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Investigation on catalyzed combustion of high ash coal by thermogravimetric analysis

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Abstract

Thermogravimetric analysis (TGA) has been used to obtain information on ignition and burnout characteristics of high ash coal (Ab. HAC) incorporating Fe_2O_3, MnO_2 and $BaCO_3$. Experiments were conducted from the ambient temperature to l273 K at a heating rate of 20 K min^{-1}. Ignition index and burnout index had been put forward to describe further the ignition and burnout characteristics. It was indicated that compared with those of HAC, the relative active sequence of catalysts to the ignition characteristics could be described as follows: $MnO_2 > BaCO_3 > Fe_2O_3$; the relative active sequence of catalysts to the burnout could be described as follows: $Fe_2O_3 > BaCO_3 > MnO_2$. Catalyzed combustion mechanisms of the coal samples were also discussed. It was also demonstrated that the catalysis of the catalysts to the HAC combustion was embodied in the enhancement of the emission of volatile matters (VM) from HAC, which reduces the ignition temperature. Another role of the catalysts to the combustion of HAC could be a carrier of oxygen that impromotes the oxygen transfer to the char of HAC.

Keywords: High ash coal (HAC); Catalyzed combustion; Ignition temperature; Burnout; Thermogravimetric analysis (TGA)

1. Introduction

Though coal resources in China is quite rich and reserves surpasses 4500 billion tonnes, distributes of coal are very imbalanced. Moreover, for coal quality, the high ash coal and high sulfur coal are higher proportion and the ash of majority coal is general above 25%. In rotary kilns low ash coal burns well. However, compared with soft coal, there are severe problems such as ignition, combustion rate and burnout if high ash coal (Ab. HAC) is used to produce cement in rotary kiln or in precalciner.

In recent years, many more investigations on coal burning process and catalytic combustion were performed successively to promote combustion efficiency and meet pollution emission requirements [1–7]. However, these findings were only used to apply in the electricity generation and the boilers, the type and quantity of the chemical additives were not completely suitable for the cement production. Therefore, in order to widely use the high ash coal in the precalcining kiln and to widen the selection scope of the coal used in the cement industry, it is necessarily to investigate the coal catalytic combustion according to the characteristics of cement production.

Thermogravimetric analysis (TGA) profiles contribute to enhance the knowledge of this process and, therefore, to establish the optimum operational conditions to develop it. Accordingly, several authors have studied the behaviour of the pyrolysis and combustion of soft coal, anthracite and other coal by TGA [8–14].

The objective of this study was to investigate ignition and burnout characteristics of HAC incorporating Fe_2O_3, MnO_2 and $BaCO_3$ by thermogravimeter analysis (TGA). Moreover, the mechanism of catalyzed combustion was also discussed. The results may be used to enhance the understanding of the characteristics of high ash coal and also provide a useful basis for further applying high ash coal in cement kilns with high-efficiency.

2. Experiments

2.1. Materials and test methods

The material whose thermal decomposition was studied consisted of HAC with or without catalysts. The samples were

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prepared HAC with 6% MnO_2, Fe_2O_3 and $BaCO_3$. HAC from a Huaxin cement plant, with ash content (Ab. A_{ad}) of 44.2%, was selected. The percentages of catalysts refer to the weight of coal and were added to the mixing. The materials were stored in the laboratory under dry conditions.

The combustion characteristics of HAC with or without catalysts were studied in a NETZSC STA-449C thermogravimetric analyzer. In an air flux of 20 mL min^{-1}, the furnace temperature was increased from the ambient temperature to l273 K using heating rate of 20 K min^{-1}. The weight of sample was monitored continuously as a function of temperature.

2.2. Determination of ignition temperature (T_e) and ignition index (D_i)

As shown in Fig. 1, the ignition temperature (T_e) was defined as following [15,16]: firstly, through the DTG peak point A, a vertical line was made upward to meet the TG oblique line at point B; secondly, a tangent line to TG curve was made at point B, which met the extended TG initial level line at point C; thirdly, another vertical line was made downwards through point C, which met the cross axle at point D. The corresponding temperature of point D was defined as T_e. Also the ignition index D_i is determined by the equation as follows [17]:

$$D_i = \frac{(dw/dt)_{max}}{t_p t_e}$$

where $(dw/dt)_{max}$ is the maximum combustion rate, t_p the corresponding time of the maximum combustion rate and t_e is the ignition time.

