Research on combustion properties and thermokinetic of pulverized coal: raw and pre-oxidized samples

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Abstract. The combustion behaviors of raw and pre-oxidized samples for two pulverized coals (PC) were investigated using a thermogravimetric (TG) analyzer. The mass variations, characteristic temperatures and combustion characteristic parameters, et al. of PC during oxidation combustion were analyzed. The results demonstrated that the ignition temperatures (T_i) and burnout temperatures (T_b) of pre-oxidized PC were lower than those of raw PC. The total mass losses of the four samples were 91.33, 92.32, 88.85, and 90.02 mass% respectively, which were consistent with the volatile matter and fixed carbon contents (V_ad+FC_ad). The calculated combustion characteristic parameters (the ignition index C_i, burnout index C_b, and comprehensive combustibility index S_n) of pre-oxidized samples were all greater than those of raw samples, which indicated that pre-oxidized PC was more prone to self-ignition than raw PC under the same conditions. The thermokinetic parameters of PC during pyrolysis and combustion were studied by Coats–Redfern method. The apparent activation energy E_a of these four PC samples ranged from 45.12 to 55.37 kJ/mol.

1. Introduction
Coal is one of the main fossil fuels in china, accounting for ca. 60% of primary energy consumption [1]. Moreover, to achieve the aims of high efficiency and cleanliness, coal is extensively used in thermal power plants and chemical industries in the form of dust (diameter less than 74 µm) [2]. However, a smaller particle size means larger surface area, which causes that pulverized coal (PC) is easier to react with oxygen and release heat, enhancing the possibility of spontaneous combustion [3]. In addition, spontaneous combustion of PC can seriously pollute the environment, even causing a dust explosion accident, which can result in equipment damage and casualties [4]. Therefore, it is necessary to understand the combustion behaviors of PC and further guide us to prevent self-ignition.

In general, to achieve maximum combustion performance, the PC needs to be milled, sieved and dried before entering the boiler [5]. However, the undesired deposition of PC occurs frequently at these zones, especially in the coal mill inlet and horizontal section of fine powder separator [6]. Furthermore, due to the effects of preheater air temperature and air leakage, the temperature in these areas is as high as 100 °C or more, which further causes that the PC is oxidized. The conclusion has also been confirmed, i.e., the reactivity of pre-oxidized PC is greater than that of the raw one [7]. Thus, the possibility of spontaneous combustion or explosion of deposited PC is increased dramatically, posing a serious threat to safe production. In addition, oxidation phenomenon often occurs in the PC...
bunker, and the risk of self-ignition can be rose if the pre-oxidized PC is directly used in production. Meanwhile, several studies on the self-ignition characteristics of pre-oxidized PC have been conducted [8]. Deng et al. [9] studied the microscopic characteristics of secondary oxidation coal and found that secondary oxidation coal was more prone to spontaneous combustion than raw coal. Zhang et al. [10] suggested that the limiting parameters of secondary oxidation coal were all higher than those of primary oxidation coal before cross temperature, and the opposite law after cross temperature. However, the comparative analysis regarding combustion behaviors between raw and pre-oxidized PC is relatively rare. Thus, further research is still necessary.

In this study, combustion characteristics of pre-oxidized and raw PC with different rank were investigated by thermogravimetric (TG) analysis. Based on numerous literature researches on PC combustion, the three combustion characteristic parameters (the ignition index $C_i$, burnout index $C_b$, and comprehensive combustibility index $S_n$) were applied to evaluate the combustion performance of PC. Moreover, the thermokinetic parameters during the pyrolysis and combustion were calculated using the Coats–Redfern method to reveal PC combustion.

2. Experiment and methods

2.1. Preparation of samples

Two coal samples were collected from Gubei coal mine (GB) and Zhiuji coal mine (ZJ) respectively, located in Huainan city, Anhui Province, China. These samples were milled and sieved into dust with diameter of 74 μm or less, and were directly regarded as raw coal sample. Subsequently, these two PC samples were heated at 100 °C in air for 1 h (simulating the actual situation) by a hot-oven test (Fig. 1) and applied as the pre-oxidized samples. These pre-oxidized samples were marked as OGB and OZJ, respectively. The results of proximate analyses are listed in Table 1. Notably, the moisture content of the pulverized coal was remarkably reduced after the pre-oxidation treatment. Moreover, the volatile matter and fixed carbon contents described a tiny increase trend.

