Combustion Performance and Kinetic Analysis of Shenhua Raw Coal Mixed Coal Gasification Slag

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Abstract: In this paper, Shenhua coal and its gasification slag (GS) in Ordos are taken as the research objects. The thermogravimetric analyzer is used to investigate the mixed combustion characteristics of different proportions. The experimental results show that Shenhua raw coal mixed with GS can improve the overall ignition and burnout characteristics of mixed coal to some extent. With the increase of the mixing amount of GS, the combustion characteristic temperature of coal samples presents an overall trend of increase in ignition point temperature ($T_i$) and burnout temperature ($T_b$). When the GS content is 50%, the maximum weight loss temperature ($T_{max}$) is the highest. The mixing amount of GS is not equal to the change of sample mass. The comprehensive combustion characteristic $S$ decreases with the increase of GS content. When the mixing amount of GS was 50%, the minimum apparent activation energy obtained was 87.11kJ/mol.

1. Introduction

China is a country rich in coal, poor in oil and little in gas, and its energy structure is dominated by coal. Coal gasification process will produce a lot of ash, including gasification coarse slag and gasification fine slag. Gasification coarse slag has low calorific value and can be used as building materials and backfill materials. The carbon content and burning loss of gasification fine slag are large, exceeding the national and industrial standards, and it is difficult to be used as building materials for roads and backfill projects [1]. Coal combustion is the main source of heat, but it also causes serious environmental problems. The carbon content of gasification fine slag is high. The reasonable combustion treatment of gasification fine slag can not only reduce its pollution to the environment, but also recover its energy and improve the economic benefits of the enterprise. However, the gasification fine slag has high water content, very low volatiles and poor ignition characteristics, so it is difficult to be directly burned as fuel. Mixing gasification fine slag with fuel coal with good combustion characteristics can improve its ignition and burnout characteristics, which is considered as a feasible technical scheme [2]. Some studies [3] have pointed out that the unburned carbon content in gasified fine slag can reach 60%, indicating that the gasified fine slag after drying still has great thermal application value. Mixing it with coal with good combustion characteristics can realize the combustion of gasified fine slag, so as to realize the resource utilization of gasified fine slag. Therefore, this paper takes Shenhua coal and its gasification slag (GS) in Ordos as the research object, and the combustion characteristics of mixed GS of different proportions were investigated by thermogravimetric analyzer,
which provided basic data and technical support for the development of reliable resource utilization technology of gasification fine slag.

2. Experiment section

2.1. Experimental Materials
The coal samples used in this experiment are from Shenhua raw coal and its gasification slag (GS) in Shanwan, Ordos, Inner Mongolia, with particle sizes of 0.15-0.75mm. GS and raw coal are mixed at 1:9, 3:7, 5:5, 7:3, 9:1 ratios respectively and labeled as GS-10, GS-30, GS-50, GS-70, GS-90 in a container protected by inert atmosphere for standby use.

2.2. Combustion reaction performance test
The thermogravimetric (TG) experiment was performed on the samples under the condition of NETZSCH 409, O₂ atmosphere, scanning temperature range from room temperature to 950℃, and heating rate of 10℃/min. In order to ensure the accuracy and repeatability of the experimental results, each group of experiments should be repeated at least three times during the experiment.

The weight loss curve and weight loss rate curve of the samples in the reaction process are automatically collected by the computer, and the coal sample combustion conversion rate \( x \) is calculated from the weight loss curve (equation (1)).

\[
x = \frac{m_0 - m_t}{m_0 - m_\infty}
\]

Where, \( m_0 \) is the initial mass of the sample, g; \( m_\infty \) is the complete weight loss mass of the sample, g; \( m_t \) is the mass at time \( t \), g.

3. Experimental results and analysis

3.1. Analysis of combustion characteristics of coal sample
In this paper, TG-DTG method [4] is adopted to define the ignition temperature \( T_i(\text{℃}) \), maximum mass loss rate peak temperature \( T_{\text{max}}(\text{℃}) \) and burnout temperature \( T_b(\text{℃}) \) of coal samples. The comprehensive combustion characteristic index \( S \) is defined as

\[
S = \left(\frac{\text{dm} / \text{dt}}{\text{max}}\right) \text{mean} \left(\frac{\text{dm} / \text{dt}}{\text{mean}}\right)^2 \left(\frac{1}{T_b^2} - \frac{1}{T_i^2} - \frac{1}{T_{\text{max}}^2}\right)
\]

Where, \( (\text{dm} / \text{dt})_{\text{mean}} \) is the average combustion rate, %/min , and \( (\text{dm} / \text{dt})_{\text{mean}} = [(\text{dm} / \text{dt})_i + (\text{dm} / \text{dt})_b] / 2 \), \( (\text{dm} / \text{dt})_{\text{max}} \) is the maximum combustion rate, % / min.