2.3. Determination of burnout index (D_f)

In this study, the burnout index is used to evaluate the burnout performance, which can be described as follows [17]:

$$D_f = \frac{(dw/dt)_{max}}{\Delta t_{1/2} t_p t_f}$$

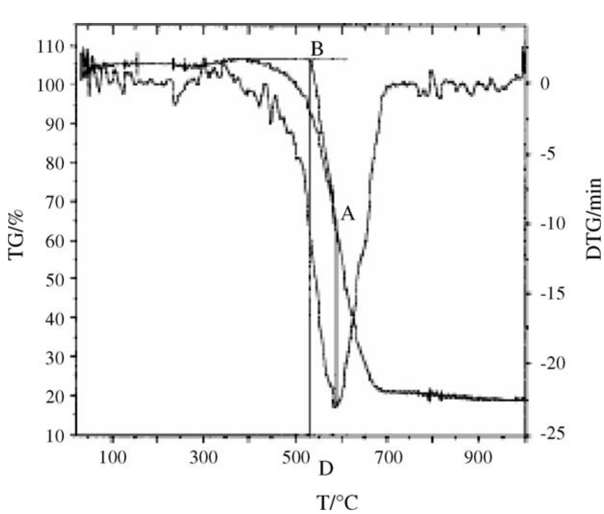

Fig. 1. Ignition temperature (T_e) definition sketch.

where $(dw/dt)_{max}$ is the maximum combustion rate, $\Delta t_{1/2}$ the time zone of $(dw/dt)/(dw/dt)_{max} = 1/2$, t_p the corresponding time of $(dw/dt)_{max}$ and t_f is burnout time.

3. Results and discussion

The combustion profiles of different blends with different catalysts have been compared with the profiles of HAC. Fig. 2(a)–(d) shows the TG–DTG profiles of the pure pulverized coal with or without catalysts.

3.1. Ignition performance of HAC containing different catalysts

The characteristic parameters of the blends with different catalysts and pure HAC were obtained from the burning profiles, as shown in Table 1.

It is indicated from Table 1 and Fig. 2 that T_e of HAC is 458.5 °C, and the catalysts used in this study can decrease T_e of HAC to a certain degree. The ignition temperature of the samples with 6% MnO_2, Fe_2O_3 and $BaCO_3$ decrease by 3.4%, 1.8% and 10.5%, respectively. Furthermore, D_i ($\times 10^{-4}$) of the pure coal is 81.66, D_i ($\times 10^{-4}$) of the blends with the additive of catalysts increase by 73.2%, 72.2% and 72.9%, respectively. When compared the ignition temperature and ignition index of the blends containing different catalysts, MnO_2 has preferable catalyzed performance to the ignition temperature of HAC. But three kinds of catalysts have similar effect to D_i. The relative active sequence of catalysts to the ignition performance of HAC can be described as follows: $MnO_2 > BaCO_3 > Fe_2O_3$.

3.2. Burnout performance of HAC containing different catalysts

Burnout temperature or time of the samples is identified the corresponding temperature or time of no weight loss in TG/DTG curves. As shown in Table 1, the influence of coal on the burnout time (t_f) is slight, so the burnout time cannot completely reflect burnout performance of waste type blends.

Table 1 and Fig. 2 show that the burnout index ($D_f \times 10^{-4}$) of high ash coal is 4.29. Compared with the burnout characteristics of HAC with different catalysts, it has been shown that the coal burnout index of the samples with 6% MnO_2, Fe_2O_3 and $BaCO_3$ increase by 217%, 230% and 228%, respectively. The relative active sequence of catalysts to the burnout performance can be described as follows: $Fe_2O_3 > BaCO_3 > MnO_2$.

