Effects of catalysts on combustion characteristics and kinetics of coal-char blends

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Abstract. The effects of Fe$_2$O$_3$, 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 improve volatile matter release, and reduce ignition point, promotes char to begin burning under lower temperature. The ignition index (C) was increased, respectively, by 27% for Fe$_2$O$_3$, 6% for CaO, 11.3% for MnO$_2$, and the combustion characteristic index (S) was increased respectively, by 29% for Fe$_2$O$_3$, 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ addition. Zou [9] investigated the influence of MnO$_2$, CaO, and Fe$_2$O$_3$ 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$_2$O$_3$, 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.](image)

| 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$_2$O$_3$, 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$_2$O$_3$”, “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$_2$O$_3$ 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.

\[
C = \frac{W_{\text{mean}}}{T_i}
\]

\[
S = \frac{W_{\text{max}}W_{\text{mean}}}{T_1^2T_f}
\]

Where; \(W_{\text{max}}\) is the maximum mass loss rate, \(W_{\text{mean}}\) 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.](image)

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 °C because of the water loss in the bituminous and char. The second stage, ranging from 200 to 500 °C, 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 °C, 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 of DSC curve without catalysts (CC). This results indicated that \(\text{Fe}_2\text{O}_3\), \(\text{CaO}\), and \(\text{MnO}_2\) 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 \((T_f)\). 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 \(\text{Fe}_2\text{O}_3\), 6% for \(\text{CaO}\), 11.3% for \(\text{MnO}_2\), and the combustion characteristic
index ($S$) was increased respectively, by 29% for Fe$_2$O$_3$, 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$_2$O$_3$, which is similar to the results of earlier researchers [9].

![Figure 2. TG-DSC and DTG curves of samples combustion.](image)

**Table 2.** The characteristic parameters for samples combustion.

| Samples     | $T_1$ ($°C$) | $T_1$ ($°C$) | $T_2$ ($°C$) | $T_f$ ($°C$) | $W_{max}$ (%·min$^{-1}$) | $W_{mean}$ (%·min$^{-1}$) | $C$ (10$^3$·°C$^{-1}$) | $S$ (10$^{-7}$·°C$^{-1}$) |
|-------------|--------------|--------------|--------------|--------------|---------------------------|---------------------------|-------------------------|-------------------------|
| CC          | 407.5        | 457.6        | 540.6        | 583.2        | 9.394                     | 5.992                     | 5.66×10$^3$             | 5.81×10$^{-7}$          |
| CC-Fe$_2$O$_3$ | 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:

$$\frac{da}{dT} = \frac{A}{\beta} \exp \left(\frac{-E}{RT}\right) f(\alpha)$$  \hspace{1cm} (3)

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

$$\ln \left(\frac{g(\alpha)}{T^2}\right) = \ln \left(\frac{4R}{E\beta}\right) - \left(\frac{E}{RT}\right)$$  \hspace{1cm} (4)

Where; $\alpha$ is extent of conversion, $\beta$ 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 | \( f(\alpha) \)             | \( g(\alpha) \)           |
|-----------------------------------------|--------|-----------------------------|-----------------------------|
| **Order of reaction**                   |        |                             |                             |
| First order                             | \( F_1 \) | \( 1 - \alpha \)            | \(- \ln(1 - \alpha) \)     |
| 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               | \( D_1 \) | \( 1/2\alpha \)             | \( \alpha^2 \)              |
| 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                           | \( R_1 \) | \( 1 \)                     | \( \alpha \)                |
| Two dimensions                          | \( R_2 \) | \( 2(1 - \alpha)^{1/2} \)    | \( 1 - (1 - \alpha)^{1/2} \) |
| Three dimensions                        | \( R_3 \) | \( 3(1 - \alpha)^{2/3} \)    | \( 1 - (1 - \alpha)^{2/3} \) |

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.

![Fitting curves of different reaction mechanisms at the different stage.](image.png)

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 Fe₂O₃ 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 exhibit 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°C    | \(1 - (1 - \alpha)^{1/2}\) | 86.000          | 0.999            |
|                 | 501.0-583.2°C    | \(-\ln(1 - \alpha)\) | 133.897         | 0.999            |
| CC-Fe\(_2\)O\(_3\) | 391.5-499.8°C | \(1 - (1 - \alpha)^{1/2}\) | 76.921          | 0.999            |
|                 | 499.8-581.2°C    | \(-\ln(1 - \alpha)\) | 128.618         | 0.999            |
| CC-CaO         | 399.1-501.8°C    | \(1 - (1 - \alpha)^{1/2}\) | 75.120          | 0.999            |
|                 | 501.8-580.5°C    | \(-\ln(1 - \alpha)\) | 127.520         | 0.999            |
| CC-MnO\(_2\)  | 398.5-498.7°C    | \(1 - (1 - \alpha)^{1/2}\) | 83.329          | 0.999            |
|                 | 498.7-582.5°C    | \(-\ln(1 - \alpha)\) | 130.688         | 0.999            |

4. Conclusion and Discussion

In this study, the effects of Fe\(_2\)O\(_3\), 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 \(T_f\). However, the reduction of the second peak temperature \(T_f\) and the burnout temperature \(T_b\) was not significant, and the peak of DSC curve with catalysts addition was lower than that of DSC curve without catalysts (CC). This results indicated that Fe\(_2\)O\(_3\), 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\(_2\)O\(_3\) 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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