Study on Spontaneous Combustion Characteristics and Oxidation Kinetic Parameters of Lignite at Different Oxygen Concentrations

Jian Chen, Baoshan Jia,* Ying Wen, Qinghe Jing, and Linjie Liu

ABSTRACT: The spontaneous combustion parameters of lignite at different oxygen concentrations and temperatures were studied by temperature-programmed oxidation experiments. The characteristic parameters, tendency, oxygen consumption rate, kinetic parameters of oxidation reaction, and heat release intensity of coal’s spontaneous combustion were studied. The results show that the variation of export oxygen volume fraction of coal samples under different oxygen concentrations is similar. It has a general s-shaped downward trend. The change trend of the CO concentration of the coal sample export is basically the same at different oxygen concentrations. The CO concentration at the outlet of the coal sample increases with the increase in coal temperature. The CO concentration at 0–200 °C increased exponentially with the coal temperature. The distribution pattern of CO/CO₂ ranging from 0 to 320 °C was similar at different oxygen concentrations. With the increase of coal temperature, CO/CO₂ first increases and then decreases after reaching the extreme point. The change curve of CH₄ with coal temperature under different oxygen concentrations meets the exponential change rule. At different oxygen concentrations, the concentration of ethylene at 0–300 °C changes exponentially, but at 300–400 °C there is no rule. When the oxygen concentration is 20.9%, according to the comprehensive judgment index method and cross temperature method, the comprehensive determination of the spontaneous combustion trend of coal samples is grade II. Under different oxygen concentrations, the oxygen consumption rate of coal increases with the increase of temperature; the oxygen consumption rate increases with the increase of oxygen concentration at the same temperature. The activation energy of coal samples increases with the decrease of oxygen supply concentration or the increase of temperature. The heat release intensity of coal samples conforms to an exponential function and polynomial function in the early and late stages, respectively.

1. INTRODUCTION

Coal spontaneous combustion not only endangers the health and safety of underground personnel but also seriously wastes resources. The essence of coal spontaneous combustion is the process of gradual heat accumulation, which has the characteristics of concealment, dynamics, and diversity. At present, the characteristics of spontaneous combustion have been fully studied and demonstrated by experts and scholars. Analysis of the lignite spontaneous combustion trend, spontaneous combustion characteristics, and oxidation kinetic parameters at different oxygen concentrations and temperatures is of great significance to the prevention and control of spontaneous combustion in coal mines. Zhang analyzed the oxidation kinetic parameters of Jurassic coal at different oxygen concentrations and temperatures. The results show that the lower the oxygen concentration is, the more activation energy is needed for the coal oxidation reaction. Studies by Qi and Liu show that the oxidation kinetics parameters decrease with decreasing oxygen concentration, and the reduction rates are different for different oxygen concentration ranges. Shen and other scholars analyzed characteristic gases of coal spontaneous combustion with different spontaneous combustion tendencies by using a temperature-programmed experimental system. The best signature gas of coal with different spontaneous combustion tendencies is obtained. Zhong et al. analyzed the coal–oxygen recombination process by using an adiabatic oxidation experiment and synchronous thermal analysis experiment. The optimal experimental and computational parameters of autothermal kinetics of coal oxidation were determined based on an equal conversion method. Zhou et al. analyzed the law of oxygen consumption rate, heat release intensity, and temperature of different coals under variable...
oxygen concentrations through a temperature-programmed test of a tubular furnace and gas chromatographic test. Zhang et al. conducted an open constant temperature heating test based on the Frank–Kamenetskii theory. The influence of different particle size, stacking state, and moisture content on lignite was studied by Xu et al., through the load pressurized coal spontaneous combustion characteristic experiment platform, using the oxygen-poor environment program heating test under 0–8 MPa. Four characteristic parameters, $T_{CO}$, $T_{HY}$, $T''_{CO}$, and $T''_{HY}$, were determined by analyzing the variation of different characteristic parameters with uniaxial stress.

