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Optimization of a Marker Gas for Analyzing and Predicting the Spontaneous Combustion Period of Coking Coal

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Abstract: The adequate assessment of the spontaneous combustion and oxidation characteristics of coking coal can help to reduce its spontaneous combustion potential. In this study, the natural ignition period of the Hex coking coal seam at Ping Coal was calculated based on the programmed-temperature-rise test and the thermal property parameters measured during the spontaneous combustion of the coal. Typical gas concentrations were measured at different oxygen concentrations and coal particle sizes to investigate the changes in the oxygen, carbon–oxygen, and hydrocarbon gas concentrations during the low-temperature oxidation of the coking coal and to determine the indicator gases at different oxidation stages. The following results were obtained: The minimum critical oxygen concentration required for spontaneous ignition was 8%, and fire prevention measures should be implemented below 200 °C. When the temperature of the coal sample reaches 50–60 °C, the rates of CO and CO_2 production increase, and when the temperature of the coal sample reaches 100–120 °C, the spontaneous combustion and oxidation of the coal generates alkane gas, in which the coal particle size has a negligible effect on the concentration of each generated gas. CO and C_2H_4 were selected as the indicator gases for different coking coal oxidation stages, and C_2H_6 and the C_2H_4/C_2H_6 ratio were used as secondary indicators to assist in the analysis. Utilizing the enhanced mathematical model for the shortest spontaneous combustion period of coal seams, in conjunction with a programmed-temperature test device, experimental calculations were conducted to determine the adiabatic spontaneous combustion period. The results indicate that the natural ignition period for the Hex coking coal seam at Ping Coal is approximately 60 days, representing a brief timeframe, and the coal seam is characterized by a high risk of spontaneous combustion.

Keywords: coal; spontaneous combustion; indicator gas; programmed temperature; critical oxygen concentration

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1. Introduction

Coal is one of the most important energy sources in the world, accounting for about 27.6% of the total primary energy consumption [1,2], and the lifeblood of China's national economy [3]. Coking coal is a scarce high-quality coal resource and an important raw material for the steel and chemical industries and plays a huge role in China's economic development. However, during mining or storage, coking coal will undergo a low-temperature oxidation reaction due to contact with air, and the accumulation of oxidation heat is very likely to cause the spontaneous combustion of the coking coal left in the mining area [4,5]. The spontaneous combustion of coal not only consumes resources [6] and pollutes the environment [7] but also may lead to severe human injuries and deaths [8]. Additionally, the low-temperature oxidation of coal also affects the physical and chemical properties of coking coal and, thus, reduces the quality of the coal. Research has shown that with the extension of the low-temperature oxidation time, the bonding and coking properties of coking coal are deteriorated. Meanwhile, low-temperature oxidation significantly reduces the heat generation of coking coal by nearly 5% after six months of storage [9]. Therefore, it is important to study the spontaneous combustion and oxidation characteristics of coking coal to guide the prediction and comprehensive prevention of the spontaneous combustion and burning of coking coal.

Among the works in the literature, the oxygen concentration was found to affect the low-temperature oxidation and spontaneous combustion of coking coal. The oxygen concentration has a considerable influence on the combustion characteristics of pulverized coal [10], while reducing the oxygen concentration can inhibit the low-temperature oxidation of coal [11] because oxygen-deficient environments inhibit the oxidation of the active structure of coal [12]. Usually, coal spontaneously combusts at low oxygen concentrations due to geological conditions, industrialization levels, and storage conditions. The incidence of spontaneous combustion is the highest at oxygen concentrations below 21.0 vol% [13]. M. Perdochova et al. [14] experimentally found that the oxygen concentration affects the release rates of CO and CO_2. At an oxygen concentration of 21.0 vol%, the release rate of CO is higher than that of CO_2; the opposite is true at an oxygen concentration of 15.0 vol%. X.Y. Qi et al. [15] investigated thermodynamic parameters during the low-temperature oxidation of coal and found that their values increased with decreasing oxygen concentration. F. Gao et al. [16] found that a reduction in the organic sulfur content could inhibit the oxidation process and spontaneous combustion tendency of coking coal.