![Fig. 1. Schematic diagram of hot oven apparatus.](image)

| Samples | $M_{ad}$ (mass%) | $A_{ad}$ (mass%) | $V_{ad}$ (mass%) | $F_{C ad}$ (mass%) |
|---------|-----------------|-----------------|-----------------|------------------|
| GB      | 2.39            | 12.73           | 30.22           | 54.66            |
| ZJ      | 3.27            | 16.10           | 26.24           | 55.39            |
| OGB     | 0.66            | 11.66           | 32.15           | 55.44            |
| OZJ     | 0.79            | 15.48           | 27.92           | 55.71            |

Notes: $M$ is moisture; $A$ is ash; $V$ is volatile matter; $F_{C}$ is fixed carbon.
2.2. Thermogravimetric test

The thermal analysis experiments were conducted by a TG thermal analyzer (PerkinElmer Pyris 1, USA) with a sensitivity of 10⁻⁷ g. To reduce heat release and satisfy experimental requirements, the initial mass of coal sample was roughly 6 mg during the experiments. The samples were heated from 30 to 800 °C at a heating rate (β) of 5 °C min⁻¹. Moreover, these pulverized coal samples were tested under air atmosphere with a flow rate of 20 mL min⁻¹. The schematic diagram of TG thermal analyzer was described in Fig. 2.

2.3. Calculation of combustion characteristics parameters

In this study, the ignition index (Ci, %/min³), burnout index (Cb, %/min⁴), and comprehensive combustibility index (Sn, %²/(°C³ min⁻²)) were adopted to evaluate the ignition, burnout and combustion performances of PC. Furthermore, coal samples with a high Sn value have a more gratifying combustion performance. These parameters could be calculated using Eqs. (1)-(3):

\[ C_i = \frac{(dw/dr)_{\text{max}}}{t_{\text{ig}, \text{max}}}, \]
\[ C_b = \frac{(dw/dr)_{\text{max}}}{\Delta t_{1/2}}, \]
\[ S_n = \frac{(dw/dr)_{\text{max}} (dw/dr)_{\text{ave}}}{T_i^{2} T_b}, \]

where (dw/dr)_{max} is the maximum mass loss rate (%/min); (dw/dr)_{ave} is the average mass loss rate (%/min); ti, tmax, and tb are the ignition time, peak time, and burnout time (min), respectively; Δt_{1/2} is the time zone of \((dw/dr)/(dw/dr)_{\text{max}} = 1/2\) (min).

2.4. Thermokinetic analysis

In this study, the Coats–Redfern integral method was applied to calculate the thermokinetic parameters during the PC oxidation combustion. The detailed calculation equations were generally described as [11]:

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

where \(\alpha\) is the conversion degree; \(T\) is the coal temperature (K); \(A\) is the pre-exponential factor (1/min); \(R\) is the universal gas constant (8.314 J/(mol K)); \(E_a\) is apparent activation energy (kg/mol); \(n\) is the reaction order; \(\beta\) is the heating rate (°C/min).

We can gain the \(E_a\) and \(A\) according to the slope and intercept of the regression line by plotting \[\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]\] versus 1/T and \[\ln\left[\frac{1-(1-\alpha)^{-n}}{T^2 (1-n)}\right]\] versus 1/T, respectively.
3. Results and discussion

3.1. TG/DTG analysis

Fig. 3(a) depicts TG and DTG curves of GB sample in the process of oxidation combustion at a heating rate of 5 °C min\(^{-1}\). Based on the variation of TG and DTG curves, five characteristic temperatures were determined during oxidation combustion of PC. The \(T_f\), \(T_m\), \(T_{ig}\), \(T_{max}\), and \(T_b\) represented respectively the temperatures of the maximum water evaporation and gas desorption, maximum oxidization mass gain, ignition, maximum mass loss rate, and burnout. In addition, according to these characteristic temperatures and the variation of TG curves, the whole oxidation combustion process of PC was divided into four stages: water evaporation and gas desorption (I), oxygen absorption mass gain (II), pyrolyzation and combustion (III), and burnout (IV).