The analysis of the absorbance and peak area of(310,279),(691,591) the characteristic functional groups was performed by Lu et al. The influence mechanism of oxygen concentration on spontaneous combustion of coal was studied. Then, the variation law of gas products with coal oxidation was analyzed based on the theory of coal combustion oxidation, and thermal strength of coal at different oxygen concentrations at low and high temperatures were studied. The influence of oxygen concentration on spontaneous combustion of coal was analyzed. It provides theoretical guidance for studying the influence mechanism of oxygen concentration on spontaneous combustion of coal.

2. EXPERIMENTAL DETAILS

2.1. Temperature-Programmed Experiments. At present, most of the coal project experiments are mainly concentrated in the range of 200 °C, focusing on particle size above 1.5 mm. There is a lack of research on spontaneous combustion oxidation characteristics of coals 1.5 mm and below. In the actual underground production environment, there is a large amount of floating coal with particle size less than 1.5 mm in the working face, inlet and return air duct, and the goaf. In order to explore the spontaneous combustion characteristics of micrograined coal at different oxygen concentrations, lignite from Lingquan Mine was selected as the experimental coal sample in this paper. During the experiment, the massive fresh coal from underground was broken and screened under an inert gas atmosphere for a particle size of 100 mesh (0–0.15 mm). The coal sample is divided into three samples with the corresponding oxygen concentration of 20.9%, 10.0%, and 7.0%, respectively. The experimental data were obtained in the temperature range from 25 to 400 °C. The temperature-programmed experiment settings are shown in Figure 1.

The oxide layer on the surface of coal sample is treated before sampling. Then, the experimental coal samples with diameters ranging from 80 to 100 mesh were crushed and selected in nitrogen atmosphere. The coal samples were put into a vacuum drying tank and dried at 50 °C for 24 h. Then the coal samples were tested.

3. RESULTS AND DISCUSSION

The coal samples were tested under different oxygen concentrations by industrial analysis and a temperature-programmed experiment. The composition, characteristic parameters of spontaneous combustion, oxygen consumption rate, oxidation kinetic parameters, and thermal strength of coal samples were studied.

3.1. Characteristic Parameters of Spontaneous Combustion of Coal. 3.1.1. Characteristic Parameters of Spontaneous Combustion Gas of Coal. The experiment was carried out under the oxygen concentration of 20.9%, 10.0%, and 7.0%, respectively. The volumetric concentrations of $O_2$, $CO$, $CO_2$, and $CH_4$ were measured at 25–400 °C at the exit. The influence of different oxygen concentration on gas products was analyzed based on the theory of coal–oxygen combination. Then, the variation law of gas products with coal temperature was explored, as shown in Figures 2–6.

The concentrations of gas products in coal oxidation and spontaneous combustion at three oxygen concentrations were treated and analyzed. The relationship between the volume concentration of oxygen at the outlet and the coal temperature is shown in Figure 2. It can be seen that the changing trend of outlet oxygen volume fraction in the heating process of...
experimental coal samples under different oxygen concentrations is the same, and it has a roughly S-shaped downward trend. Simultaneously, they all conform to the polynomial fitting function

\[ y = A + (B_1 \times x^2) + (B_2 \times x^3) + \ldots + (B_5 \times x). \]

The specific piecewise fitting curve and fitting formula are shown in Figure 2 and Table 2.

At a lower oxygen concentration (7.0%), the decrease rate of oxygen volume fraction at the outlet has an obvious lag phenomenon. When the coal sample temperature reaches 250 °C, the chemical adsorption is enhanced and the oxygen concentration at the outlet decreases rapidly. At 10.0% and 20.9% oxygen volume fractions, the oxygen concentration begin to decrease significantly at 225 and 165 °C, respectively.
When the oxygen volume fraction was low in the experiment, the oxygen concentration at the outlet decreased and lagged obviously, as shown in Figure 2 and Table 2. The change curve of CO concentration under variable oxygen concentration during coal sample heating is shown in Figure 3. It can be seen from Figure 3 that the variation trend of CO concentration under different oxygen concentrations is basically the same, and it increases with the increase of coal temperature. The change rate of CO concentration in coal samples is different under the same temperature and different oxygen concentration, which is positively correlated with the oxygen concentration. However, when the temperature is less than 100 °C, the oxygen concentration has less influence on the CO concentration. With the increase of temperature, CO concentration is the highest at 20.9% oxygen concentration at the same temperature. There is little difference in CO concentration between 10% and 7% oxygen. The main reason is that the temperature rises in the later stage, the oxidation rate increases, and oxygen concentration becomes the main factor restricting the increase of CO concentration.