Accurate prediction is essential to prevent the spontaneous combustion of coal. In this regard, the determination of the indicators for the spontaneous combustion of coal has been a hot topic of recent research [17,18]. To gain insight into the mechanism of the spontaneous combustion of coal, techniques such as programmed temperature rise have been employed to simulate the low-temperature oxidation process of coal [19], and the concentrations of gaseous compounds, such as CO, CO_2, CH_4, C_2H_4, and C_2H_6, were found to be positively correlated with the temperature of the coking coal [20]. These gases are usually used as indicator gases for predicting the spontaneous combustion of coal [21]. J. Guo et al. [22] evaluated CO and C_2H_4 formation rates, as well as various gas ratios, to predict the spontaneous combustion of coal. X.Y. Guo et al. [23] found that olefin-index gases were more accurate predictors of the spontaneous combustion of coal than alkane-index gases under low-oxygen-concentration conditions. H. Wen et al. [24] developed a model for predicting the CO concentration in the return air angle of coal mines, which can be used to accurately assess the degree of the spontaneous combustion of coal. Q.Q. Liu et al. [25] found that CO production, C_2H_4 concentrations, and Graham's fire coefficient (R2, R3) could be used as indicators to predict the CSC process. In addition, variations in the active functional groups and molecular structure were analyzed during the oxidation of coking coal, and the relationship between the thermodynamic behavior and the microscopic characteristics of coal was systematically studied to prevent spontaneous combustion [26].

The mines of the China Ping Coal Shenma Group are rich in coking coal resources, with proven reserves accounting for 62.1% of all the coal produced in Henan Province, and are the largest producer and main supplier of high-quality coking coal in China. These twelve mines are the first "industry-level" double-high mines among Ping Coal's high-profile mines and are known as the "Pearl of the Orient" of Ping Coal. The key working face of Twelve Mine, Hex16-17-31020, started to be mined back in August 2021, and it encountered a fault situation during the process of advancement soon after mining. We adopted the coal seam of this working face as the research object to calculate the natural ignition period of the coal seam through programmed temperature rises and measured the thermal properties of the coal during spontaneous combustion to evaluate the probability of natural coal ignition. Additionally, the combustion parameters of the coking coal were studied during the low-temperature oxidation stage, the release mechanism was revealed for the main gases, and the indicator gases were determined for the different oxidation stages of the coking coal. The results of this study are important for gaining insight into the low-temperature oxidation behavior of the coking coal at Ping Coal, determining the appropriate mining and storage methods, and predicting and preventing the spontaneous combustion of coal.

2. Materials and Methods

2.1. Coal Samples

A coal sample from the hexagonal group of Ping Coal is taken as the object of the study. The hexagonal group sample is a low ash, extra-low sulfur, low phosphorus, and high calorific coal, and its specific characteristic indexes are shown in Table 1.

Table 1. Coal quality characteristics.

Moisture M_{ad}/%	Ash A_d/%	Volatile V_{daf}/%	Sulfur S_{td}/%	Phosphorus P_d/%	Heat Generation Q_{bd}/%	Colloid Layer Thickness Y/mm	Adhesion Index G
6	10–20	27.13	0.5	0.01	27.21–30.90	11–37	64–74

