:1.5	400	2
3	HNO_3	20%	1:2	600	3
4	HNO_3	25%	1:2.5	800	4
5	H_2O_2	10%	1:1.5	600	4
6	H_2O_2	15%	1:1	800	3
7	H_2O_2	20%	1:2.5	200	2
8	H_2O_2	25%	1:2	400	1
9	H_3PO_4	10%	1:2	800	2
10	H_3PO_4	15%	1:2.5	600	1
11	H_3PO_4	20%	1:1	400	4
12	H_3PO_4	25%	1:1.5	200	3
13	H_2SO_4	10%	1:2.5	400	3
14	H_2SO_4	15%	1:2	200	4
15	H_2SO_4	20%	1:1.5	800	1
16	H_2SO_4	25%	1:1	600	2

EXPERIMENTAL SECTION

Modified pyrolysis tar preparation

The materials used in this study were rice husk coke, coal tar, trash, coke and red mud at 600°C. Used oxidation modification method to deal with pyrolysis tar, mixed pyrolysis tar and modified solution according to a certain proportion, heat reflux 2h then take out the sample washed to neutral, dried 12h at 120°C and calcinated in the tube furnace under inert gas.

The experimental design

Orthogonal experiment of 5 factors 4 levels was designed in this work, selecting different modification solution, solid-liquid ratio to pyrolysis tar and modification solution, calcination temperature, calcination time and modified solution concentration as 5 factors. The modified solution selected dilute nitric acid, phosphoric acid, hydrogen peroxide and sulfuric acid, solid-liquid ratio to pyrolysis tar and modification solution selected 1:1, 1.5:1, 2:1, 2.5:1, calcination temperature selected 200°C, 400°C, 600°C, 800°C and calcination time selected 1h, 2h, 3h, 4h, the modified solution concentration selected 10%, 25%, 20%, 25%. Orthogonal experiment table was showed in Table 1.

The testing device of modified pyrolysis tar performance

Experiments were conducted in the fixed adsorption column at constant temperature and adsorption column was in a quartz tube 20 mm in diameter 50 cm in height. The testing device (Testo350XL) of modified pyrolysis tar performance was shown in Fig. 1.

RESULT AND DISCUSSION

The influence of different modified pyrolysis tar on the desulfurization efficiency

Analysis results by orthogonal experiment were shown in Table 2.

Table 2: Visual analysis of orthogonal experiment.

sample	modified solution type	concentration	S/L	temperature(°C)	time(h)	desulfurization efficiency
1	1	10%	1:1	200	1	300
2	1	15%	1:1.5	400	2	305
3	1	20%	1:2	600	3	660
4	1	25%	1:2.5	800	4	670
5	H_2O_2	10%	1:1.5	600	4	270
6	H_2O_2	15%	1:1	800	3	215
7	H_2O_2	20%	1:2.5	200	2	230
8	H_2O_2	25%	1:2	400	1	275
9	H_3PO_4	10%	1:2	800	2	200
10	H_3PO_4	15%	1:2.5	600	1	225
11	H_3PO_4	20%	1:1	400	4	165
12	H_3PO_4	25%	1:1.5	200	3	760
13	H_2SO_4	10%	1:2.5	400	3	223
14	H_2SO_4	15%	1:2	200	4	290
15	H_2SO_4	20%	1:1.5	800	1	200
16	H_2SO_4	25%	1:1	600	2	190
K_1	483.750	248.250	217.500	395.000	250.000	
K_2	247.500	258.750	383.750	242.000	231.250	
K_3	337.500	313.750	356.250	336.250	464.500	
K_4	225.750	473.750	337.000	321.250	348.750	
Range	258.000	225.500	166.250	153.000	233.250	