The fitting formula and goodness of fit of the curve of CO concentration changing with coal temperature are shown in Table 3. In the process of the temperature-programmed system with 20.9% oxygen concentration, the CO concentration increases exponentially, and it conforms to the exponential function \( y = y_0 + A_1 e^{a_1 x} / t^4 \). There is a linear correlation with the temperature of coal in the process of accelerated oxidation and spontaneous combustion, and it fits with the linear function \( y = A + (B \times x) \). When the oxygen concentration is 10.0% and 7.0%, the relation between CO concentration and coal temperature conforms to the exponential function \( y = y_0 + A_1 e^{a_1 x} / t^4 \). The \( R \)-square of the fitted curve is close to 1, and the goodness of fit is high. Therefore, CO concentration index can be used to predict coal spontaneous combustion before 200 °C.

The change curve of CO/CO\(_2\) with coal temperature under variable oxygen conditions is shown in Figure 4, and the CO/CO\(_2\) does not have the obvious function rules. The distribution characteristics show that CO/CO\(_2\) has a similar distribution rule under different oxygen concentrations before 320 °C. With the increase of coal temperature, CO/CO\(_2\) first increases and then decreases after reaching the highest point. The inflection point temperature at 7% oxygen concentration is obviously higher than that at 10% and 20.9% oxygen concentration, indicating that only a higher temperature in an oxygen-poor environment can meet the external conditions required by the coal–oxygen complex reaction. The inflection point of CO/CO\(_2\) indicates that coal has entered the stage of high temperature oxidation. When the oxygen concentration is 7.0% and the coal temperature is greater than 300 °C, the concentration of CO in the oxygen-poor condition increases exponentially, resulting in a sudden increase of CO/CO\(_2\). Because the distribution of carbon dioxide in goaf is affected by many factors, it can only be used as an auxiliary index for the early warning for the coal spontaneous combustion stage.

The curves, fitting curves and goodness of fit of methane with coal temperature at different oxygen concentrations, are shown in Figure 5. Meanwhile, CH\(_4\) concentration accords with exponential function \( y = A \times e^{b_1 x} + B \) at oxygen concentrations of 10.0% and 20.9%; when the oxygen concentration is 7.0%, the methane concentration conforms to an exponential function at 1−321 °C and a linear function at 322−400 °C. Although the variation of CH\(_4\) concentration is quite regular, most of it comes from CH\(_4\) released by the adsorption of coal itself. Therefore, CH\(_4\) C\(_2\)H\(_4\)/CH\(_4\) and C\(_3\)H\(_8\)/CH\(_4\) are not suitable as the indicators of the spontaneous combustion of coal. After 300 °C, the generation of methyl radical was severely inhibited at 10.0% and 7.0% oxygen concentrations, and the lower the oxygen concentration was, the more severely it was inhibited. Therefore, after 300 °C, the CH\(_4\) concentration shows a downward trend at low oxygen concentration, as shown in Figure 5 and Table 4.

### Table 3. Fitting Formula of CO Concentration of Coal Oxidation Spontaneous Combustion

| oxygen concentration (%) | temperature (°C) | fitting formula | \( R^2 \) |
|--------------------------|-----------------|----------------|---------|
| 7.0                      | 1−400           | \( y = 9.57 e^{−121.46} + 16.54 \) | 0.99888 |
| 10.0                     | 1−400           | \( y = 28.07 e^{−181.99} + 41.51 \) | 0.99415 |
| 20.9                     | 0−200           | \( y = 2.62 e^{−56.27} + 6.60 \) | 0.99334 |
|                          | 200−400         | \( y = 1.28 x + 6489.78 \) | 0.99511 |

The \( C_3H_4 \) concentration of 0−300 °C under the variable oxygen concentration meets the change law of the exponential function \( y = A \times e^{b_1 x} + B \), and at 300−400 °C, there is no obvious rule, as shown in Figure 6. After 300 °C, the formation of aldehyde group was inhibited at 10% and 7% oxygen concentrations. Therefore, \( C_3H_4 \) concentration tends to decrease under high temperature and low oxygen concentration. At the same temperature, the concentration of ethylene increased with the increase of oxygen concentration, but it was not significant. The variation index of ethylene concentration is shown in Table 5.