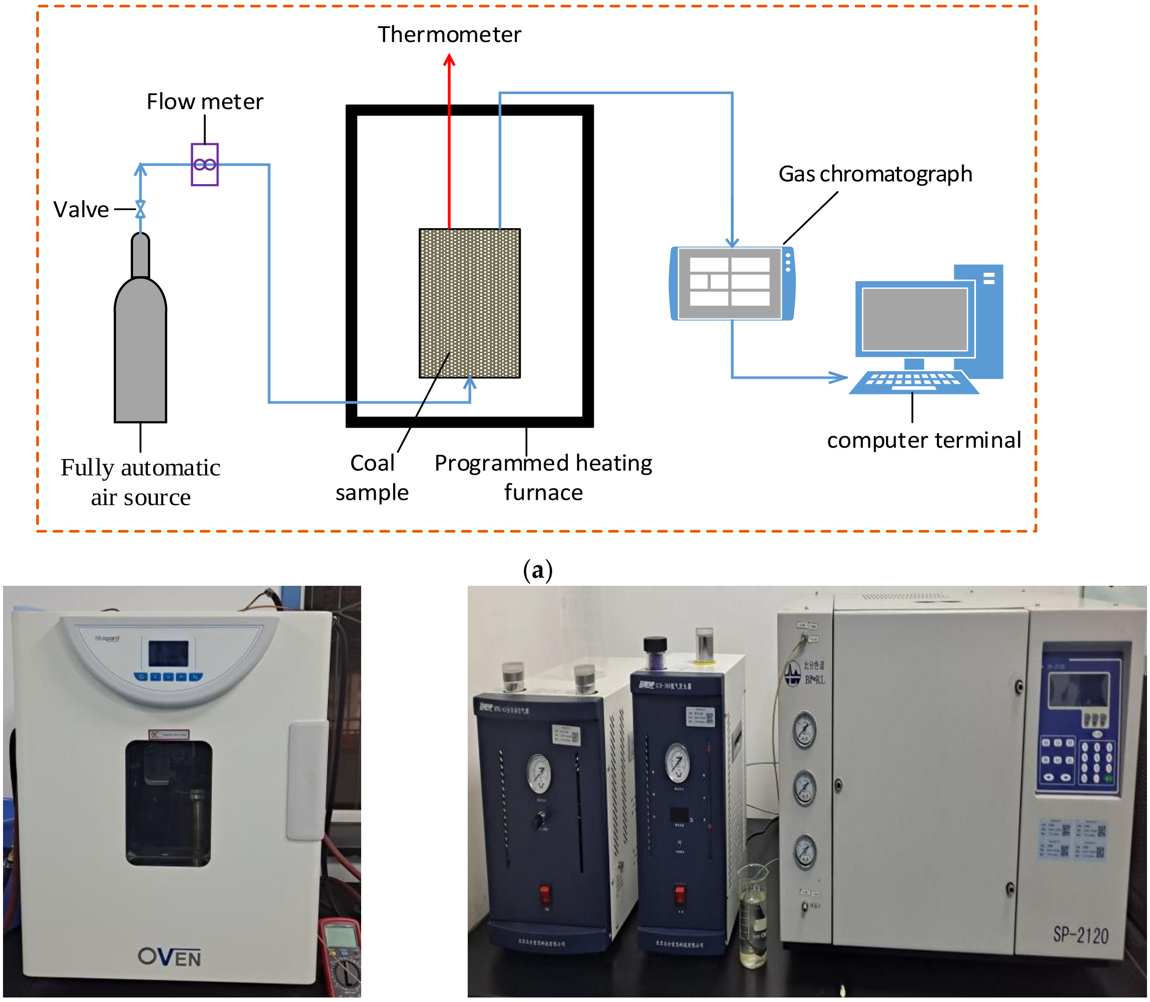
The coal samples used for the tests were collected in accordance with GB/T 482-2008 [27] “Sampling of coal seams”. To prevent oxidation during transportation, the collected coal samples were sealed in bags. In addition, to meet the test requirements, the collected coal samples were crushed and sieved before the test, and three coal samples with particle sizes in ranges 0–0.9, 0.9–3, and 3–5 mm were prepared for the tests. The sieving process is shown in Figure 1. The preparation process of the test coal samples strictly followed the relevant requirements in GB/T 474-2008 [28] “Method for preparation of coal sample”.

Figure 1. Sieving of test coal samples.

2.2. Programmed-Temperature-Rise Test

The spontaneous combustion process of coal mainly includes the preparation period, self-heating period, and combustion period, and the oxygen consumption rate and the indicator gases produced in different stages are different. Therefore, to study the combustion parameters of the coking coal in the low-temperature oxidation stage and determine the indicator gases corresponding to the different oxidation stages, this experiment was conducted to test the spontaneous combustion characteristics of the coal at different oxygen concentrations with a closed programmed heating device and investigate the effects of the different particle sizes on the spontaneous combustion characteristics of the coking coal.

