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# THERMOGRAVIMETRIC INVESTIGATION ON COMBUSTION CHARACTERISTICS OF OIL SHALE AND HIGH SULPHUR COAL MIXTURE

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Co-combustion experiments of mixture of Huadian oil shale and Heshan coal with high sulphur content have been conducted using a thermogravimetric analyzer. The effects of five different Ca/S mol ratios on the combustion characteristics of mixture fuel are analyzed using TG and DTG curves. The results show that the initial temperature of combustion of mixture fuel is decreased with an increase in the oil shale content of mixture fuel. The combustion characteristic of mixture fuel is superior to that of Heshan coal. Adding about 20 mass% Huadian oil shale into Heshan coal is feasible for desulfurization of mixture fuel during combustion.

***Keywords:*** *co-combustion, high sulphur coal, mixture fuel, oil shale, thermogravimetric analysis*

## Introduction

High sulphur coal can produce a great quantity of $SO_2$ in the combustion process. Adding calcium based sorbents such as limestone and shell [1] is common desulphurization methods. Other sorbents include natural manganese ores [2], zinc oxide based sorbents [3] etc. In addition, adding all sorts of additives is also studied in order to improve the desulfurization efficiency or modify the sorbent. The additives include NaCl, $CaCl_2$ and NaOH [4–6], NaCl, KCl, calcium lignosulfonate [7], some compound additives [9], $MnO_2$ and CuO powders [10], a new sorbent prepared from fly ash and lime [11], N-150 sorbent [12], appropriate modifying agent and active agent [13, 14], CuO/$\gamma$-$Al_2O_3$ [15].

Desulfurizing additive added into boiler brings about the following disadvantages: boiler heat efficiency decreases, power consumption increases, the load of separation and recirculation rises, and running costs rise. It is a key research subject that finding a high performance desulfurizer adaptable to the local resource condition, which will not bring about an increase in the heat loss of boiler and running costs. Since oil shale contains rich carbonates within which $CaCO_3$ is main component, it is expected that using it as desulfurizer can get good desulphurization effect. $CaCO_3$ decomposes at high temperature and produces CaO which is good desulfurizer. In addition, because oil shale is an additive with high volatile content and low ignition temperature, it will have better effects than limestone on boiler combustion efficiency and heat efficiency.

The researches on mixture of oil shale and coal with high sulphur content are less carried out. Johnson *et al*. considered that pyrolyzing coal and oil shale together could have many advantages [16], for example the carbonate minerals found in oil shale can act as scavengers of hydrogen sulfide during pyrolysis and hydrodesulphurization. They studied the co-pyrolysis of coal and oil shale. Using laboratory scale reactors Avid *et al.* did tests to explore the performance of a sub-bituminous coal and an oil shale from Mongolia, under conditions simulating gasification, pyrolysis and combustion process [17].

The geological prospecting studies indicate that oil shale has wide distribution in the world and its heat producing capability converted from its storage capacity ranked the second of fossil fuels, only next to coal. Oil shale can apply widely as desulfurizing additive. Using a thermogravimetric analyzer the experimental investigation on the combustion of mixture of Huadian oil shale and Heshan coal with high sulphur content is studied. The effects of different Ca/S mol ratios on the combustion characteristics of the mixture fuel are analyzed.

## Experimental

### *Sample*

Oil shale and high sulphur coal are obtained from Huadian and Heshan, China, respectively. Their analysis data are shown in Tables 1–3. The samples of mixture fuel are made through the following steps. First,

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**Table 1** Proximate and ultimate analysis of Huadian oil shale

| Proximate analysis[a] | | Ultimate analysis[a]/ mass% | |
|---|---|---|---|
| Moisture/ mass% | 2.90 | C | 31.63 |
| Volatile matter/ mass% | 41.89 | H | 4.37 |
| Ash/ mass% | 51.61 | O | 7.76 |
| Fixed carbon/ mass% | 3.60 | N | 0.73 |
| Net calorific value/ kJ $kg^{-1}$ | 8374 | S | 1.00 |

[a]air dry base

**Table 2** Ash contents (mass%) analysis of Huadian oil shale

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $TiO_2$ | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|
| 52.90 | 17.74 | 6.56 | 14.78 | 2.99 | 0.55 | 0.89 | 1.27 |

massive oil shale is broken pieces, then is grinded by miniature type coal grinding machine. Next, mix it with high sulphur coal in several specified proportion. Finally, grind the mixture separately by hand agate bowl. The grinding can make oil shale and coal mix sufficiently, and make their grain sizes more homogeneous. No screen separation is done to the samples, which ensures the experimental data can reflect the combustion characteristic of mixture fuel exactly.

The Ca/S mol ratios of the samples are 2.0, 1.5, 1.0, 0.5, 0.33 individually. The last sample only contains Heshan coal. The sample masses and mass ratios between Huadian oil shale and Heshan coal are shown in Table 4.