![TG and DTG curves of the PC during oxidation combustion at a heating rate of 5 °C min\(^{-1}\): (a) GB, (b) GB versus OGB.](image)

The contrasts analysis of TG and DTG curves between GB and OGB samples in the process of oxidation combustion at a heating rate of 5 °C min\(^{-1}\) is presented in Fig. 3(b). When the temperature was below approximately 250 °C, the TG and DTG curves of these two samples embodied an extremely similar variation due to the low coal temperature and oxidation reaction rate. Moreover, the reaction intensity between coal and oxygen increased gradually with the temperature increased, and depicted a mild raise in mass loss rate from DTG curves. Subsequently, the coal samples entered into the acute combustion period after the temperature exceeded \(T_{ig}\) of coal, and the mass loss rate reached the maximum through a tiny time. It is transparent that the \(T_{ig}\) values of GB and OGB samples were 380.6 and 362.9 °C respectively, differing by ca. 18 °C. And the \(T_{max}\) value of OGB sample was less than approximately 7 °C from GB sample. Generally, the high moisture content could affect the thermal conductivity of oxidation combustion [12]. Thus, the GB sample reached the \(T_{ig}\) and \(T_{max}\) later. Meanwhile, the endothermic evaporation of moisture could also delay the PC combustion process. Besides, a portion of steady functional groups in the GB sample were activated as activating molecules that readily reacted with oxygen upon pre-oxidation treatment. This caused that the OGB sample could be ignited at a relatively lower temperature.

The detailed information of combustion characteristic parameters of samples is listed in Table 2. The \(T_m\) values of the four PC samples ranged from 247.8 to 290.4 °C. Meanwhile, the \(T_m\) values of OGB and OZJ samples were 247.8 and 269.5 °C, respectively, which were lower than those of raw samples (i.e., GB and ZJ) of 263.6 and 290.4 °C. A high ash content can affect the oxygen diffusion efficiency, and hindering the oxidation reaction of raw samples. Therefore, the GB and ZJ sample achieved \(T_m\) later. The \(T_{ig}\) values of GB, ZJ, OGB and OZJ samples were 380.6, 404.9, 362.9, and 389.2 °C, respectively; Meanwhile, the \(T_{max}\) values were 447.7, 453.6, 440.6, and 446.2 °C, respectively. Based on the previous study, the volatile matter was a key component that caused self-ignition; Its high content could boost the oxidation reaction intensity, and cause that the characteristic temperatures were reached early [13]. In addition, the \(T_b\) values ranged from 504.3 to 534.1 °C. Notably, besides the ash and volatile matter, the fixed carbon and oxygen adsorption can also effect the characteristic temperature and oxidation combustion process of PC.
Table 2 Characteristic parameters of the PC samples during oxidation combustion.

| Sample | GB | ZJ | OGB | OZJ |
|--------|----|----|-----|-----|
| $T_f$ (°C) | 120.3 | 144.9 | 112.5 | 130.3 |
| $T_m$ (°C) | 263.6 | 290.4 | 247.8 | 269.5 |
| $T_{ig}$ (°C) | 380.6 | 404.9 | 362.9 | 389.2 |
| $T_{max}$ (°C) | 447.7 | 453.6 | 440.6 | 446.2 |
| $T_b$ (°C) | 522.4 | 534.1 | 504.3 | 521.7 |
| I mass loss (%) | 1.19 | 1.23 | 1.03 | 0.89 |
| II mass loss (%) | -2.58 | -2.31 | -1.76 | -1.56 |
| III mass loss (%) | 90.63 | 92.83 | 87.85 | 90.21 |
| IV mass loss (%) | 2.09 | 0.57 | 1.73 | 0.48 |
| Total mass loss (%) | 91.33 | 92.32 | 88.85 | 90.02 |

The mass losses in each period during oxidation combustion are also presented in Table 2. As the increase in temperature, each sample experienced a tiny mass loss at the initial phase and hereafter steep mass loss until burnout. The mass loss values in phase I, II, III, and IV ranged from 0.89 to 1.23, -1.56 to -2.58, 87.85 to 92.83, and 0.48 to 2.09, respectively. The mass loss values in stage I of the pre-oxidized PC were below than its raw PC, which might be related to a decrease in moisture content. For all four samples, the maximum mass losses were observed in phase III, indicating that vigorous combustion occurred at this stage. Notably, a tiny mass loss occurred in phase IV, and high temperature pyrolysis of ash was the main factor for this phenomenon. The total mass losses of GB, ZJ, OGB, and OZJ samples were 91.33, 92.32, 88.85, and 90.02 mass%, which were consistent with volatile matter and fixed carbon contents. Nevertheless, the sample mass applied in TG test was relatively low and cannot entirely represent the actual situation. Thus, it is essential to conduct a larger-scale simulation experiment or a field industrial test for gaining the more precise result.