The test device is shown in Figure 2a and mainly consists of four parts: a gas supply system, a programmed heating system, a gas analysis system, and a computer terminal. The gas supply system includes a flow meter (with a range of 30–300 mL/min), a preheating copper pipe, a high-temperature-resistant gas pipe, and a fully automatic air source (with a supply pressure of 0.4 MPa) and is used to ensure that sufficient air is in the coal sample tank and promote full contact between the test coal sample and the air. The programmed heating system includes the coal-sample tank, temperature-measuring instrument, and programmed heating furnace, as shown in Figure 2b. The coal-sample tank is made of stainless steel, with an inner diameter of 10 cm, a height of 23 cm, and a volume of 1800 mL. The programmed heating furnace is automatically controlled by a silicon-controlled regulator, with an inner space of 50 × 40 × 30 cm^3. In the upper and lower ends of the sample tank, a certain amount of free space needs to be reserved to ensure uniform ventilation. The gas analysis system includes a drying tube (with a length of 1 m and an inner diameter of 2 mm), a syringe, and a gas chromatograph, as shown in Figure 2c. The collected gases are injected into the SP-2120 gas chromatograph(Beijing Beifen-Ruili Analytical Instrument(Group)Co., Ltd., Beijing, China), which can accurately determine the gas composition and corresponding concentration.



(**a**)

(**b**) (**c**)

Figure 2. Programmed-temperature-rise test device: (**a**) schematic diagram; (**b**) programmed heating furnace; (**c**) gas chromatograph.

During the tests, 330 g each of three coal samples with different particle size ranges, 0–0.9, 0.9–3, and 3–5, mm were mixed thoroughly in the coal-sample tank. Then, gas was introduced to the copper pipe for preheating to ensure the gas tightness of the test device. Then, a certain amount of dry air was introduced to the coal-sample tank at a flow rate of 130 mL/min, and the programmed-temperature-rise test was started. After the temperature reached the specified temperature, a gas sample was withdrawn after 2 min at a constant temperature for testing and analysis. After the completion of the tests for determining the characteristics of the spontaneous combustion of coal at oxygen concentrations of 21%, 18%, 15%, 10%, 8%, and 5%, 1000 g of each of the three samples with different particle size ranges was selected for comparison tests to investigate the effects of different particle sizes on the spontaneous combustion characteristics of the coking coal. In this test, an oxygen concentration of 21% was used. In all the above tests, the maximum temperature of the test was kept constant at 400 °C.

2.3. Test of Thermal Property Parameters during Spontaneous Combustion of Coal

The LFA457 laser thermal conductivity analyzer(NETZSCH Scientific Instruments (Shanghai) Co., Ltd., Shanghai China) was used for this test, and the instrument and test principle are shown in Figure 3. The instrument mainly includes a laser generator, a furnace body, and an infrared detector. The laser generator is used to emit the laser beam, the furnace is used to control the sample temperature, and the infrared detector is used to detect the temperature change. The instrument is equipped with a gas supply system, water circulation system, and controller. The test can be used to obtain thermal property parameters, such as the thermal diffusion coefficient, thermal conductivity, and specific heat capacity, of the coal.

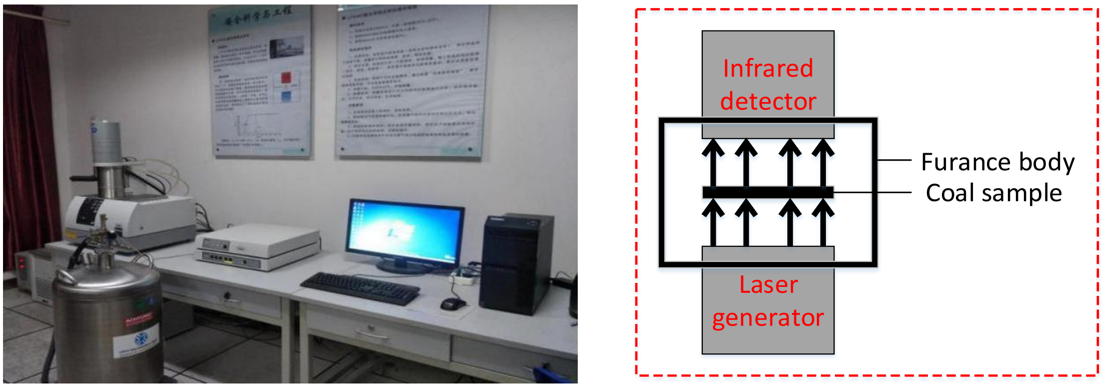


Figure 3. LFA457 laser thermal conductivity analyzer and test principle.

