The Combustion Characteristics of Coal Blends under Low Oxygen Atmosphere Using the Thermogravimetric Analyzer

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Abstract. Experiments on coal blends combustion were carried out using simultaneous TGA dynamic runs under low oxygen atmosphere. With the increasing of bituminous coal, the initial combustion temperature increases, however there is no obvious change in the burnout temperature. During coal blends combustion, lignite is dominant in the ignition stage, while bituminous coal has more influence on the burnout stage. The combustion characteristic index (S) indicates that adding bituminous coal will reduce the combustion characteristic of coal. The activation energy (E) is calculated by Coats–Redfern method. The results indicate that with the addition of bituminous coal, the activation increases from 12.58 to 38.4 KJ/mol.

1. Introduction

China is the world’s largest consumer of coal, and it is difficult to change the dominant position of coal power in the short term. However, low energy efficiency, and high pollutant emissions restrict the coal-based energy production and consumption [1]. Dynamic coal blending is a clean coal technology suitable for China’s national conditions, which is conducive to improving the utilization rate of coal thermal energy and reducing the emission of pollutants from coal burning [2].

Domestic and foreign scholars have conducted a series of researches on the combustion characteristics and the release of NOx of mixed coal. Tianyang Chi [3] investigated the characteristic parameters (i.e., relative ignition temperature, maximum ignition points, oscillation frequency, and fluctuation ratio and combustion dynamic energy) with the flame monitoring system. Anxin Weng [4] surveyed the burn-out performance of mixed coal can be improved with the graded combustion. And when the proportion of bituminous coal was 25%, the NOx emission was the lowest. Fernando Rubiera [5] researched the combustion behavior of coal blends in TGA.

Coal pyrolysis is the initial stage of gasification, liquefaction and combustion, which is very important for its transformation. Pyrolysis will vary depending on the conditions (coal type, final temperature, particle size, atmosphere, heating rate, pressure) used in the pyrolysis process [6-10]. However, most of the current investigations are focusing on pyrolysis under inert conditions and combustion with oxygen-rich conditions [11-12]. According to efficient low-nitrogen combustion technology [13] proposed by our research group, coal will be first pyrolyzed under the low-oxygen tail gas, and then burned out in the furnace. Therefore, it is necessary to study the pyrolysis characteristics of coal under the atmosphere of low oxygen.
In this research, the pyrolysis characteristics of lignite, bituminous coal and their blends under 8% O$_2$ atmosphere were studied using TGA analysis. In addition, a reasonable evaluation of coal pyrolysis and kinetic analysis were used to calculate the activation energy of the process.

2. Experimental

2.1. Materials
The lignite and bituminous coal were ground to 80-100 mesh sizes. According to mass ratio, the coal samples were mixed evenly. The coal ratio and serial number of mixed coal were shown in Table 1. Ultimate and proximate analysis of coal samples were shown in Table 2.

Table 1. The serial number of coals

| Samples  | S1  | S2  | S3  | S4  | S5  |
|----------|-----|-----|-----|-----|-----|
| Lignite, | 100%| 70% | 50% | 30% | 0%  |
| Bituminous | 0%  | 30% | 50% | 70% | 100% |

Table 2. Proximate and ultimate analysis of the samples

|                | Ultimate analysis | Proximate analysis |
|----------------|-------------------|--------------------|
|                | C$_{ad}$,%        | H$_{ad}$,%         | N$_{ad}$,%         | S$_{ad}$,% | O$_{ad}$,% | M$_{ad}$,% | A$_{ad}$,% | V$_{ad}$,% | FC$_{ad}$,% |
| S1             | 69.41             | 2.27               | 0.92               | 0.37       | 27.03       | 30.6       | 6.46       | 58.2       | 34.92       |
| S2             | 69.11             | 2.89               | 0.95               | 0.47       | 26.58       | 22.47      | 7.8        | 51.93      | 39.38       |
| S3             | 70.44             | 3.3                | 0.99               | 0.51       | 24.76       | 17.39      | 8.6        | 48.64      | 44.14       |
| S4             | 70.78             | 3.65               | 1.02               | 0.54       | 24.01       | 12.91      | 9.27       | 44.12      | 45.40       |
| S5             | 70.64             | 4.32               | 1.04               | 0.7        | 23.3        | 4.23       | 10.38      | 37.43      | 52.55       |

2.2. Experimental Method
Pyrolysis behavior of two coals and the blends were studied with 50 ml/min flow in a simultaneous thermal analyzer (model TGA/SDTA851e). Samples were submitted to dynamic runs carried out up to 900°C at the heating rate (β=dT/dt) of 15°C/min.