### Table 4. \( C_3H_4 \) Concentrations as a Function of Temperature

| oxygen concentration (%) | temperature (°C) | fitting formula | \( R^2 \) |
|--------------------------|-----------------|----------------|---------|
| 7.0                      | 1−321           | \( y = 0.027 e^{47.65} + 47.91 \) | 0.98761 |
|                          | 322−400         | \( y = 1.05 x + 287.98 \) | 0.99743 |
| 10.0                     | 1−400           | \( y = 2.39 x + 412 \) | 0.99139 |
| 20.9                     | 0−400           | \( y = 5.29 x + 297 \) | 0.99742 |

The \( C_2H_4 \) concentration of 0−300 °C under the variable oxygen concentration meets the change law of the exponential function \( y = A \times e^{b_1 x} + B \), and at 300−400 °C, there is no obvious rule, as shown in Figure 6. After 300 °C, the formation of aldehyde group was inhibited at 10% and 7% oxygen concentrations. Therefore, \( C_2H_4 \) concentration tends to decrease under high temperature and low oxygen concentration. At the same temperature, the concentration of ethylene increased with the increase of oxygen concentration, but it was not significant. The variation index of ethylene concentration is shown in Table 5.

### Table 5. Law of Exponential Change of \( C_2H_4 \) Concentration

| oxygen concentration (%) | temperature (°C) | fitting formula | \( R^2 \) |
|--------------------------|-----------------|----------------|---------|
| 7.0                      | 1−300           | \( y = 0.02409 e^{0.95} + 0.27780 \) | 0.99832 |
|                          | 1−300           | \( y = 0.02296 e^{0.379} + 0.23653 \) | 0.99770 |
|                          | 1−300           | \( y = 0.07053 e^{0.6} + 0.43639 \) | 0.99079 |

### 3.1.2. Spontaneous Combustion Tendency of Coal

1. Comprehensive determination index method of coal spontaneous combustion tendency:

The coal spontaneous combustion trend is an intrinsic attribute of coal oxidation capacity and an important index to evaluate the risk degree of coal spontaneous combustion.\(^{18−21}\) The comprehensive measurement index of coal spontaneous combustion trend is calculated as follows.\(^{22,23}\)
In the formula, $\alpha$ is the calculation factor of oxygen volume fraction at outlet, $\alpha = 15.5$; $\beta$ is the CPT (crossing point temperature) factor, $\beta = 140$; $\gamma$ is the magnification factor (MF), $\gamma = 40$; $\theta$ is the correction factor, $\theta = 300$; $\phi(O_2)$ is the volume fraction of oxygen at the exit when the temperature of coal is 70 °C; $I(O_2)$ is the volume fraction index of oxygen at coal outlet at 70 °C; $I$ is the comprehensive judgment index; $T_{cpt}$ is the crossing point temperature, °C; $I_{cpt}$ is the index of $T_{cpt}$; $W(O_2)$ is the weight of the low temperature oxidation stage, W($O_2$) = 0.6; $W_{cpt}$ is the weight of heating and accelerating oxidation stage, $W_{cpt}$ = 0.4.

The result of calculation is $I = 1116.98$. It can be seen that the lignite spontaneous combustion tendency of Lingquan Mine is classified into class II, as shown in Table 6.

### Table 6. Classification Index of Spontaneous Combustion Tendency of Coal

| grade of spontaneous combustion tendency | composite decision index ($I$) |
|------------------------------------------|-------------------------------|
| class I easy spontaneous combustion       | $I < 600$                     |
| class II spontaneous combustion           | $600 \leq I < 1200$          |
| class III not easy spontaneous combustion| $1200 \leq I$                |

(2) Cross-point temperature method of coal spontaneous combustion tendency:

Because of its high reliability and applicability, CPT has been widely used in the identification of the spontaneous combustion tendency of coal. Under the oxygen concentration of 20.9%, the temperature at the intersection point of the temperature-programmed coal sample is CPT = 154 °C, as shown in Figure 7. As CPT = 154 °C, it can be seen that the spontaneous combustion tendency of the coal samples in Lingquan Mine is class II. This is consistent with the above calculation and experimental results of comprehensive measurement index $I$.