![Figure 1. Effect of mixing ratio on TG curve of GS and raw coal co-combustion](image1)

![Figure 2. Effect of mixing ratio on DTG curve of GS and raw coal](image2)
Table 1. Characteristic parameters of co-combustion of GS and raw coal.

| Samples | Weight loss (%) | $T_i$ (°C) | $T_{\text{max}}$ (°C) | $T_b$ (°C) | $s \times 10^{11}$ |
|---------|-----------------|------------|-----------------------|------------|--------------------|
| GS-10   | 82              | 393.6      | 457.6                 | 675.2      | 0.0135             |
| GS-30   | 62              | 407.3      | 448.5                 | 708.1      | 0.0176             |
| GS-50   | 47              | 413.0      | 498.4                 | 727.6      | 0.0070             |
| GS-70   | 35              | 423.1      | 485.7                 | 736.3      | 0.053              |
| GS-90   | 13              | 428.2      | 497.5                 | 748.4      | 0.014              |

Figure 1 shows the combustion weight loss curve TG of samples with different proportions of mixed GS, and Figure 2 shows the first derivative DTG curve of combustion weight loss. It can be seen from Figure 1 that the whole oxidizing combustion process of coal samples can be divided into four stages, namely, water evaporation and desorption stage (starting temperature to about 170°C), oxidation weight gain stage (170°C-317°C), intense combustion stage (317°C-517°C), and burnout stage (temperature greater than 517°C). The DTG curve of Shenhua raw coal and its GS blended combustion presents bimodal distribution, corresponding to the combustion process of raw coal and GS respectively. The specific parameters are listed in Table 1.

As can be seen from Table 1, with the increase of the mixing amount of GS, the combustion characteristic temperature of coal samples, the ignition point $T_i$, the fastest combustion rate temperature $T_{\text{max}}$, and the burnout temperature $T_b$, all show an overall rising trend. Among them, $T_i$ and $T_b$ almost linearly increase (see Figure 3). The main reason is that the higher the GS content is, the less combustible components are in the sample and the more difficult it is to ignite. Therefore, the $T_i$ increases with the increase of the GS content. At the same time, as the content of GS increases, the number of non-combustible minerals increases, therefore, $T_b$ increases with the increase of GS content.

With the increase of the amount of GS, the $T_{\text{max}}$ did not change linearly. When the content of GS is low, the $T_{\text{max}}$ is mainly within the range of 440-460°C. When the content of GS is greater than or equal to 50%, the $T_{\text{max}}$ is within the temperature range of 480-500°C. When the content of GS is 50%, the $T_{\text{max}}$ is the highest, reaching 498.4°C.
It can be seen from Table 1 and Figure 4 that the weight loss of coal sample decreases almost linearly with the increase of mixing amount of GS (see Figure 4). When the mixing amount of GS increases from 10% to 30%, 50%, 70% and 90%, the sample weight loss decreases from 82% to 62%, 47%, 35% and 13% respectively. The mixing amount of GS is not equal to the change amount of sample weight loss, which indicates that the interaction between GS and raw coal leads to oxidation combustion weight loss reaction. It has been reported in some literatures that gasification fine slag and fuel coal mixed combustion show significant synergistic effect [5]. Zhang et al [6] research bituminous coal and semi-coke blended combustion and found that there is a significant interaction promotion effect in the blending process.

The maximum rate of mass change is thought to be proportional to the reactivity of the sample. As can be seen from Table 1 and Figure 5, with the increase of mixing amount of GS, the maximum mass change rate \((\text{dm/dt})_{\text{max}}\) of the sample decreases successively. This indicates that after ignition, the sample with high GS content has a lower combustion rate and less heat release, and the higher the GS content is, the more unfavorable the combustion [7]. In other words, the comprehensive combustion characteristic index \(S\) also decreases with the increase of GS content.

### 3.2. Calculation method of thermal analysis kinetic

Thermal kinetic is a method of applying thermal analysis technology to study the physical changes of substances and the rate mechanism of chemical reactions [8]. Two different equations can be used for the rate of loss (or gain) of coal weight:

\[
\frac{dx}{d(t)} = kf(x) \tag{3}
\]

\[
G(x) = kt \tag{4}
\]

\[
f(x) = \frac{1}{G(x)} = \frac{1}{d[G(x)/d(x)]} \tag{5}
\]

Here \(x\) is the weight fraction of coal loss (or gain) at time \(t\), which is calculated on a dry basis. \(k\) is the kinetic mechanism function of rate constant, \(f(x)\) and \(G(x)\) in differential and integral form respectively. The rate constant \(k\) usually assumed to conform to the Arrhenius equation.

\[
k = A \exp\left(-\frac{E}{RT}\right) \tag{6}
\]

By combining formulas (3), (4), (5) and (6), the following formula can be obtained

\[
\frac{dx}{f(x)} = \frac{A}{\beta} e^{-E/RT} dT \tag{7}
\]

In the equation (7), \(A\) is pre-exponential factor, \(E\) is reaction activation energy (kJ/mol), \(R\) is gas constant, the value is 8.314J/ (K·mol). The heating rate was \(dT/dt = \beta\).