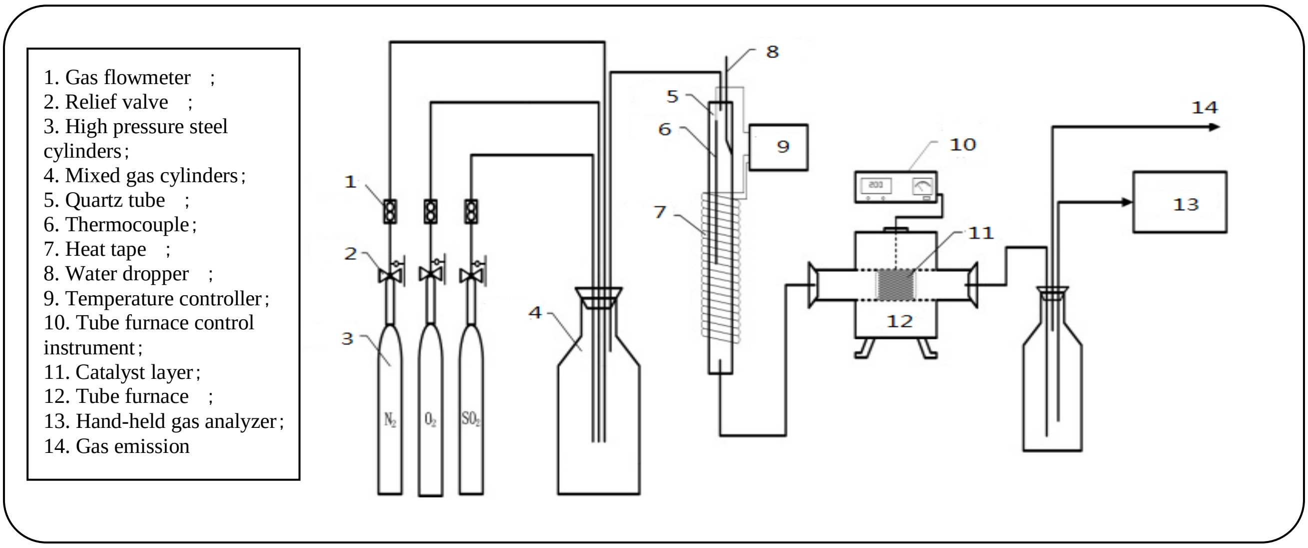

Figure.1 The testing device of modified pyrolysis tar performance

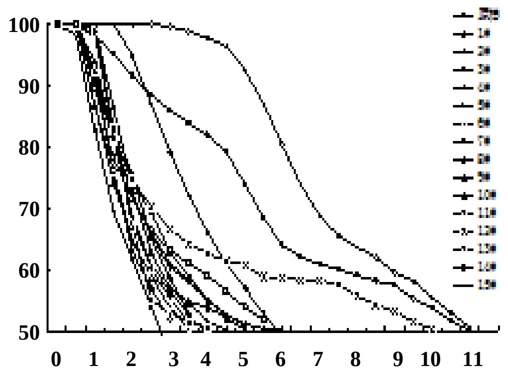

Fig. 2: the influence of different modified pyrolysis tar on the desulfurization efficiency.

Table 2 shows that five factors had influenced on the desulfurization efficiency, and the modified solution types were the most critical influences on desulfurization efficiency. Because the nitric acid has strong oxidizing property, which makes acid oxygenous, groups on the surface of pyrolysis tar increase significantly, and then achieve the goal of modification. Although sulfuric acid is the strong acid, but modified effect is bad for its oxidation. Secondly, solution concentration also plays a very important role. Nitric acid, for example, the stronger the acid concentration, the more its oxidation, and it has a positive impact on oxygen containing functional group and pore structure. It is showed that calcination temperature and calcination time are not the main reason from Table 2, which caused the pyrolysis tar desulfurization performance increased, but they are the important aspects. With the volatilization of impurities in the pyrolysis tar, the specific surface area increased with the number of the internal pore increasing under the high temperature, so the desulfurization efficiency can increased accordingly. The roles that the solid liquid ratio and the acid concentration play are the same. By improving the surface oxygen groups of pyrolysis tar, such as phenol hydroxyl, carboxyl and ketone to influence the modified pyrolysis tar desulfurization efficiency[9-13]. From the range analysis, modified pyrolysis tar desulfurization efficiency is influenced by five factors which in the order is acid type > calcination time > acid concentration > solid-liquid ratio > calcination temperature.