*Equipment and procedure*

Using a STA409 thermogravimetric analyzer the experimental research on the combustion characteristic of mixture fuel at different Ca/S mol ratios is studied. The thermogravimetric analysis is very useful for comparison between samples [18–20]. In this work the heating rate is 20°C $min^{-1}$, the gas is composed of 20% oxygen and 80% nitrogen, and the gas flux is 100 mL $min^{-1}$.

## Results and discussion

*TG and DTG*

The TG curve and DTG curves of mixture of oil shale and coal at different Ca/S mol ratios are shown in Figs 1

**Table 3** Proximate and ultimate analysis of Heshan coal

| Proximate analysis[a] | | Ultimate analysis[a]/ mass% | |
|---|---|---|---|
| Moisture/ mass% | 2.91 | C | 33.45 |
| Volatile matter/ mass% | 14.85 | H | 1.97 |
| Ash/ mass% | 51.52 | O | 4.72 |
| Fixed carbon/ mass% | 30.72 | N | 0.64 |
| | | S | 4.79 |

[a]air dry base

and 2, respectively. The TG curves indicate the same trend at different Ca/S mol ratios. Before the decomposition of samples, there is a distinct mass growth, which can sustain until 60°C. The causes may be that the sample adsorbs moisture from ambient atmosphere, or the temperature and pressure increase in the analyzer at the beginning of heating. The former is more possible. The initial temperature of combustion decreases with increasing Ca/S, which indicates that the ignition temperature is lowered and combustion characteristic improves. The final temperatures of all samples are near to 750°C basically, which indicates that Ca/S mol ratio has not great effect on the final temperature.

The DTG curves show that the initial temperature of mass loss decreases and the maximum combustion rate increases as Ca/S increases below 450°C. Volatile with high mass content is main combustible matter of oil shale, which makes oil shale ignite easily at the lower temperature and burn strongly at the early stage of combustion, but weakly at the following stage of char burning. Thus, oil shale will have greater effect on the low temperature combustion process of mixture fuel than on the high temperature combustion process. The DTG curves also show that the maximum combustion rate reduces as Ca/S increases above 450°C. The effect of oil shale on the combustion of coal will become small with combustion progressing. Above 450°C, coal will become the main combustible matter of mixture fuel and an increase of Ca/S mol ratio has little effect on the final temperature.

*Combustion characteristic*

The combustion characteristic parameters of TG and DTG curves include: the initial temperature of mass loss $T_s$, maximum combustion rate $(d\alpha/d\tau)_{max}$ and the

**Table 4** Sample masses and mass ratios between Huadian oil shale and Heshan coal

| Ca/S mol ratio | 2.0 | 1.5 | 1.0 | 0.5 | 0.33 |
|---|---|---|---|---|---|
| mass ratio (oil shale:coal) | 77.23:22.77 | 66.21:33.79 | 48.86:51.14 | 17.43:82.57 | 0:100 |
| Sample mass/mg | 4.6 | 5.0 | 4.9 | 4.8 | 4.8 |

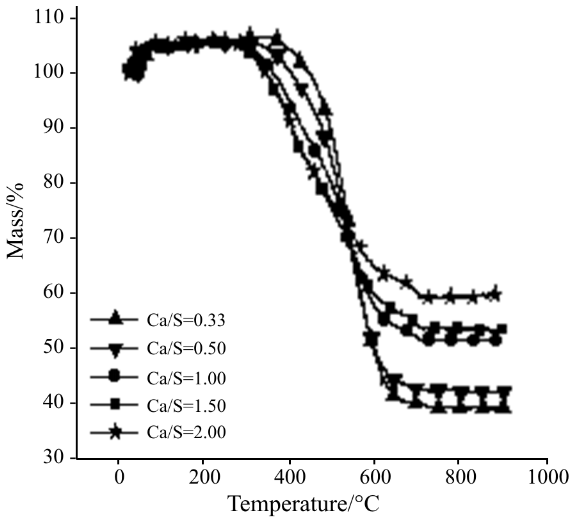


**Fig. 1** Combustion TG curves at different Ca/S mol ratios

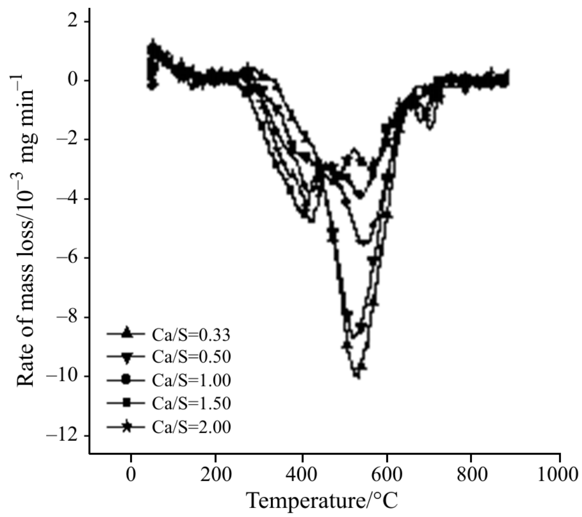


**Fig. 2** Combustion DTG curves at different Ca/S mol ratios

corresponding temperature $T_{max}$ at this rate, and $\Delta T_{1/2}$ which is the temperature difference between two temperatures at $(d\alpha/d\tau)/(d\alpha/d\tau)_{max}$ is 1/2. $\Delta T_{1/2}$ is named as half peak width, which represents concentrated degree of combustion product releasing. $T_s$ is calculated by computer through monitoring the differential scanning calorimetric curve. The release property index $r$ of combustion product can be calculated by $r=(d\alpha/d\tau)_{max}/T_s\Delta T_{1/2}T_{max}$ [21]. Index $r$ is based on the results of a lot of combustion tests using computer thermal balance, and reflects the combustion characteristic of mixture fuel. With index $r$ increased, combustion characteristic of mixture fuel becomes better, and heat release becomes more concentrated.