The kinetic calculation methods of coal sample combustion include integral method and differential method [9], and there are dozens of specific solving methods in each method. In this paper, Coats-Redfern [10] integral method was used to calculate the combustion kinetic
of blended GS coal sample.

The experiment was carried out under the condition of constant temperature rise. Assume that \( f(x) = (1-x)^n \), the equation (7) can be written as

\[
\frac{dx}{dT} = \frac{A}{\beta} (1-x)^n \exp\left(-\frac{E}{RT}\right)
\]

or

\[
\int_{x}^{1} \frac{dx}{(1-x)^n} = \frac{A}{\beta} \int_{0}^{T} \exp\left(-\frac{E}{RT}\right) dT
\]

Integrate and arrange equation (9), and then take the logarithm of both sides of the equation, and get

\[
\frac{\ln (1-x)^{1-n}-1}{n-1} = \ln \frac{ART^2}{\beta E} \left(1-\frac{2RT}{E} \right) - \frac{E}{RT} \quad (n \neq 1)
\]

\[
\ln \frac{-\ln(1-x)}{T^2} = \ln \frac{AR}{\beta E} \left(1-\frac{2RT}{E} \right) - \frac{E}{RT} \quad (n = 1)
\]

For the general reaction temperature region and most \( E \) values, \( E/RT \approx 1 \), \( 1-2RT/E \approx 1 \), equation (11) can be rewritten as

\[
\ln \frac{-\ln(1-x)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (n = 1)
\]

3.3. Combustion kinetic analysis of coal samples

The oxidation and combustion process of coal samples is generally considered as a first-order reaction [11], so according to equation (12), the figure of \( \ln(-\ln(1-x)/T^2) \sim 1/T \) is drawn (see Figure 6). The slope of the linear fitting is \(-E/RT\), and the intercept is \( \ln(AR/\beta E) \). According to the value of the intercept and slope, the combustion activation energy \( E \) and pre-exponential factor \( A \) can be calculated (see Table 2). In this paper, the main reaction area of the sample combustion was selected as the research object, and the combustion reaction kinetic of the sample was investigated at 317-517°C with the combustion conversion rate \( x \) between 1% and 98%.
Table 2. Kinetic parameters of co-combustion of GS and raw coal.

| Samples | $E$ [kJ mol$^{-1}$] | $A$ [min$^{-1}$] | $R^2$ | Fitting equation |
|---------|-------------------|----------------|-------|-----------------|
| GS-10   | 99.97             | 2.90E+06       | 0.9923| $y=-12024.08x+3.18$ |
| GS-30   | 99.46             | 2.40E+06       | 0.9912| $y=-11962.36x+3.00$ |
| GS-50   | 87.11             | 1.55E+05       | 0.9936| $y=-10477.81x+0.39$ |
| GS-70   | 91.82             | 5.01E+05       | 0.9915| $y=-11044.12x+1.51$ |
| GS-90   | 91.25             | 3.66E+05       | 0.9894| $y=-10975.64x+1.20$ |

It can be seen from Table 2 that the correlation coefficients of the combustion kinetic parameters of the samples fitted by the Coats-Redfern integral method were all greater than 0.98 by using the first-order kinetic equation, indicating good fitting results. The combustion activation energy $E$ decreases first and then increases with the increase of the mixing amount of GS. When the mixing amount of GS is 50%, the minimum apparent activation energy obtained is 87.11kJ/mol. The results show that when the ratio of GS to raw coal is 1:1, the activation energy required to overcome combustion is the lowest. As can be seen from Table 2 and Figure 7, the change trend of pre-exponential factor $\ln A$ of coal sample combustion also decreased first and then increased with the mixing amount of GS. The fitting result accords with the compensation effect between activation energy and pre-exponential factor [12], that is, the change law of activation energy and pre-exponential factor was consistent.

4. Conclusion
In this paper, the combustion characteristics and kinetic of gasification slag (GS) mixed with different proportions in Shenhua raw coal were investigated by thermogravimetric analysis. Shenhua raw coal mixed with GS can improve the overall ignition and burnout characteristics of mixed coal to some extent. When the GS content is 50%, the maximum weight loss temperature $T_{\text{max}}$ is the highest, reaching 498.4°C. The mixing amount of GS is not equal to the change of mass weight loss. Both the maximum mass change rate $(\text{dm/dt})_{\text{max}}$ and the comprehensive combustion characteristic index $S$ decreases with the increase of the content of GS. When the mixing amount of GS was 50%, the minimum apparent activation energy obtained was 87.11kJ/mol.

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