It is also indicated that the maximum combustion rate ($(dw/dt)_{max}$) of coal samples increase with the incorporation of catalysts in HAC. And the corresponding time (t_p) and temperature (T_p) decrease. These indicate that catalysts can facilitate combustion of HAC.

4. Catalyzed mechanism analyses

As shown from the above analyses, catalysts in this study have catalytic action to the release process of the coal volatile

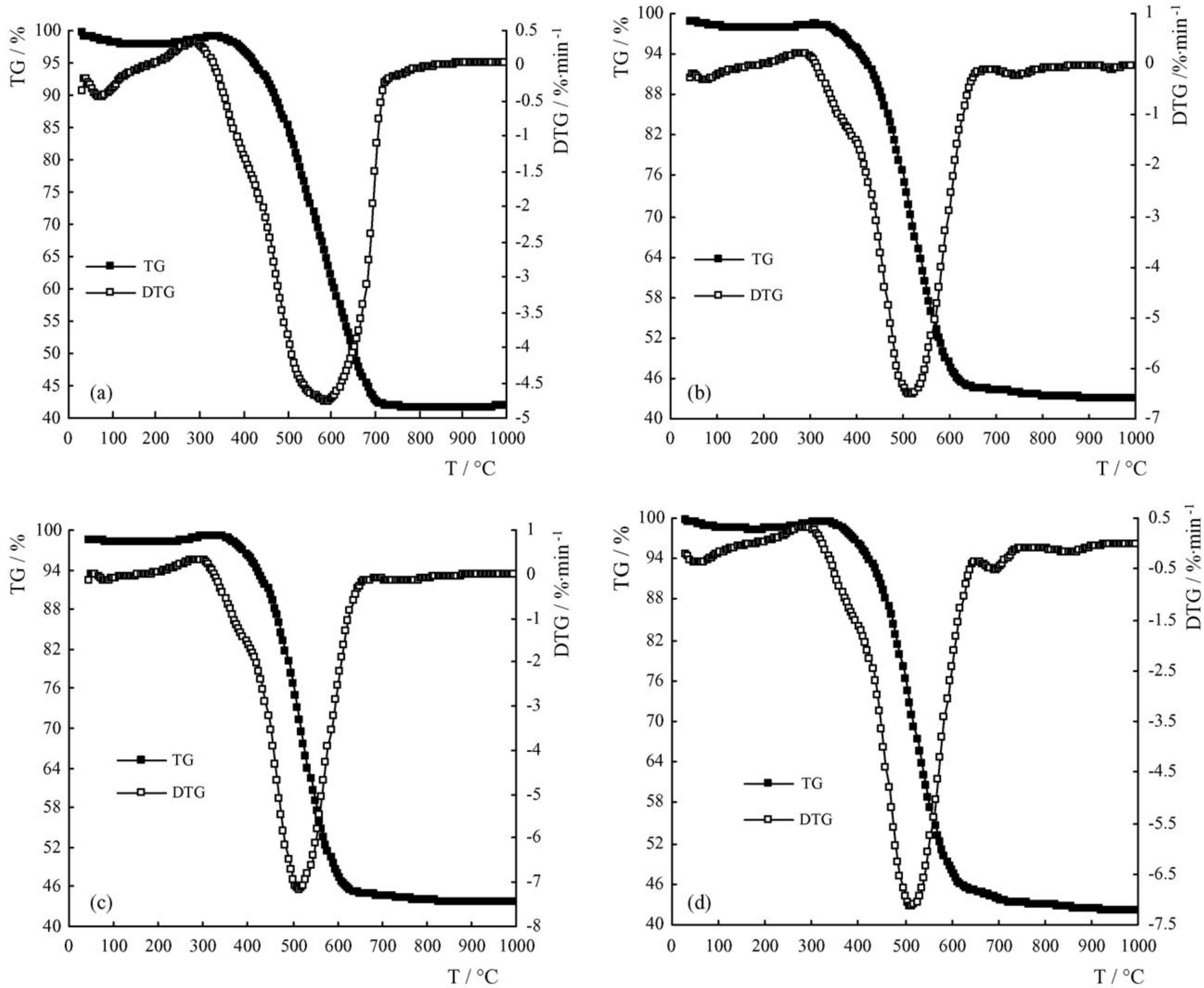

Fig. 2. TG–DTG of combustion of samples: (a) HAC; (b) HAC + 6% MnO_2; (c) HAC + 6% Fe_2O_3; (d) HAC + 6% $BaCO_3$.

