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Abstract. The effects of Fe_2O_3, CaO, and MnO_2 on the combustion characteristics and kinetics of coal-char blends were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results indicated that catalysts exhibited positive effects on the combustion characteristics of coal-char blends, especially in the initial period of coal-char blends combustion. With catalysts addition (mass 1.5%), it could improves volatile matter release, and reduces ignition point, promotes char to begin burning under lower temperature. The ignition index (C) was increased, respectively, by 27% for Fe_2O_3, 6% for CaO, 11.3% for MnO_2, and the combustion characteristic index (***S***) was increased respectively, by 29% for Fe_2O_3, 5% for CaO, 8.3% for MnO_2. In addition, two kinetic models (R_2 and F_1) were adopted to calculate the kinetic parameters in different stage of combustion processes. The results showed that with Fe_2O_3 or CaO addition, the activation energy at second stage decreases from 86.0 KJ/mol to 76.92 KJ/mol and 75.12 KJ/mol, respectively. There are no obvious decreases at the third stage of samples combustion process.

1. Introduction

Coal-Based Co-production is the important directions of clean coal technology in future development due to its high efficiency and good environmental performance for electricity generation [1]. A large amount of char are produced in the pyrolysis process, and using this char for combustion and power generation is emerging as viable methods. However, the char is difficult to ignite and burnout as a result of its low volatile and high ash content [2]. At present, there are two different way to solve this problem: preheating combustion [3-4] and co-combustion [5].

Besides, catalytic combustion was regarded as the most promising approaches to raise combustion rate of the pulverized coal and decrease contaminant emission [6]. At present, AAEM (alkaline and alkaline earth compounds) and some transition metal compounds were widely used as catalysts for catalytic combustion of pulverized coal [7]. Gong [8] adopted the differential thermal analysis (DTA) method to study the effects of CeO_2 and Fe_2O_3 on heat release during anthracite combustion. The results of the

study showed that ignition temperature decreased and residual carbon decreased with CeO_2 or Fe_2O_3 addition. Zou [9] investigated the influence of MnO_2, CaO, and Fe_2O_3 on the combustion reactivity of anthracite and coal char using thermogravimetric analysis (TGA) and a drop tube furnace (DTF). The DTF results indicated the maximum burnout rate of anthracite and char both increased with catalysts addition. Much research has been aimed to explore the chemical additive effects on coal and char combustion. However, the effects of catalysts on combustion characteristics and kinetics of coal-char blends has not yet been reported.

In this work, effects of Fe_2O_3, CaO, and MnO_2 which were used as catalysts, on coal-char blends combustion were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) technique. The main purpose of the work is to investigate the combustion characteristics and kinetics of coal-char blends with the addition of catalysts.

2. Experimental

The experimental coal used in this work is Shenmu bituminous coal, and the char was produced by a low-temperature pyrolysis method used to process coal. Both the bituminous and char samples were ground to 0.048–0.074 mm. Proximate-ultimate analysis results of both the bituminous and char samples were given in Table 1. The bituminous and char samples were blended in same mass weights (1:1), and named it “CC”.

Table 1. The proximate-ultimate analysis of bituminous and char.

Proximate analysis (%)	Moisture	Ash	Volatile matter	Fixed carbon	
bituminous	12.22	4.51	32.79	60.48	
char	2.18	19.54	3.31	82.35	
Ultimate analysis (%)	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
bituminous	75.19	5.87	1.15	0.16	12.61
char	81.47	0.37	0.85	0.59	7.13

The three chemical compounds, Fe_2O_3, CaO, and MnO_2 as catalysts (mass 1.5%), all over 99% in purity with particle size of -0.048 mm, were mixed with coal-char blends by hand for 10 min physically at mortar. Then named them “CC- Fe_2O_3”, “CC- CaO”, and “CC- MnO_2” respectively.

Experiments were performed using TGA/DSC simultaneous thermal analyzer, by which the mass loss curve (TG curve) and heat flow curve (DSC curve) could be obtained. About 10±0.02 mg of samples were placed in an Al_2O_3 crucible and combusted under air atmosphere (50 ml/min), from 30 °C to 850 °C at 15 °C /min.

