Thermogravimetric analysis of combustion characteristics of coal gangue and petroleum coke mixture

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Abstract. In order to improve the comprehensive combustion efficiency of the steam coal and reduce waste of resources, combustion experiments of petroleum coke and coal gangue were carried out by thermogravimetric analyser at different proportions and heating rates. Combustion characteristic curves (TG, DTG, DTA) and combustion characteristic parameters of the blended samples were analysed by thermogravimetric analysis and thermogravimetric analysis. The optimum combustion ratio and combustion characteristic parameters of the blended samples were explored. Experiments show that the combustion performance of petroleum coke and coal gangue is the best when the mixture ratio of petroleum coke and coal gangue is 4:1 in air atmosphere and the flow rate is 30ml/min, and the combustion characteristics of petroleum coke and coal gangue are better than that of single sample. The burning effect of the mixed fuel is the best. The exothermic area of 15℃/min and 25℃/min is greater than that of 20℃/min, which indicates that the heating rate of 20℃/min is not conducive to exothermic.

1. Introduction

Petroleum coke is the final byproduct of petroleum refining. The actual amount of petroleum coke is very limited, and a large part is piled up as waste. Therefore, petroleum coke is used as an alternative or supplementary fuel for coal, and combustion for power generation is an important way to utilize petroleum coke [1-3]. Since the petroleum coke has a low volatile content, the ignition point is high and it is difficult to burn out, its combustion characteristics are greatly affected by the heating rate. Shen Boxiong [4] studied the ignition and burnout characteristics of petroleum coke, and defined the temperature at which the sample began to lose weight as the ignition temperature, and considered that the heating rate had no effect on the ignition temperature. However, Zhou Jun [5] drew different conclusions when studying the combustion characteristics of petroleum coke at different heating rates. Zhou Jun believes that the increasing heating rate will cause the combustion temperature of petroleum coke to rise to the high temperature zone. The ignition temperature, the burnout temperature, and the maximum combustion rate will increase. The above studies are just all petroleum coke burning. Coal gangue is now mixed with petroleum coke. Coal gangue is industrial solid waste that is washed out during coal washing [6-7], which has low calorific value, low volatile content and high ash content, therefore it is difficult to burn. Considering the advantages and disadvantages of two kinds of inferior combustion, the combination of coal gangue and petroleum coke can effectively reduce the ignition temperature, improve the ignition performance and combustion stability, thereby improving the
comprehensive combustion efficiency of coal gangue and petroleum coke, reducing resource waste and preventing Pollution.

2. Experimental part

2.1. Experimental materials

The experiment used 140 mesh Liaohua petroleum coke and 140 mesh Inner Mongolia Ximeng coal gangue as experimental materials. The elemental analysis and industrial analysis are shown in Table 1. The calorific value data is shown in Table 2. It can be seen from Table 1 that petroleum coke has a high carbon content, which is twice more than that of coal gangue, with little volatile matter and low ash. Coal gangue has a high ash content and contains less than half of the carbon coke. Elemental analysis shows that the elemental composition of petroleum coke is mainly composed of carbon, hydrogen, oxygen, nitrogen and sulfur, and the five elements in coal gangue only account for about 50%.

| Table 1. Elemental Analysis and industrial analysis of test samples. |
|---------------------------------------------------------------|
| Industrial analysis/% | Elemental analysis/% |
| Mad | Aad | Vad | FCad | Cad | Had | Oad | Nad | Sad |
| Petroleum | 2.73 | 0.79 | 12.85 | 83.63 | 87.87 | 2.75 | 2.25 | 2.06 | 1.63 |
| Coal gangue | 0.58 | 52.5 | 12.56 | 34.36 | 44.85 | 5.93 | 6.18 | 1.19 | 0.11 |

| Table 2. Experimental data of calorific value of samples. |
|---------------------------------------------------------------|
| Coal sample | Bullet barrel heat (kJ/kg) | Low level receives base |
| Coal gangue | 12802.51 | 9746.35 |
| Petroleum coke | 36430.48 | 31483.24 |

2.2. Experimental instruments and methods

In this paper, Seycheldam's Setsys Evo synchronous thermogravimetric analyzer is used to separate and mix petroleum coke with coal gangue. The sample quality is about 10 mg, and the mixing ratio is 1:4, 2:3, 3:2, 4:1 (petroleum coke: coal gangue). High purity argon was used as the shielding gas. The combustion test was carried out under an air atmosphere at a flow rate of 30 mL/min. The temperature programming rate is: 10℃/min, 15℃/min, 20℃/min, 25℃/min, and the combustion temperature ranges from 40 ℃ to 1400 ℃.