During the test, a certain mass of the coal powder (about 160 mg) was weighed and pressed in the tablet press to form a disc with a diameter of about 12.8 mm and a thickness of about 1.2 mm. The pressing process should ensure that the two surfaces of the discs are flat and that the discs have the same thickness. The pressed samples were weighed, and the diameter and thickness were measured to calculate the density of the samples. During the experiment, the sampling temperature points were set at 10 °C intervals. At each sampling temperature point, the laser was flashed three times, and the average value was taken as the thermal property parameter at that temperature. The blowing gas was air at a constant flow rate of 100 mL/min. The experimental conditions for measuring the thermal property parameters are shown in Table 2.

Table 2. Experimental conditions of test for measuring thermal physical parameters.

Fineness (mesh)	Particle Size (mm)	Quality (mg)	Diameter (mm)	Thickness (mm)	Experimental Temperature (°C)	Heating Rate (°C/min)	Air Flow (mL/min)
200	0.074	160	12.83	0.94	30–170	1	100

3. Results

3.1. Spontaneous Combustion Characteristics of Coking Coal

3.1.1. O_2 Concentration

The natural firing period of the coal seam is the theoretical time calculated under the condition of a sufficient oxygen content. However, in the actual production process, the oxygen content is an important index affecting the oxidation state of the coal left in the mining area and is an important basis for dividing the mining area into three zones. Therefore, it is important to study the oxidation characteristics of coking coal at different O_2 concentrations and determine the critical O_2 concentration for its oxidation and spontaneous combustion. It is very important to prevent the spontaneous combustion and ensure the safe production of coal. The O_2 concentration plotted as functions of the coal temperature during the test is shown in Figure 4. The oxidation of the coking coal samples accelerated with increasing environmental temperature. However, with decreasing initial O_2 concentration, the oxygen consumption rate of the oxidation reaction of the specimen decreased, indicating that the oxidation reaction of the coking coal became slower.

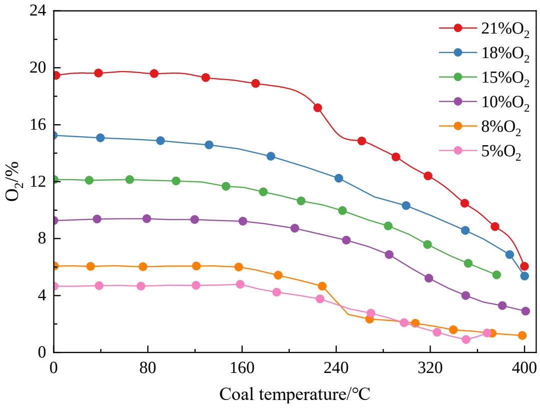


Figure 4. O_2 concentration plotted as functions of coal temperature.

Studies have shown that CO is a gas that is continuously produced during coal oxidation and is one of the gases that mark the beginning of the oxidation reaction of coal. The concentration of CO in a certain range can characterize the stage of coal oxidation. The CO concentration plotted as functions of the coal temperature during the test is shown in Figure 5. As the O_2 concentration decreases, the starting temperature at which CO gas is detected increases. The temperature at which CO is first detected increases by 10–15 °C for each reduction in the O_2 concentration. When the O_2 concentration is greater than 10%, the CO concentration increases rapidly with increasing coal temperature, indicating the existence of the conditions required for a violent oxidation reaction, and the probability of the spontaneous combustion and ignition of the coal seam is greater. When the O_2 concentration is less than 8%, the CO concentration changes less with increasing coal temperature, and the total concentration of CO is lower, which means the oxidation activity of the coal is already very low.

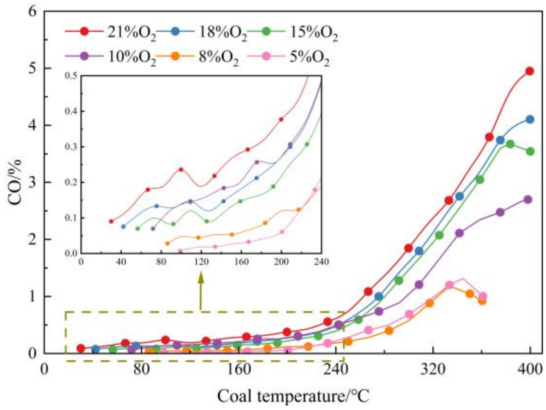


Figure 5. CO concentration plotted as functions of coal temperature at different oxygen concentrations.