3. Results and Analysis

3.1. TG-DSC analysis

The characteristic parameters of the samples obtained from TG-DSC curves may be used to compare the effects of catalysts on combustion characteristics of coal-char blends. The TG-DTG and DSC curves of coal-char blends are shown in Figure 1. The ignition temperatures (T_i) and the burnout temperature (T_f) can be determined by TG–DTG tangent method [10]. In addition, an ignition index (C)

and combustion characteristic index (***S***) is also determined using the below mentioned equations to evaluate the ignition and combustion performance of the samples. The higher ***C*** the better the ignition reactivity and the higher ***S*** the better the combustion reactivity.

$$C=\frac{W_{mean}}{T_i^2} \tag{1}$$

$$S=\frac{W_{max}W_{mean}}{T_i^2 T_f} \tag{2}$$

Where; W_{max} is the maximum mass loss rate, W_{mean} is the average mass loss rate from T_i to T_f, T_1 and T_2 are the first and second peak temperature.

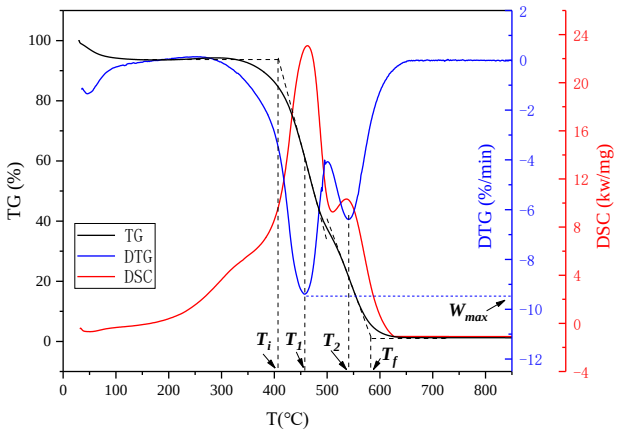

Figure 1. TG-DTG and DSC curves of coal-char blends combustion.

As shown in Figure 1, three mass loss stages were observed. In the first stage, a mass loss less than 8% was observed for combustion temperature up to 200 ℃ because of the water loss in the bituminous and char. The second stage, ranging from 200 to 500 ℃, corresponded to the combustion process of bituminous. And this stage included volatiles combustion and fixed carbon combustion. The third stage, in the temperature range from 500 to 700 ℃, corresponded to the combustion process of char. In addition, the weight loss peak temperature was almost equal to the exothermic peak temperature.

A comparison of the reduction degree of the ignition temperature of the four fuels is shown in Figure 2. Besides, the characteristic parameters for samples combustion are listed in Table 2. As shown in Figure 2, with catalysts addition, there are an obvious weight loss peak came before the first weight loss peak in the DTG curve. But the peak of DSC curve with catalysts addition was lower than that the peak of DSC curve without catalysts (CC). This results indicated that Fe_2O_3, CaO, and MnO_2 can improves volatile matter release and reduces kindling point in coal-char blends combustion. Zou [9] considered that the catalytic effect on oxidation reaction occurring on the char particles could reduce the ignition temperature.

As shown in Table. 2, with catalysts addition, the coal-char blends had the lower ignition temperature (T_i) and a lower first peak temperature (T_1). However, the reduction of the second peak temperature (T_1) and the burnout temperature (T_f) was not significant. In addition, the ignition index (C) was increased, respectively, by 27% for Fe_2O_3, 6% for CaO, 11.3% for MnO_2, and the combustion characteristic

index (***S***) was increased respectively, by 29% for Fe_2O_3, 5% for CaO, 8.3% for MnO_2.

Summarizing, the catalysts had a very meaningful effect on coal-char blends combustion, especially in the second stage. It could improves volatile matter release, and reduces ignition point, promotes char to begin burning under lower temperature. In addition, the catalytic activity of the three catalysts on coal-char blends was (in order): MnO_2<CaO <Fe_2O_3, which is similar to the results of earlier researchers [9].