Quantitative analysis of desulfurization mechanism of the pyrolysis tar

（1）the influence of nitric acid modified for desulfurization efficiency

It is showed from Fig. 3 that desulphurization efficiency of the four modified samples presented an increasing trend. That is, with the increase of nitric acid concentration, the desulfurization efficiency is also enhanced. Combined with all kinds of modified functional group content can be seen that with the increasing of nitric acid concentration, acid group on the surface of the pyrolysis tar increased significantly. Because the nitric acid has strong oxidization, it can improve the oxygen containing functional groups of pyrolysis tar, which caused the surface acidity and acid adsorption increase, so modified pyrolysis tar desulfurization efficiency was improved [14-18].

Besides, in addition to the acidic groups gradually increased, so did carboxyl. In comparison, phenolic hydroxyl had no obvious increasing trend, which was also belong to acidic groups. Thus it can improve the desulphurization efficiency with the amount of carboxylic acid groups increasing. [19-23]

（2）the influence of hydrogen peroxide modified for desulfurization efficiency

It can conclude from Fig. 4 that the desulfurization efficiency of modified pyrolysis tar prepared at different conditions may not vary much, and there is no obvious regularity under the condition of hydrogen peroxide modification. Compared with the result of nitric acid modified, the modification of hydrogen peroxide is not obvious. Contrast the desulfurization efficiency curve and number of functional groups can also see that the closely relative to the number of carboxyl and desulfurization efficiency. Thus it can be considered carboxyl of the acidic groups on the pyrolysis tar surface plays a main role. Overall, the modified effects of hydrogen peroxide was undesirability as good as nitrate. It is because hydrogen peroxide modification is relatively mild that caused slight damage to the pore structure on the surface of the pyrolysis tar. It impacts the effect of sulfur dioxide removal.

(3) the influence of phosphate modified for desulfurization efficiency

It was showed from Fig. 5 that sample 12 had the best desulfurization efficiency, and higher than other modified samples .The phosphoric acid concentration of sample 12

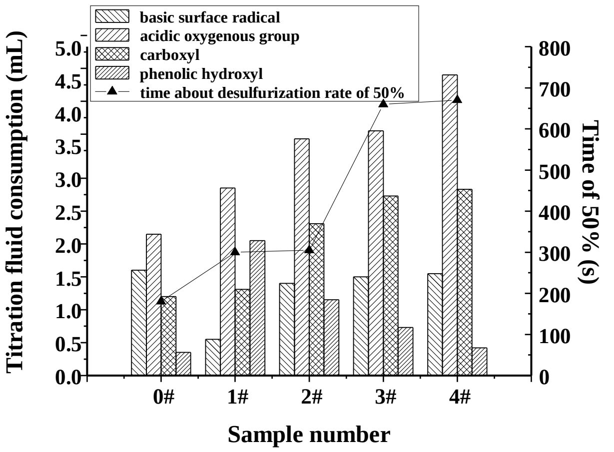

Fig. 3: The comparison of oxygen containing functional groups modified with nitric acid.

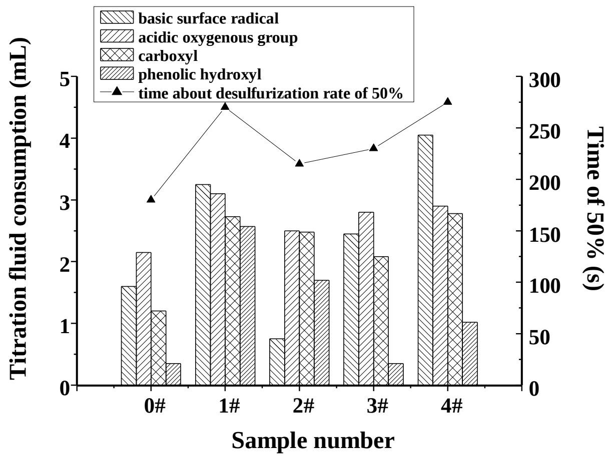

Fig. 4: The comparison of oxygen containing functional groups modified with hydrogen peroxide.