matter and the ignition time and temperature of the fixed carbon. Therefore, MnO_2 has the most obvious catalytic effect on the ignition temperature; moreover, Fe_2O_3 has the most remarkable catalytic action to the burnout characteristic.

It can be seen that the catalyst effect mainly manifests in two aspects: firstly, the catalysis of the catalysts to the HAC combustion is embodied in the enhancement of the emission of volatile matters (VM) from HAC, which reduces the ignition temperature. In a certain degree, the catalysts promoted the coal decomposition reaction, resulted in the oxidative and transformed reaction of the matter which is difficult to oxidize and transform, accelerated the tar and the crude benzene to be decomposed easily, and increased the release of the coal volatile matter.

Secondly, the catalysts to the combustion of HAC may be a carrier of oxygen that impromotes the oxygen transfer to the char of HAC, which attributed to the char combustion of HAC. The surface complex salts were formed between these ions in the catalysts and oxo groups of the coal surface. Due to the electron donating effect of the divalent ion, they were transmitted to the homocycle or the carbon chain by the oxygen, which made the homocycle or the carbon chain become instability and burst and emit CO and CO_2. Under the effect of H_2O, the surface complex salts were reform again. The surface complex salts

Table 1
The influences of different catalysts on the ignition and burnout performance of HAC

No.	T_e (°C)	$(dw/dt)_{max}$ (% min^{-1})	t_e (min)	$\Delta t_{1/2}$ (min)	t_p (min)	T_p (°C)	t_f (min)	T_f (°C)	D_i (×10^{-4})	D_f (×10^{-4})
1	458.5	−4.77	20.99	11.67	27.83	587.9	34.20	715.7	81.66	4.29
2	442.8	−6.74	20.15	6.91	23.65	517.6	30.38	636.6	141.43	13.58
3	450.1	−7.07	20.86	6.86	24.10	515.9	30.25	632.9	140.63	14.14
4	448.0	−7.05	20.75	7.01	24.06	515.2	29.7	626.2	141.21	14.07

Notes: 1, HAC; 2, HAC + 6% MnO_2; 3, HAC + 6% Fe_2O_3; 4, HAC + 6% $BaCO_3$; T_p, the corresponding temperature of $(dw/dt)_{max}$; T_e, the ignition temperature; t_f and T_f, the burnout time and the corresponding temperature; D_i, the ignition index; D_f, the burnout index.

acted as the oxygen carrier, and promoted the oxygen transfer, which contributed to the burnout and combustion of the fixed carbon. But the metallic ion can also combine with the coal oxo groups. Simultaneously, it also reacts with the mineral of coal during combustion process. Therefore, the use of the catalysts should be paid attention to the influence of the content to the catalyzed effect.

5. Conclusions

Influences of different catalysts in this study on the HAC combustion characteristics are more remarkable. Compared with combustion characteristics of HAC, the ignition index of the samples with 6% MnO_2, Fe_2O_3 and $BaCO_3$ decrease by 73.2%, 72.2% and 72.9%, respectively. And the coal burnout index of the samples increase by 217%, 230% and 228%, respectively.

The relative active sequence of catalysts to the ignition performance is described as follows: $MnO_2 > BaCO_3 > Fe_2O_3$. And the relative active sequence of catalysts to the burnout performance is described as follows: $Fe_2O_3 > BaCO_3 > MnO_2$.

The catalysts mechanism shows that the catalysis of the catalysts to the ignition characteristics is embodied in the enhancement of the emission of volatile matters from HAC, which attributes to reduce the ignition temperature. And the catalysts to burnout may be a carrier of oxygen that impromotes the oxygen transfer to the char of HAC.

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