3. Results and analysis

3.1. Analysis of combustion characteristics of different mixing ratio samples

3.1.1. Analysis of TG curves with different mixing ratios. Petroleum coke is difficult to burn alone. So the combustion process is unstable and exhibits multiple stages of combustion [8-10]. The petroleum coke and coal gangue are now mixed at a ratio of 1:4, 2:3, 3:2, 4:1 respectively. The difference between the combustion characteristics of the mixed sample and the combustion characteristics of the single sample was analyzed. The TG curves of different mixing ratios are shown in Figure 1. It can be seen from Figure 1 that the weight loss curves of the four mixing ratios are generally consistent, but the burnout temperatures are different. Before the temperature reaches the ignition temperature, when the temperature is heated to about 400℃, the curve in the TG diagram has some obvious rise, and the slight increase in weight. Because when the temperature rises slowly, the sample is thermally expanded, in the meanwhile a chemisorption reaction occurs in combination with oxygen, causing the
TG curve to rise, resulting in weight gaining. When the temperature reaches about 500℃, the sample is volatilized and analyzed for combustion, and the TG curve shows obvious weight loss.

**Figure 1.** TG curves of samples with different mixing ratios.

In this paper, we use the TG-DTG joint definition method [11-12], that is, on the DTG curve, the over-peak point is perpendicular to the TG curve at point A, and the point A is the tangent to the TG curve, which is parallel to the beginning of the weight loss. The intersection temperature of the line is the ignition temperature. The burnout temperature is the temperature at which the mass of the substance burns and never changes. The combustion characteristic parameters of the sample are shown in Table 3. The combustion conversion rates of the six groups of samples are 45.81%, 47.43%, 60.01%, 67.05%, 85.94%, 80.64%. The mixed sample with a mixing ratio of 4:1 has the highest combustion conversion rate. Coal gangue has the lowest conversion rate and shortest burning time, and the burnout temperature is about 805℃. With the increase of petroleum coke content in the mixed sample, the conversion rate gradually increases, the combustion curve of the mixed fuel moves to the right, and the burnout temperature rises to the high temperature region. This is mainly due to the high combustion temperature zone of petroleum coke. It can be shown that the mixed combustion of coal gangue and petroleum coke can improve the combustion quality of a single sample, but the mixing ratio of the sample is required, and the comprehensive combustion characteristics of the 4:1 mixed sample is the best.

**Table 3.** Combustion characteristic parameters of samples.

| Sample ratio     | Ignition temperature T_i/°C | Peak temperature T_p/°C | Burnout temperature T_f/°C | Weight loss rate α/% |
|------------------|-----------------------------|--------------------------|-----------------------------|----------------------|
| Coal gangue      | 425                         | 620                      | 805                         | 45.81                |
| 80% coal gangue  | 440                         | 550                      | 865                         | 47.43                |
| 60% coal gangue  | 446                         | 626                      | 889                         | 60.01                |
| 40% coal gangue  | 450                         | 604                      | 1146                        | 67.05                |
| 20% coal gangue  | 451                         | 607                      | 1040                        | 85.94                |
| Petroleum coke   | 454                         | 652                      | 1048                        | 80.64                |

**3.1.2. Analysis of DTG curves with different mixing ratios.** It can be seen from the DTG graph that the coal gangue has only one obvious weight loss peak, which is caused by the combustion of the volatile analysis, while the fixed carbon portion is not burned vigorously, and no weight loss peak is formed on the DTG graph. Figure 2 is a DTG curves of samples with different mixing ratios. There are two obvious weight loss peaks at 650℃ and 1050 ℃ on the DTG curve, but the difference between the two peaks is large, and the temperature difference between the two peaks is very large, indicating that
the volatiles need time and temperature reserve energy after combustion. Fixed carbon fires and burns. In the mixed sample, two significant weight loss peaks appeared in the DTG curve. As the petroleum coke content increased, the second peak became more obvious. This phenomenon is mainly due to the large volatile matter content of coal gangue, the volatile matter is easy to burn, but the impurities are more, and the content of combustible part is less. The petroleum coke has a small volatile content and a large fixed carbon content. The fixed carbon has a large heat release but is not easy to catch fire. This reflects the fact that the petroleum coke is difficult to burn but has a high calorific value.