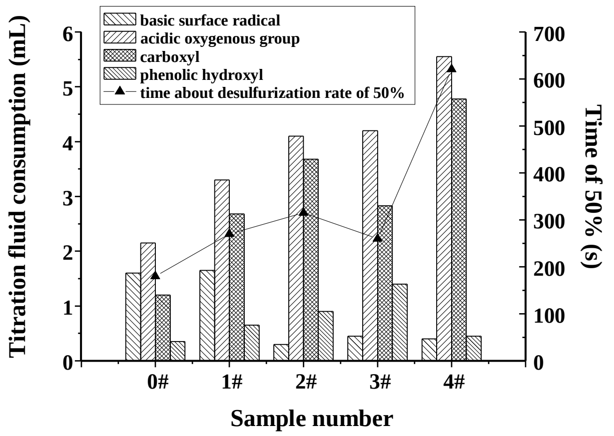

Fig. 5: The comparison of oxygen containing functional groups modified with phosphoric acid.

was the highest, it showed that acid concentration is an important factor in the process of phosphoric acid modification. Phosphoric acid is not very strong acid, but when its concentration increased, the desulfurization efficiency also had greatly improved. Compared with the sample 12, desulfurization efficiency of the other three samples had no obvious improvement. It showed that phosphoric acid modification needs to be done under the condition of appropriate concentration.

Compared with the number of functional groups can be obtained that acidic groups of sample12 was the highest of all the modified pyrolysis tar and it had the best desulfurization efficiency accordingly. Acidic carboxyl also had a main influence, while phenolic hydroxyl and alkaline groups had no obvious regularity. As a result, phosphoric acid modification improved the desulfurization efficiency by increasing surface acidic groups of the pyrolysis tar.

(4) the influence of sulfuric acid modified for desulfurization rate

It was shown from Fig. 6 that desulfurization efficiency of sample 14 was best, but the sample 13 maintained the desulfurization rate of 100% was the longest. In addition to sample13 sample 14, desulfurization efficiency of the other two samples had no obviously increased. Although sulfuric acid is strong acid, but only play a role of acid in low concentrations, so the degree of oxidation was not better than oxidation of nitric acid.

The sample 13 and 14 acid group and carboxylic content were the highest, and phenolic hydroxyl groups improved after modification. Compared with the Fig. 3, figure.4 and figure.5 can be found that acid sulfate groups had been increased after modification, but compared with nitric acid and phosphoric acid modification; acidic group increased was not significant. It is showed that strength of the oxidation was the important factors, which influenced the modification results of good or bad.

Qualitative analysis of desulfurization mechanism of the modified pyrolysis tar

Infrared spectroscopy can be qualitative characterization of oxygen-containing functional groups on the surface of the pyrolysis tar. According to the influence of different modified pyrolysis tar for desulphurization efficiency and Boehm titration analysis

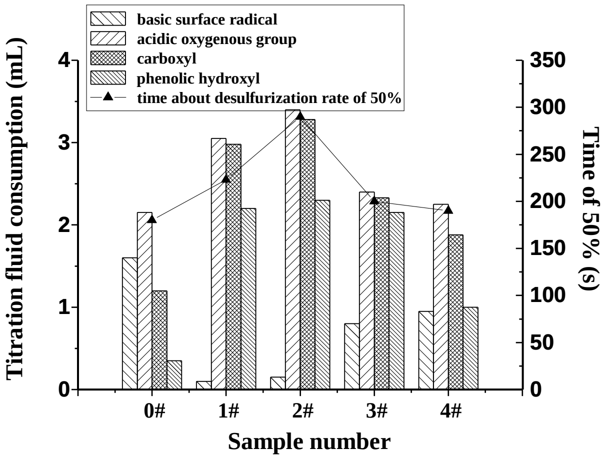

Fig. 6: The comparison of oxygen containing functional groups modified with sulfuric acid.