#### 3.2. Oxygen Consumption Rate

One can assume that the coal–oxygen composite reaction in this experiment belongs to the first order reaction, and the oxygen concentration is evenly distributed across the test tube. The oxygen consumption rate is calculated according to the following formula.

$$v_{O_2}(T) = \frac{Q \times C_0}{SH(1 - n)} \ln \left( \frac{C_0}{C_1} \right)$$

(4)

In the formula, $v_{O_2}(T)$ is the oxygen consumption rate; $Q$ is the supply air quantity, cm$^3$ s$^{-1}$; $C_0$ is the initial oxygen concentration, mol cm$^{-3}$; $S$ is the cross-sectional area in the tube, cm$^2$; $H$ is the height of the coal sample, cm; $n$ is the coal sample gap rate; and $C_1$ is the exports oxygen concentration, mol cm$^{-3}$.

According to the data of temperature-programmed experiment, the oxygen consumption rates of coal samples under three different oxygen concentrations can be solved by using eq 4. The oxygen consumption rate of coal at different oxygen concentrations increases with the increase of temperature, as shown in Figure 8. At the same temperature, the oxygen consumption rate of coal sample increases with the increase of oxygen concentration.

The fitting curve in Figure 8 is combined with the fitting formula in Table 7. It can be seen that the oxygen consumption rate of coal samples in the early stage under different oxygen concentrations conforms to the exponential fitting formula $y = A \times e^{\Delta t} + y_0$. The rate of oxygen consumption at a later stage follows a polynomial function $y = B_1x^5 + B_2x^4 + B_3x^3 + B_4x^2 + ... + B_n$, where $x$ is the gas in the tank is uniform and consistent. According to the oxidation reaction equation of coal, the oxygen consumption rate equation of the solid coal sample in unit height at $x$ is shown in eq 5.

$$-\frac{dC_{O_2}}{dx} = (1 - n)Y_{O_2}(T)S \, dx$$

(5)

In the formula, $n$ is the void fraction of coal sample, %; $S$ is the cross-sectional area of the coal sample tank, cm$^2$; $Y_{O_2}(T)$ is the oxygen consumption rate of coal at different oxygen concentrations.
Table 7. Fitting Equation of Segmentation Curve of
Relations between Oxygen Consumption Rate and Oxygen
Concentration

| oxygen | temperature | fitting formula | R² |
|---|---|---|---|
| concentration (%) | (°C) | | |
| 7.0 | 1–275 | \( y = 3.65 \times 10^{-4} e^{35.21} \) | 0.98031 |
| | 276–400 | \( y = 6.12 \times 10^{-5} x^2 + 0.042 \times x - 0.026807 \) | 0.9916 |
| 10.0 | 1–280 | \( y = 0.00244 e^{34.65} - 0.00738 \) | 0.99729 |
| | 281–400 | \( y = 6.28 \times 10^{-5} x^2 - 6.45 \times 10^{-4} x + 0.22276x - 21.61 \) | 0.99145 |
| 20.9 | 0–290 | \( y = 0.00637 e^{34.65} - 0.06740 \) | 0.99949 |
| | 291–400 | \( y = 2.90 \times 10^{-5} x^2 - 5.16 \times 10^{-4} x + 0.00366x^2 - 1.29x^2 + 228.26x - 16045.96 \) | 0.999873 |

the oxygen consumption rate at \( x \), mol cm\(^{-3} \) s\(^{-1} \); \( Q_{\text{inlet}} \) is the gas flow rate, cm\(^3\) s\(^{-1}\); \( C_{O_2}^m \) is the oxygen concentration at \( x \), mol cm\(^{-3}\); \( dC_{O_2} \) is the decrease value of \( O_2 \) concentration in \( dx \), mol cm\(^{-3}\).