The kinetic parameters of mixture fuel in low temperature and high temperature are shown in Tables 5 and 6, respectively. In Table 5, when Ca/S ratio is low, combustion of mixture fuel is not distinct. When increasing Ca/S, the maximum combustion rate $(d\alpha/d\tau)_{max}$ increases slightly, the temperature $T_{max}$ at maximum combustion rate is stable basically, the initial temperature of combustion $T_s$ reduces apparently, half peak width $\Delta T_{1/2}$ increases a little, and index $r$ increases. These results represent that as $r$ increased, the ignition temperature is lowered, the combustion characteristic of mixture fuel improves, and heat release becomes more concentrated.

In Table 6, when Ca/S mol ratios are 0.33 and 0.5, the combustion characteristics of mixture fuel have many differences with ones at other three Ca/S mol ratios. A small amount of oil shale mixed in coal makes the temperature $T_{max}$ at maximum combustion rate decrease, and makes index $r$ reduce a little. When the proportion of oil shale increases, the initial temperature of combustion $T_s$ increases, half peak width $\Delta T_{1/2}$ increases apparently, the temperature $T_{max}$ at maximum

**Table 5** Kinetic parameter of mixture of oil shale and coal in low temperature

| Ca/S mol ratio | $(d\alpha/d\tau)_{max}$/mg min$^{-1}$ | $T_{max}$/°C | $T_s$/°C | $\Delta T_{1/2}$/°C | $r\cdot10^9$/mg $T^{-3}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 0.33 | – | – | – | – | – |
| 0.5 | – | – | – | – | – |
| 1.0 | –3.75 | 409 | 288 | 116 | 0.27 |
| 1.5 | –4.54 | 409 | 263 | 123 | 0.34 |
| 2.0 | –4.78 | 410 | 256 | 131 | 0.35 |

**Table 6** Kinetic parameter of mixture of oil shale and coal in high temperature

| Ca/S mol ratio | $(d\alpha/d\tau)_{max}$/mg min$^{-1}$ | $T_{max}$/°C | $T_s$/°C | $\Delta T_{1/2}$/°C | $r\cdot10^9$/mg $T^{-3}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 0.33 | –10.02 | 543 | 367 | 130 | –0.39 |
| 0.5 | –8.70 | 532 | 329 | 130 | –0.34 |
| 1.0 | –5.53 | 541 | 676 | 228 | –0.07 |
| 1.5 | –3.99 | 545 | 686 | 287 | –0.04 |
| 2.0 | –3.03 | 543 | 687 | 304 | –0.03 |

combustion rate reduces apparently, and index *r* reduce apparently. These results represent that plenty of oil shale added have great influence on the combustion characteristic of mixture fuel. Thus the proportion of oil shale has an appropriate value.

As a practical experience, it is feasible that about 20 mass% other substance is added into a fuel as an additive. When Ca/S mol ratio of mixture fuel is 0.5, the mass ratio of Huadian oil shale is 17.43% and is less than one quarter of Heshan coal mass. At this mol ratio, the combustion characteristics of Heshan coal improve. Therefore Huadian oil shale can be added into Heshan coal as an additive, which can reduce $SO_2$ emission of high sulphur coal due to self-desulphurization of oil shale. Because Huadian oil shale is a high volatile fuel and Heshan coal is a high ash anthracite coal, the combustion substances at low temperature are the volatile mainly from oil shale and less one from coal, on the other hand, combustion substances at high temperature are coke particles mainly from coal and a few from oil shale.

Analyzing from above results, it is practical and appropriate that 20 mass% of Huadian oil shale add into Heshan coal with high sulphur content.

## Conclusions

This paper studied the co-combustion characteristic of Huadian oil shale and Heshan coal with high sulfur content by using thermogravimetric analysis and the following conclusions are obtained:

- An increase in the oil shale content of mixture fuel makes the initial temperature of mass loss of mixture fuel decrease, but has little influence on the final temperature.
- The combustion characteristic of mixture of Huadian oil shale and Heshan coal is superior to Heshan coal. Less than 20 mass% oil shale content can improve slightly the combustion characteristic of Heshan coal. And the effect will become great when Huadian oil shale content is above 20 mass%.
- About 20 mass% of Huadian oil shale added into Heshan coal is feasible for desulphurization of mixture fuel during combustion.

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