Heat accumulation is an important external condition for the accelerated oxidation of coal, and it is an important indicator to judge whether the coal is close to its ignition point. The thermodynamic characteristic curves of coal samples at different O_2 concentrations are shown in Figure 6.

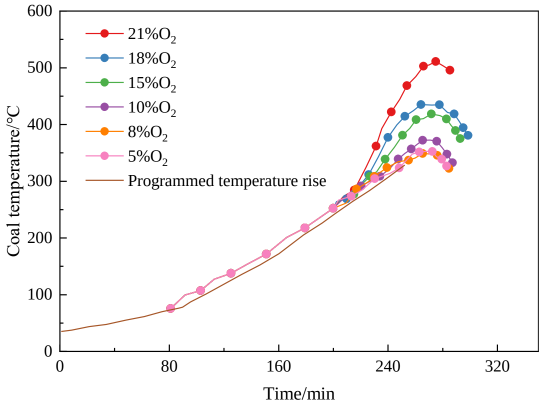


Figure 6. Coal temperature plotted as functions of time at different oxygen concentrations.

The curves representing the production of CO gas during the temperature rise and oxidation of coal samples at different O_2 concentrations are shown in Figure 7. When the temperature of the coal sample is 30–110 °C, the CO production rate is very low, and the curve rises more gently. As the temperature continues to rise, the curve changes significantly, and the CO production rate increases sharply.

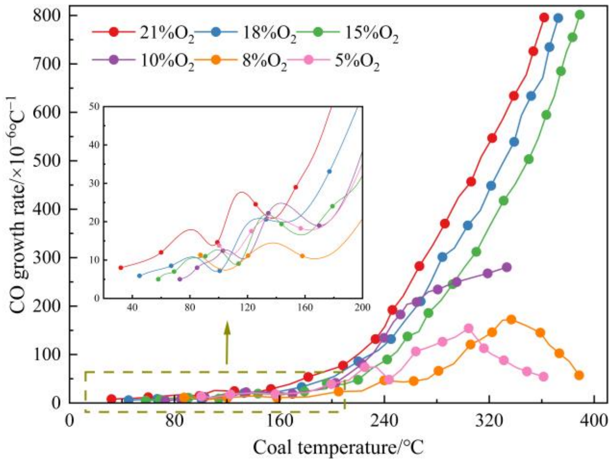


Figure 7. CO production rate plotted as functions of coal temperature at different oxygen concentrations.

3.1.2. CO and CO_2 Gas Concentrations

It is very difficult to use the CO concentration alone to determine the stage of the coal oxidation. In fact, other gases, such as CO_2, CH_4, C_2H_4, and other hydrocarbon gases, are also produced during the oxidation and temperature rise of coal, and these gases appear at different oxidation stages and show some differences. Understanding these differences can help us to infer more accurately the oxidation stage of the coal seam so that we can take different intervention measures.

The CO concentrations produced by different coal particle-size ranges at different coal temperatures are shown in Figure 8. The particle size of the coal sample has less influence on the pattern of the CO gas generation. CO gas was already generated at a coal temperature of 30 °C, indicating that the oxidation reaction of the coal samples had started at low temperatures, but it was difficult to detect CO gas in the wind-leakage environment in the field. The CO concentration is low and increases slowly below 60 °C. When the coal temperature exceeds 60 °C, CO production is accelerated, indicating that the coal oxidation reaction is accelerated. When the coal temperature exceeds 110 °C, the CO concentration increases rapidly, and the coal oxidation continues to accelerate. Therefore, the critical temperature for the appearance of CO in the Hex coal sample from Ping Coal is 60 °C, and the critical temperature for the accelerated oxidation of the coal sample is around 110 °C.