3.1.3. Analysis of DTA curves with different mixing ratios. The thermal difference analysis method is that the measured substance changes in a certain environment, and a thermal effect is generated, and a peak appears on the thermal difference analysis curve. In the thermal difference analysis, it is generally prescribed that the peak at the top of the peak is an exothermic peak. The larger the thermal effect is, the larger the area of the peak is. The area of the exothermic peak is the exothermic zone. Figure 3 is a DTA graph of different mixing ratios of petroleum coke and coal gangue. Table 4 Exothermic regions of DTA curves. It can be seen from the figure that the peak point of the 60% coal gangue curve is the highest, followed by 20% coal gangue and single petroleum coke. The peak point of the single coal gangue curve is higher than 80% coal gangue, while 40% coal gangue peak point is the lowest. As the blending ratio of petroleum coke in coal gangue increases, the exothermic peak of the sample does not increase proportionally. When the mixing ratio is too small, the exothermic peak point is significantly lower than the single sample, and the heat release will decrease. Conducive to
heat release, such as 40%, 80% coal gangue exothermic peak is lower than a single coal gangue. With the increase of the blending ratio of petroleum coke in coal gangue, the exothermic peak of DTA curve appears to shift to the right, indicating that with the increase of petroleum coke blending ratio, the end temperature of the sample exotherm is very high. Compared with the heat release area of DTA curve of different mixing ratio samples, the heat release area of petroleum coke is the largest, indicating that the calorific value of petroleum coke is higher, followed by 20% coal gangue and 60% coal gangue, indicating that the amount of petroleum coke increases. It is beneficial to the exothermic heat of the mixed sample.

Table 4. Exothermic regions of DTA curves.

| Sample ratio   | Vertex | Peak      | Highest exotherm/(J.g⁻¹) |
|----------------|--------|-----------|--------------------------|
| Coal gangue    | 753    | 523-823   | 38.63                    |
| 80% coal gangue| 630    | 482-915   | 29.68                    |
| 60% coal gangue| 805    | 597-859   | 51.77                    |
| 40% coal gangue| 717    | 492-984   | 25.55                    |
| 20% coal gangue| 992    | 532-1004  | 47.70                    |
| Petroleum coke | 1024   | 596-1062  | 46.33                    |

3.2. Analysis of combustion characteristics of mixed samples at different heating rates

3.2.1. Analysis of TG curves with different heating rates. From the above analysis of the experimental data, it can be known that the petroleum coke and coal gangue have the best combustion performance at a ratio of 4:1, and the ignition characteristics and ignition stability are better than those of a single sample. In this experiment, the effect of different heating rates on the combustion characteristics of the mixed samples was studied under the condition of 4:1 mixing ratio. The TG curves for different heating rates are shown in Figure 4. It can be seen from the TG curve that the TG curves of the four groups of samples are roughly the same. As the heating rate increases, the initial temperature and the burnout temperature of the four groups of samples also increase, and the temperature is exhausted at 10°C/min. The lowest temperature is about 650°C; the second is 15°C/min, 20°C/min and 25°C/min; the highest burnout temperature is about 1100°C, which can be seen that the burnout temperature difference is about 450°C, indicating that this stage of temperature rise. The rate has a great influence on the combustion temperature. As the heating rate increases, the combustion of the mixed sample requires a higher temperature, that is, at a faster heating rate, the corresponding combustion temperature is higher, otherwise the reaction efficiency will be affected.

Figure 4. TG curves of different heating rates.
The temperature and quality of the burning characteristics of the sample are shown in Table 5. As can be seen from Table 5, the combustion conversion rates of the four groups were 34.52%, 48.83%, 45.16%, and 62.55%, and the conversion rate was the lowest at 10°C/min. The conversion rate at 15°C/min was higher than at 20°C/min, but the conversion rate at 25°C/min is the highest. Combined with the TG and DTG curves, it can be seen that as the heating rate increases, the conversion rate of the sample is not linearly related to the heating rate, and the conversion rate of 15°C/min is significantly higher than 10°C/min and 20°C/min. The conversion rate at 10°C/min is the lowest. Because the heating rate is low, the temperature of the sample rises slowly, and the combustion is analyzed with the volatilization, so that a substance that hinders the contact of oxygen with the sample is formed on the surface of the sample particle, resulting in insufficient combustion of the fixed carbon, which affects the overall combustion efficiency of the sample. Although the conversion rate at 25°C/min is the highest, the temperature, at which the combustion reaction is severe, is also the highest. Because the increase in the heating rate causes the heat transfer efficiency of the sample particles to decrease, the heat cannot be transferred to the center of the particles in time [13-14], that is, heat. The hysteresis makes the central temperature of the coal sample not as high as the outside, inhibits the internal volatilization analysis, and does not provide enough heat for the subsequent fixed carbon cracking combustion, so that the fixed carbon cracking combustion requires additional energy from the outside. Based on the above analysis, the combustion effect at 15°C/min is the best.