3.2. Analysis of combustion characteristic parameters

According to the Eqs. (1)-(3), we calculated $C_i$, $C_b$, and $S_n$ to evaluate the combustion performance of PC, and their detailed values are listed in Table 3. The DTG$_{max}$ values of GB, ZJ, OGB, and OZJ samples were 3.64, 3.19, 6.13, and 4.43 %/min, respectively. Therefore, the DTG$_{max}$ values of pre-oxidized samples were higher than those of raw samples, indicating that pre-oxidized PC had a larger volatile release rate at their peak temperatures. Moreover, the ignition index $C_i$ and burnout index $C_b$ of pre-oxidized samples were all greater than its raw samples, which might be attributed to the increase in DTG$_{max}$ and the decline in $T_{ig}$, $T_{max}$, and $T_b$. The high $C_i$ suggested that the PC was readily to be ignited and the high $C_b$ could cause a lengthened combustion process, which indicated that the pre-oxidation PC was more prone to spontaneous combustion. Similarly, the results of comprehensive combustibility index $S_n$ were in accordance with those of $C_i$ and $C_b$.

Table 3 Combustion characteristic parameters of PC samples.

| Sample | DTG$_{max}$ (%/min) | DTG$_{ave}$ (%/min) | $C_i \times 10^4$ (%/min$^3$) | $C_b \times 10^4$ (%/min$^4$) | $S_n \times 10^8$ %$^2$/(°C$^3$ min$^2$) |
|--------|----------------------|----------------------|-------------------------------|-------------------------------|----------------------------------|
| GB     | 3.64                 | 0.57                 | 5.34                          | 0.79                          | 3.74                             |
| ZJ     | 3.19                 | 0.58                 | 3.57                          | 0.61                          | 2.44                             |
| OGB    | 6.13                 | 0.53                 | 8.58                          | 1.03                          | 4.89                             |
| OZJ    | 4.43                 | 0.56                 | 4.61                          | 0.75                          | 2.89                             |
Referring to the previous study [14], the relevance between the combustion characteristic parameters (i.e., \( C_i \), \( C_b \), and \( S_n \)) and \((\text{Vad} + \text{FCad})/\text{Aad}\) was delved, and the results were illustrated in Fig. 4. Fig. 4(a) demonstrates that the \( S_n \) had a high linear correlation with \((\text{Vad} + \text{FCad})/\text{Aad}\) (\( R^2=0.965 \)), indicating that the method was feasible. \( S_n \) enhanced with the increasing \((\text{Vad} + \text{FCad})/\text{Aad}\). Moreover, the variations of \( C_i \) and \( C_b \) had a high consistency with that of \( S_n \) (Fig. 4(b)). For PC combustion, the oxidation process was influenced by the synergy of Ash, fixed carbon, and volatile contents. In addition, the combustion performance of pre-oxidized PC was more satisfactory because of its high volatile and fixed carbon contents and the low ash content.

### 3.3. Thermokinetic analysis

The \( E_a \) and \( A \) during pyrolysis and combustion (stage III) were calculated using Eqs. (4) and (5) to evaluate the thermokinetic characteristics of raw and pre-oxidized PCs. Fig. 5 illustrates the Arrhenius plots of the GB and ZJ samples using different reaction orders. The detail values of \( E_a \) and \( A \), and the mechanisms that generated the highest \( R^2 \) are listed in Table 4. Overtly, the \( R^2 \) value of each sample was higher than 0.98, which suggested that the calculation results were reliable. For these four PC samples, the calculated values were the most precise when \( n = 1.5 \). The \( E_a \) values of GB, ZJ, OGB, and OZJ samples were 48.35, 55.37, 45.112, and 51.95 kJ/mol, respectively. The \( E_a \) of OGB sample was lower than that of GB sample by 3.23 kJ/mol; Similarly, the \( E_a \) of OZJ sample was also below than that of ZJ sample by 3.42 kJ/mol. The low \( E_a \) value meant a higher reactivity and combustion performance [15]. Thus, it was concluded that the pre-oxidized PC was prone to spontaneous combustion. In addition, the variation of \( A \) values was consistent with that of \( E_a \).

![Fig. 4 Relationship between combustion characteristic parameters and \((\text{Vad} + \text{FCad})/\text{Aad}\).](image)

![Fig. 5 Fitting plots of the GB and ZJ samples using various reaction rates.](image)

\[
Y = \ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right] (n = 1), \quad Y = \ln \left[ \frac{1-(1-\alpha)^{1-n}}{T^{2-n}(1-n)} \right] (n \neq 1)
\]
Table 4 Thermokinetic parameters of PC samples during pyrolyzation and combustion.