3. Results and Discussion

3.1. Thermal Analysis of Samples
Fig.1a and b shows the weight loss and the instantaneous weight loss rate along with different oxygen concentrations. The separate combustion characteristics of lignite and bituminous coal were greatly different, which indicated that coal rank had great influence on combustion characteristics.
In this paper, the ignition temperature (Ti) was defined by the TG-DTG tangent method [14]. The burnout temperature (Tb) was detected as temperature of 98% of the final weight loss. DTGmax was maximum weight loss rate, Tmax was temperature of maximum weight loss rate and DTGmean was the average weight loss rate. In addition, the combustion characteristic index (S) is also determined using the below mentioned equations to evaluate the combustion performance of the samples and the higher S the better the combustion reactivity.

\[
S = \frac{\frac{dw}{dt}}{\frac{dw}{dt}_{\text{max}} \cdot \frac{dw}{dt}_{\text{mean}}} \frac{1}{T_i \cdot T_b}
\]  

(1)

These characteristic parameters of TG-DTG curves were shown in Table3, which showed more evident differences between the samples. As shown in Table3, with bituminous coal ratio increasing, Ti increased from 330°C to 439°C. The change of ignition temperature may be caused by the volatile content of the coals. However, Tb had similar temperatures at about 880°C except the S1, which indicates that the bituminous coal has great effect on the burnout temperature. Tmax rose from 430°C to 583°C with the bituminous coal ratio increasing. In addition, the combustion characteristic index (S) had a downward trend with the bituminous coal ratio increasing.
Table 3. The characteristic parameters of TG-DTG curves

| Samples | $T_{\text{max}}$ (°C) | $(\text{dw/dt})_{\text{max}}$ (%·°C$^{-1}$) | $(\text{dw/dt})_{\text{mean}}$ (%·°C$^{-1}$) | Ti (°C) | Tb (°C) | $S_{2\cdot °C - 5\cdot 10^{-10}}$ |
|---------|---------------------|---------------------------------|---------------------------------|--------|--------|-------------------------------|
| S1      | 430                 | 0.2798                          | 0.1024                          | 330    | 810    | 3.25                          |
| S2      | 448                 | 0.2597                          | 0.0989                          | 341    | 884    | 2.5                           |
| S3      | 493                 | 0.2506                          | 0.1014                          | 363    | 879    | 2.19                          |
| S4      | 583                 | 0.2417                          | 0.0992                          | 391    | 879    | 1.78                          |
| S5      | 583                 | 0.2644                          | 0.1016                          | 439    | 884    | 1.58                          |

3.2. Kinetic Analysis

Generalizing, the rate of macromolecular compound can be generally described by:

$$\frac{d\alpha}{dt} = kf(\alpha)$$  \hspace{1cm} (2)

where $\alpha$ is the conversion degree; $t$ is time; $k$ the temperature-dependent constant. $\alpha$ and $f(\alpha)$ is defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_{\infty}}$$  \hspace{1cm} (3)

$$f(\alpha) = (1 - \alpha)^n$$  \hspace{1cm} (4)

where $m_0$ is the mass of initial sample; $m_t$ is the mass of $t$ time sample; $m_{\infty}$ is the mass of experiment ended sample; $n$ is the reaction series.

According to the Arrhenius:

$$k = A\exp(-E/RT)$$  \hspace{1cm} (5)

where $A$ is the frequency factor; $E$ is the activation energy; $R$ is the ideal gas constant and $R = 8.3145$ J/(mol·°C).

The above rate expression can be transformed into a non-isothermal rate expression describing reaction rate as a function of temperature at a constant $\beta$ ($\beta = \frac{dT}{dt}$):

$$\frac{d\alpha}{dt^\beta} = A\beta^{-1}\exp(-E/RT)f(\alpha)$$  \hspace{1cm} (6)

Coats-Redfern method [15] was used to process the experimental data and obtain the inverse of coal kinetic parameters. First, the data after processing is fitted with linear relevancy. The $n$ value corresponding to the line closest to 1 was the reaction series, and then the $n$ value of the line is used. The activation energy $E$ was calculated.

The activation energy ($E$) and correlation coefficients ($R^2$) for samples are shown in Table 4. With the bituminous coal ratio increasing, the activation energy increases from 12.58 kJ/mol to 38.4 kJ/mol.

Table 4. E and $R^2$ of the samples

| Samples | S1 | S2 | S3 | S4 | S5 |
|---------|----|----|----|----|----|
| E(KJ/mol) | 12.58 | 23.42 | 30.83 | 35.07 | 38.4 |
| $R^2$ | 0.998 | 0.997 | 0.995 | 0.995 | 0.999 |

4. Conclusions

In this study, the combustion characteristics and kinetics of coal blends were investigated by TGA.

With the increase of bituminous coal, there are other obvious changes in the TG-DTG curves. The lignite had the lower ignition temperature ($T_i$) and burnout temperature ($T_b$). As the proportion of bituminous coal increases, the initial combustion temperature increases (from 330°C to 439°C), however there is no obvious change in the burnout temperature at about 880°C. In the process of coal blends combustion, lignite plays a leading role in the ignition stage, while bituminous coal has more
influence on the burnout stage. The combustion characteristic index (S) (from $3.25 \times 10^{-10}$ down to $1.58 \times 10^{-10}$) indicates that higher proportion of bituminous coal and the worse combustion of coal blend.

In addition, the activation energy (E) was calculated by Coats–Redfern method. The results indicated that with the addition of bituminous coal, the activation energy goes higher, which increases from 12.58 KJ/mol to 23.43 KJ/mol, 30.83 KJ/mol, 35.07 KJ/mol and 38.4 KJ/mol, respectively.

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