Table 5. Combustion characteristic parameters of samples.

| Heating rate/(°C·min⁻¹) | Ignition temperature T_i/°C | Peak temperature T_p/°C | Burnout temperature T_f/°C | Weight loss rate α/% |
|--------------------------|-----------------------------|--------------------------|---------------------------|---------------------|
| 10                       | 458                         | 522                      | 668                       | 34.52               |
| 15                       | 465                         | 531                      | 685                       | 48.83               |
| 20                       | 473                         | 540                      | 782                       | 45.16               |
| 25                       | 490                         | 630                      | 1097                      | 62.55               |

3.2.2. Analysis of DTG curves with different heating rates. It can be seen from the Figure 5 is a DTG graph that there are two significant weight loss peaks at 10 °C/min and 15°C/min in the four samples. The first weight loss peak is caused by the combustion of the volatile analysis, and the second weight loss peak is fixed. Due to carbon cracking and combustion, the two weight loss peaks are close to each other, and the temperature difference is about 100°C, indicating that the combustion and fixed carbon combustion occur successively in the volatilization analysis. At 20°C/min, only a significant weight loss peak appeared on the DTG curve, indicating that the heating rate increased. The sample was only burned violently during the volatile analysis stage, and the generated heat could not be transferred to the inside of the sample in time, resulting in a fixed carbon burning station. Insufficient heat requirement causes the sample to react less strongly during the stationary carbon combustion phase, forming a half-shoulder peak on the DTG curve. The temperature of the two weight loss peaks in the DTG curve at 25°C/min is very different, about 400°C, indicating that the heat supplied by the volatiles is not enough to support the fixed carbon combustion of the latter sample, so it takes time and temperature to reserve energy with the purpose of fixing carbon ignition and combustion, which is consistent with the above TG curve analysis, that is, the thermal hysteresis effect makes combustion difficult.

3.2.3. Analysis of DTA curves with different heating rates. Figure 6 is a DTA curve of mixed combustion of petroleum coke and coal gangue at different heating rates (10, 15, 20, 25°C/min) at the same particle size (140 mesh). The peak point of the 10°C/min curve is the lowest, the peak point of the 15°C/min curve is higher than that of the 20°C/min curve, and the peak point of the 25°C/min curve is the highest. It can be seen that the increase of the heating rate has a certain promoting effect on the exothermic, but it is not a positive correlation increase. When the heating rate is within...
20℃/min, the exotherm decreases and the exothermic peak decreases. It can be seen from the DTA graph that as the temperature rises, the exothermic peaks of the different heating rate curves are obviously shifted to the right, while the leftward shift phenomenon is smaller, indicating that the heating rate change is from the exothermic. The initial and termination temperatures have a greater impact, which is contrary to the conclusions by Wang Ruijie [15] in the influence of heating rate on pyrolysis of mixed coal samples and kinetic analysis. The total exothermic area of the sample at 15℃/min and 20℃/min is similar, the exothermic area at 10℃/min is the smallest, and the exothermic area at 25℃/min is the largest, indicating that the heating rate is 25℃/min. Well, the rate of temperature rise is too small to help the heat release. Table 6 is the exothermic regions of DTA curves.

![Figure 5. DTG curves of different heating rates.](image)

![Figure 6. DTA curves of different heating rates.](image)

| Heating rate/(℃·min⁻¹) | Vertex | Peak temperature/℃ | Highest   |
|-------------------------|--------|---------------------|-----------|
| 10                      | 620    | 504-680             | 15.31     |
| 15                      | 650    | 497-695             | 30.24     |
| 20                      | 752    | 598-804             | 27.96     |
| 25                      | 1035   | 655-1103            | 50.89     |

4. Conclusions
After several experiments, the particle size and air flow of the above-mentioned coal sample were selected reasonably, and the experimental results were reproducible, and the following conclusions were drawn:
(1) By analyzing the combustion characteristic curves of different mixing ratio samples, it can be seen that as the petroleum coke content increases, the conversion rate of the mixed sample gradually increases, and the burnout temperature moves to the high temperature region, and the fixed carbon combustion of the sample also comes. As the heat supplied by the former volatiles is increasingly needed, the exothermic peak of the DTA curve appears to shift to the right, indicating that as the petroleum coke blending ratio increases, the end temperature of the sample exotherm is greatly affected, and the ratio is too small. It is not conducive to exotherm, and the best exothermic effect is 20% coal gangue, which is consistent with the conclusion of the TG curve. The 4:1 mixed sample has the best comprehensive combustion characteristics.

(2) By analyzing the combustion characteristic curves of mixed samples with different heating rates, it is known that as the heating rate increases, the initial temperature, burn-out temperature and conversion rate of the sample also increase, although the conversion rate at 25℃/min is the largest, but the required combustion temperature is also the largest, and the combined combustion efficiency at 15℃/min is the best, indicating that the change in heating rate has a greater impact on the combustion reaction. It can be seen from the DTA curve that the increase of the heating rate has a certain promoting effect on the exothermic, but it is not a positive correlation increase. The exothermic heat of 15℃/min and 25℃/min is higher than that of 20℃/min, indicating that the heating rate of 20℃/min is not conducive to heat release.

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