According to the kinetics and theory of coal-oxygen combined oxidation, the relationship between oxygen consumption rate and oxygen concentration is shown in eq 6.\(^{31,32}\)

\[
V_{O_2} = k_{O_2} C_{O_2}^m \tag{6}
\]

In the formula, \( C_{O_2} \) is the oxygen consumption, mol cm\(^{-3}\); \( k_{O_2} \) is the reaction rate coefficient, s\(^{-1}\); \( m \) is the reaction order, \( m = 1 \).

The oxygen consumption rate of the unit volume solid coal sample at \( x \) was obtained by the Arrhenius equation, as shown in eq 7.\(^{33}\)

\[
V_{O_2}^x(T) = C_{O_2}^x A \exp(-E/RT) \tag{7}
\]

In the formula, \( A \) is the pre-exponential factor, s\(^{-1}\); \( R \) is the gas constant, 8.3144 J K\(^{-1}\) mol\(^{-1}\); \( T \) is the temperature, K; \( E \) is the activity energy, J mol\(^{-1}\).

Equation 8 is obtained through the compound operation of eqs 4 and 2, and the relation equation of activation energy is obtained.\(^{34}\)

\[
\ln \left( \frac{SAH(1 - n)}{Q_{\text{inlet}}} \right) - \frac{E}{RT} = \ln \left( \frac{C_{O_2}^m}{C_{O_2}^H} \right) \tag{8}
\]

In the formula, \( C_{O_2}^0 \) is the initial oxygen concentration of the mixture, mol cm\(^{-3}\); \( C_{O_2}^H \) is the oxygen concentration at height \( H \) of the coal sample, mol cm\(^{-3}\).

For this, one plots \( \ln(C_{O_2}^0/C_{O_2}^H) \) and \( T^{-1} \) as the vertical and horizontal coordinates, respectively, and performs piecewise linear fitting. The activation energy and pre-exponential factor of coal samples at oxygen concentration of 20.9%, 10.0%, and 7.0% can be calculated by slope and intercept, as shown in Figure 9 and Table 8.

The overall trend of reaction activation energy of coal samples under different oxygen concentrations is basically the same, showing a change trend of rising first and then decreasing, as shown in Table 8 and Figure 10. In the slow oxidation stage, the physical and chemical adsorption of coal samples releases a lot of adsorption heat, and the activation energy demand is low.

Figure 9. Relationship curve between \( T^{-1} \) and \( \ln(C_{O_2}^0/C_{O_2}^H) \) varying with oxygen concentration at 20.9%, 10.0%, and 7.0%.

In the accelerated oxidation stage, various active groups in coal samples need more energy to be activated, and the activation energy increases gradually. In the ignition stage, the activation energy continues to rise and reaches the inflection point, and the heat generation of coal sample itself begins to play a leading role. In the combustion stage, the heat generated
Table 8. Table of Reaction Kinetics Parameters of Coal Samples at Different Stages under Different Oxygen Concentrations

| Oxygen concentration (%) | Reaction stage | Temperature range (°C) | Activation energy E (kJ mol⁻¹) | Pre-exponential factor A (min⁻¹) | Goodness of fit R² |
|---------------------------|----------------|------------------------|-------------------------------|---------------------------------|------------------|
| 7.0                       | eremacausis    | 25.00–63.38            | 16.57                         | 0.43                            | 0.99224          |
|                           | accelerated oxidation | 83.06–162.79    | 14.56                         | 0.11                            | 0.99799          |
|                           | ignition       | 183.50–239.98          | 25.85                         | 1.64 × 10⁵                     | 0.99974          |
|                           | burn           | 247.04–268.05          | 75.24                         | 1.71                            | 0.93290          |
|                           |                | 278.10–400.00          | 14.84                         | 0.29                            | 0.99224          |
| 10.0                      | eremacausis    | 25.00–83.06            | 9.52                          | 0.02                            | 0.95417          |
|                           | accelerated oxidation | 102.73–220.84    | 29.20                         | 0.03                            | 0.99828          |
|                           | ignition       | 232.02–282.76          | 60.66                         | 9.13 × 10³                     | 0.99569          |
|                           | burn           | 300.04–400.00          | 2.47                          | 0.03                            | 0.95886          |
| 20.9                      | eremacausis    | 25.00–124.89           | 24.49                         | 1.05                            | 0.95786          |
|                           | accelerated oxidation | 145.15–214.32    | 36.57                         | 29.63                           | 0.99395          |
|                           | ignition       | 230.41–276.48          | 66.02                         | 3.56 × 10⁴                     | 0.95635          |
|                           | burn           | 290.37–400.00          | 4.26                          | 0.06                            | 0.97331          |