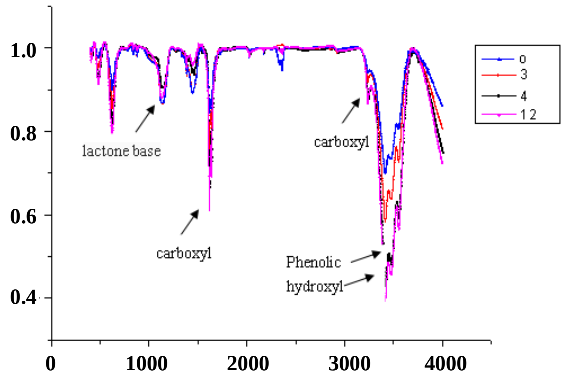

Fig. 7: The infrared spectrogram of pyrolysis tar.

of oxygen-containing functional groups on the surface of the pyrolysis tar, selected the best desulfurization efficiency of sample 2, 3, 4 and 12 for infrared spectroscopy analysis. It was shown in Fig. 7. According to the infrared absorption peak frequency table of the functional groups to find out the phenol hydroxyl, lactone and carboxyl peak position and to prove the existence of the three groups.

By the quantitative analysis of the pyrolysis tar can be obtained that the desulfurization efficiency of modified pyrolysis tar was mainly due to the surface acidic groups increased. Acid group titrated by the Boehm titration mainly included: carboxyl group, phenolic hydroxyl and lactone, acid carboxylic was the strongest. Infrared spectrum detection can qualitative analysis the desulfurization mechanism of the pyrolysis tar, if the strength of the group increased by modification, it proved that the quantitative analysis conclusion was correct. That is the improvement of desulfurization efficiency mainly related to its surface acid groups.

It was shown as Fig. 7, the original sample and the three samples, which had better modified affect all existed carboxyl group, phenolic hydroxyl and lactone. The stretching vibration peak of lactone base was found between $1000cm^{-1}$~$1250cm^{-1}$, there was carboxyl of characteristic peak in $1500cm^{-1}$~$1600cm^{-1}$ and $3000cm^{-1}$ ~$3250cm^{-1}$, phenolic hydroxyl absorption peak was existed in $3250cm^{-1}$~$3500cm^{-1}$. Infrared spectra analyzed different pyrolysis tar surface acidic groups, confirmed there had carboxyl, lactones and phenolic hydroxyl group in the pyrolysis tar surface.

It was found that the absorption peak intensity of carboxyl group from Fig. 7, phenolic hydroxyl and lactone were better than original sample. It was showed that acidic groups on the surface of modified pyrolysis tar had increased relatively. The absorption peak intensity of sample12 (phosphoric acid modified pyrolysis tar) was the largest. By compared with the desulfurization efficiency diagram, meanwhile the time of sample 12 which the desulfurization rate maintained more than 50% was the longest. It was showed that carboxyl was the main factors of desulphurization efficiency increased in the process of modification.

CONCLUSIONS

(1) Modified pyrolysis desulfurization efficiency influenced by five factors which in the order was acid type > calcination time > acid concentration > solid-liquid ratio > calcination temperature.

(2) The effect of nitric acid and phosphoric acid modification were the best, the former had the longest desulfurization efficiency and the latter had the longest time, which maintained more than 50% of desulfurization efficiency.

(3) The higher nitrate concentration, the better-modified effect of pyrolysis tar and the ability to remove sulfur dioxide.

(4) The desulfurization efficiency increased was mainly associated with acidic groups on the surface of the pyrolysis tar, desulfurization efficiency got better along with the increasing of acidic groups.

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