| Sample | Temperature range | $E_a$ (kJ/mol) | $A$ (1/min) | $n$ | $R^2$ |
|--------|-------------------|----------------|-------------|-----|-------|
| GB     | 263.6-522.4       | 48.35          | 345.47      | 1.5 | 0.985 |
| ZJ     | 290.4-534.1       | 55.37          | 1003.33     | 1.5 | 0.988 |
| OGB    | 247.8-504.3       | 45.12          | 279.33      | 1.5 | 0.987 |
| OZJ    | 269.5-521.7       | 51.95          | 789.42      | 1.5 | 0.991 |

4. Conclusions

(1) Based on the TG and DTG curves, the whole combustion process of PC can be divided into four stages, and the total mass losses of GB, ZJ, OGB, and OZJ samples were 91.33, 92.32, 88.85, and 90.02 mass%, respectively. Pre-oxidized treatment resulted in a mild increase in volatile matter and fixed carbon, as well as a decrease in moisture and ash contents.

(2) The characteristic temperatures of pre-oxidized PCs were below than those of raw samples; meanwhile, the combustion characteristic parameters ($C_i$, $C_b$, and $S_n$) of pre-oxidized sample were higher than those of raw sample because of its high volatile matter and fixed carbon contents and low ash content.

(3) The thermokinetic parameters $E_a$ and $A$ of PC were the most accurate when $n$ was 1.5, and the apparent activation energy $E_a$ of OGB and OZJ samples (45.12 and 51.95 kJ/mol) were higher than those of GB and ZJ samples (48.35 and 55.37 kJ/mol).

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References
[1] Deng J., Lei C., Xiao Y., Cao K., Ma L., Wang W., Laiwang B. (2018) Determination and prediction on "three zones" of coal spontaneous combustion in a gob of fully mechanized caving face. Fuel, 211:458–470.
[2] Du R., Wu K., Zhang L., Xu D., Chao C., Zhang B. (2017) A sectioning method for the kinetics study on anthracite pulverized coal combustion. J. Therm. Anal. Calorim., 130:2293–2299.
[3] Ma L., Zou L., Ren L., Wang J., Wang W. (2019) Reactivity and spontaneous combustion characteristics of high-sulphur coal during low-temperature oxidation. Int. J. Oi Gas Coal T., 21:375–389.
[4] Feng G., Wu Y., Zhang C., Hu S., Shao H., Xu G. (2017) Changes on the low-temperature oxidation characteristics of coal after CO$_2$ adsorption: a case study. J. Loss Prevent. Proc. 49:536–544.
[5] Ueki Y., Yoshiie R., Naruse I., Matsuzaki S. (2017) Effect of hydrogen gas addition on combustion characteristics of pulverized coal. Fuel Process. Technol., 161:289–294.
[6] Xiao Y., Ren S., Deng J., Shu C. (2018) Comparative analysis of thermokinetic behavior and gaseous products between first and second coal spontaneous combustion. Fuel, 227:325–333.
[7] Song Z., Kuenzer C. (2014) Coal fires in china over the last decade: a comprehensive review. Int. J. Coal Geol., 133:72–99.
[8] Yi B., Zhang L., Mao Z., Huang F., Zheng C. (2014) Effect of the particle size on combustion characteristics of pulverized coal in an O$_2$/CO$_2$ atmosphere. Fuel Process. Technol., 128:17–27.
[9] Deng J., Zhao J., Zhang Y., Wang C., Wang K. (2016) Experiment on secondary oxidation spontaneous combustion characteristics of low metamorphic degree coal. Coal Sci. Technol. 44:49–54.
[10] Zhang X., Li Q., Xiao Y., Lu J., Deng J. (2016) Experiment study on the limit parameters of the forsaken coal spontaneous combustion in the re-oxidation process. J. Saf. Environ., 16:101–106.
[11] Coats A., Redfern J. (1964) Kinetics parameters from thermogravimetric data. Nature, 201:68–69.

[12] Wang C., Yang Y., Tsai Y. (2016) Spontaneous combustion in six types of coal by using the simultaneous thermal analysis–Fourier transform infrared spectroscopy technique. J. Therm. Anal. Calorim., 126:1–12.

[13] Wang H., You C. (2014) Experimental investigation into the spontaneous ignition behavior of upgraded coal products. Energ. Fuel., 28:2267–2271.

[14] Deng J., Li B., Xiao Y., Ma L., Wang C., Laiwang B., Shu C. (2017) Combustion properties of coal gangue using thermogravimetry–Fourier transform infrared spectroscopy. Appl. Therm. Eng., 116:244–252.

[15] Wang Z., Hong C., Xing Y., Li Y., Feng Y., Jia M. (2018) Combustion behaviors and kinetics of sewage sludge blended with pulverized coal: With and without catalysts. Waste Manage., 74:288–296.