The exothermic intensities of coal samples in the early and late stages meet the functions of $y = A \times e^{x/\tau} + y_0$ and $y = B_1x^2 + B_2x^3 + B_3x^2 + B_4x + C$, respectively, at different oxygen concentrations. In addition, the heat release intensity and oxygen consumption rate of coal samples under different oxygen concentrations are consistent, as shown in Figures 8 and 11.

by the oxidation reaction of coal itself will stimulate the active groups to participate in the reaction, and the activation energy begins to decline rapidly.

3.4. The Intensity of Heat. The heat release intensity reflects the overall capacity of coal itself to generate heat, and the calculation formula of oxygen consumption rate and heat release intensity is shown in eqs 9 and 10.

$$V_{O_2}(T) = \frac{Q}{S} \ln \frac{C_{O_2}^{t_i}}{C_{O_2}^{t_e}}$$

(9)

$$V_{O_2}(T) = \frac{Q}{S} \ln \frac{C_{O_2}^{t_i}}{C_{O_2}^{t_e}}$$

(10)

$$q = \Delta H[V_{O_2}(T) - V_{CO}(T) - V_{CO_2}(T)] + \Delta H_{CO}V_{CO}(T) + \Delta H_{CO_2}V_{CO_2}(T)$$

(11)

In the formula, $L$ is the coal body height, cm; $S$ is the coal tank bottom area, cm²; $V_{O_2}(T)$ is the oxygen consumption rate at temperature $T$, mol/(cm² s); $Q$ is the total amount of gas supplied to the mixture, mL/min; $C_{O_2}^{t_i}$ and $C_{O_2}^{t_e}$ represent the oxygen concentration at the inlet and outlet, respectively, mol/cm³; $\Delta H = 284.97$ kJ/mol; $\Delta H_{CO} = 311.9$ kJ/mol; $\Delta H_{CO_2} = 446.7$ kJ/mol.

The exothermic intensities of coal samples in the early and late stages meet the functions of $y = A \times e^{x/\tau} + y_0$ and $y = B_1x^2 + B_2x^3 + B_3x^2 + B_4x + C$, respectively, at different oxygen concentrations. In addition, the heat release intensity and oxygen consumption rate of coal samples under different oxygen concentrations are consistent, as shown in Figures 8 and 11.

4. CONCLUSIONS

(1) In the process of coal oxidation and spontaneous combustion with different oxygen concentration, the change trend of oxygen concentration at the outlet with coal temperature is consistent. At 0–200 °C, the relationship between CO concentration and coal temperature at different oxygen concentrations conforms to the exponential function $y = y_0 + A_1e^{x/t_1}$. Therefore, the CO concentration index can be used to predict coal’s spontaneous combustion in the range 0–200 °C.

(2) The change curve of CO/CO₂ from 0 to 320 °C at different oxygen concentrations first increases with coal temperature, and then it decreases. The lower the oxygen concentration is, the higher the inflection point temperature is. CO/CO₂ can be used as an auxiliary index of coal spontaneous combustion warning.

(3) In the range of 0–300 °C with different oxygen concentrations, the methane and ethylene concentrations accord with the change rule of the exponential function, but there is no obvious change rule under the
condition of 300–400 °C. Methane is not suitable as the indicator of the spontaneous combustion of coal, while ethylene can be used as the indicator of the accelerated oxidation of coal.

(4) Through the comprehensive determination method of the coal spontaneous combustion trend index, the comprehensive judgment index is calculated as $I = 1116.98$. CPT = 154 °C was calculated by the cross-point temperature method to determine the spontaneous combustion trend of coal.

(5) The oxygen consumption rate of the first and last two stages satisfies the exponential function and polynomial function, respectively, under different oxygen concentrations. Under different oxygen concentrations, the reaction activation energy of the coal samples increases first and then decreases in three stages: slow, accelerated, and ignition. The heat release intensity of coal sample is consistent with the change trend of the oxygen consumption rate.

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