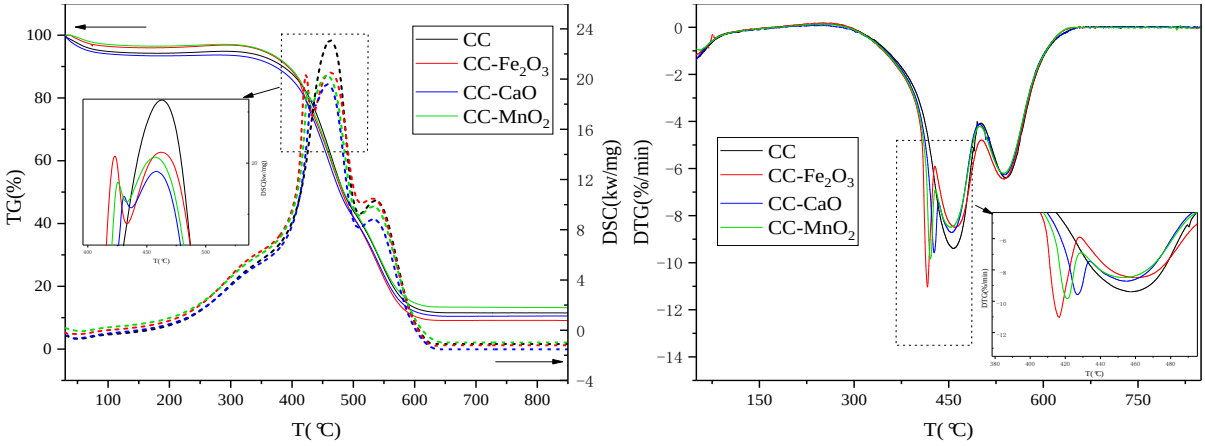

Figure 2. TG-DSC and DTG curves of samples combustion.

Table 2. The characteristic parameters for samples combustion.

Samples	T_i	T_1	T_2	T_f	W_{max}	W_{mean}	C	S
	(℃)	(℃)	(℃)	(℃)	(% min^{-1})	(% min^{-1})	(% min^{-1} ·℃$^{-2}$)	(% min^{-1} ·℃$^{-2}$)
CC	407.5	457.6	540.6	583.2	9.394	5.992	5.66×10^{-5}	5.81×10^{-7}
CC-Fe_2O_3	391.5	416.6	537.7	581.2	11.031	6.107	7.20×10^{-5}	7.56×10^{-7}
CC-CaO	399.1	427.0	537.8	580.5	9.582	5.874	6.02×10^{-5}	6.09×10^{-7}
CC-MnO_2	395.5	421.1	537.9	582.5	9.837	5.821	6.30×10^{-5}	6.29×10^{-7}

3.2. Kinetic analysis

Due to the reaction mechanisms are quite different in different stages, a sectioning method was adopted to study the kinetics in different stage of combustion processes [11]. In addition, the activation energy (***E***) and Arrhenius constants (***A***) can be calculated using TGA date of single heating rate test by Coats–Redfern method. The coal-char blends combustion was supposed to be governed by the first-order Arrgenius law. And when the heating rate is a constant during combustion, the kinetics of reaction is described as:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{3}$$

An asymptotic approximation for the resolution of Eq. (3) was used by Coats–Redfern:

$$\ln\left(\frac{g(\alpha)}{T^2}\right)=\ln\left(\frac{AR}{E\beta}\right)-\left(\frac{E}{RT}\right) \tag{4}$$

Where; α is extent of conversion, β is the heating rate, R is the gas constant, $g(\alpha)$ is a function depended by mechanism controlling the reaction.

The general solid-state rate expressions for different mechanisms were given in Table 3.

Table 3. General solid-state rate expressions for different mechanisms

Mechanisms	**Symbol**	***f(α)***	***g(α)***
Order of reaction			
First order	F_1	1-α	$-\ln(1-\alpha)$
Second order	F_2	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third order	F_3	$(1-\alpha)^3$	$[(1-\alpha)^{-1}-1]/2$
Diffusion			
One-dimensional diffusion	D_1	$1/2\alpha$	α^2
Two-dimensional diffusion	D_2	$[1-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion	D_3	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{2/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Limiting surface reaction between both phases			
One dimension	R_1	1	α
Two dimensions	R_2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Three dimensions	R_3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

According to Table 3, the experimental data of two stage of coal-char blends combustion process were fitted by Eqs.4 by different reaction models. The activation energy (***E***) can be calculated from the slope $\ln(g(\alpha)/T^2)$ versus $1000/T$. Meanwhile, the linear correlation coefficient (R^2) was calculated for different reaction models. The results are shown in Figure 3. The results shows that the line R_2 in Figure 3(a) and F_1 in Figure 3(b) have much higher parallelism, and the correlation coefficients (R^2) of two lines both exceed 0.999. Therefore, the mechanisms of R_2 and F_1 model are suitable for describing the corresponding stage of coal-char blends combustion process.

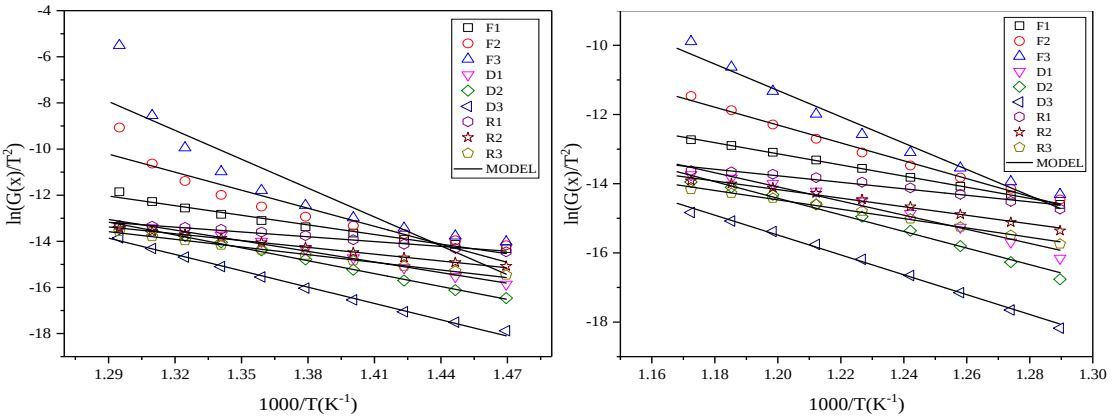

Figure 3. Fitting curves of different reaction mechanisms at the different stage.

The activation energy (**E**) at different stages of samples combustion process are shown in Table 4. With Fe_2O_3 or CaO addition, the activation energy at second stage decreases from 86.0 KJ/mol to 76.92 KJ/mol and 75.12 KJ/mol respectively. However, there are no obvious decreases at the third stage of

samples combustion process. It may be concluded that the catalysts exhibits higher catalytic activity at the second stage than the third stage.

Table 4. General solid-state rate expressions for different reaction models.

Samples	Temperature range	$g(\alpha)$	E (KJ/mol)	R^2
CC	407.5-501.0 ℃	$1-(1-\alpha)^{1/2}$	86.000	0.999
	501.0-583.2 ℃	$-\ln(1-\alpha)$	133.897	0.999
CC-Fe_2O_3	391.5-499.8 ℃	$1-(1-\alpha)^{1/2}$	76.921	0.999
	499.8-581.2 ℃	$-\ln(1-\alpha)$	128.618	0.999
CC-CaO	399.1-501.8 ℃	$1-(1-\alpha)^{1/2}$	75.120	0.999
	501.8-580.5 ℃	$-\ln(1-\alpha)$	127.520	0.999
CC-MnO_2	398.5-498.7 ℃	$1-(1-\alpha)^{1/2}$	83.329	0.999
	498.7-582.5 ℃	$-\ln(1-\alpha)$	130.688	0.999

4. Conclusion and Discussion

In this study, the effects of Fe_2O_3, CaO, and MnO_2 on the combustion characteristics and kinetics of coal-char blends were investigated by TGA-DSC.

With catalysts addition, there are other obvious weight loss peak came before the first weight loss peak in the DTG curve, and the coal-char blends had the lower ignition temperature (T_i) and a lower first peak temperature (T_1). However, the reduction of the second peak temperature (T_1) and the burnout temperature (T_f) was not significant, and the peak of DSC curve with catalysts addition was lower than that the peak of DSC curve without catalysts (CC). This results indicated that Fe_2O_3, CaO, and MnO_2 can improves volatile matter release and reduces burnout point in coal-char blends combustion.

In addition, the activation energy (E) was calculated by Coats–Redfern method. The results indicated that the mechanisms of R_2 and F_1 model are suitable for describing the corresponding stage of coal-char blends combustion process. With Fe_2O_3 or CaO addition, the activation energy at second stage decreases from 86.0 KJ/mol to 76.92 KJ/mol and 75.12 KJ/mol, respectively.

The next work is to investigate the effects of different ratios of catalysts on the combustion and kinetics of coal-char blends. Meanwhile, the release of gases during coal-char blends combustion also will be studied by TGA-DSC-FTIR.

Acknowledgments

This work was sponsored by the The National Key Research and Development Program of China (Contract No. 2017YFB0602002).

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