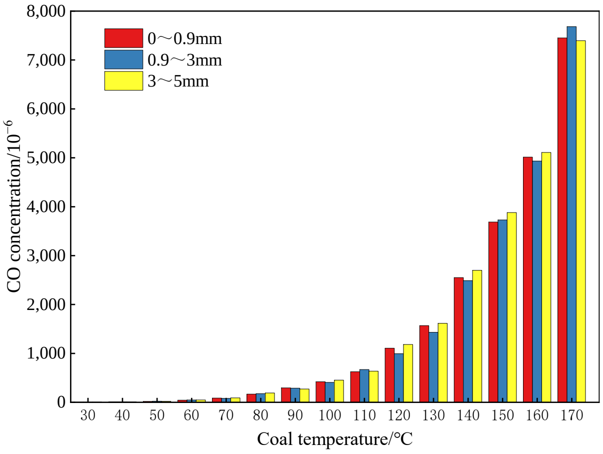


Figure 8. CO concentrations produced at different coal temperatures by different coal particle-size ranges.

The CO_2 concentrations produced by different coal particle-size ranges at different coal temperatures are shown in Figure 9. CO_2 was detected at a coal temperature of 30 °C. The CO_2 concentration increased slowly during the temperature rise from 30 °C to 60 °C, which indicates that the coal oxidation reaction rate was low. CO_2 production accelerated when the temperature of the coal sample continued to rise to about 110 °C, indicating that the coal temperature was higher than the critical temperature and that the coal oxidation reaction intensified, but the overall change in the CO_2 concentration was negligible.

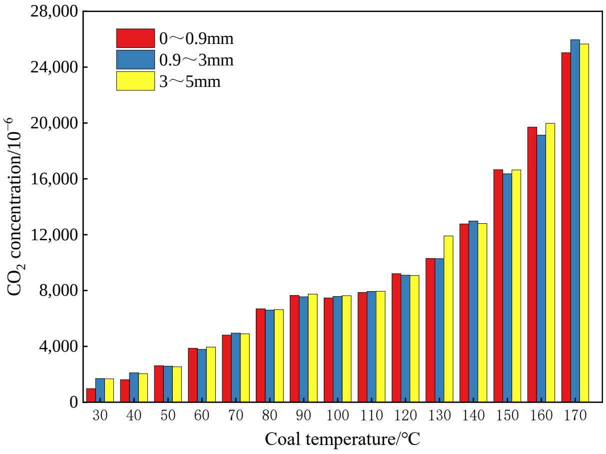


Figure 9. CO_2 concentrations produced at different coal temperatures by different coal particle-size ranges.

3.1.3. Hydrocarbon Gas Concentrations

Hydrocarbon gases are important products of the spontaneous combustion and oxidation of coal, which are very active in the high-temperature stage and are often used as indicator gases to assist in defining the degree of danger of coal approaching the ignition point. The CH_4 gas concentrations generated by the different particle-size ranges of the coking coal samples at different coal temperatures during the test are shown in Figure 10. CH_4 gas was produced at a coal temperature of 30 °C, and the production accelerated above 70 °C and then became stable above 120 °C.

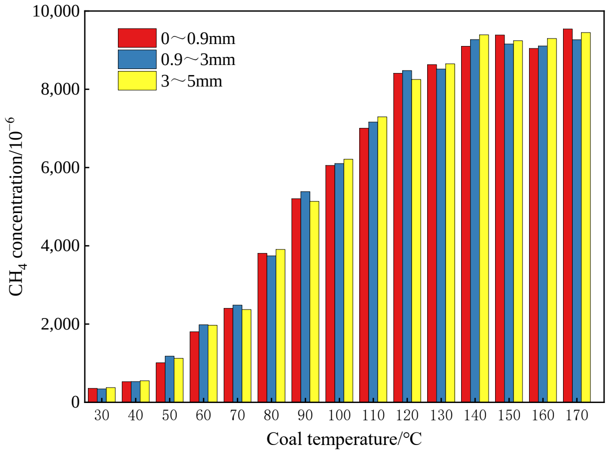


Figure 10. CH_4 concentrations generated by different coal particle-size ranges at different coal temperatures.

The C_2H_4 gas concentrations generated by the different particle-size ranges of the coking coal samples at different coal temperatures during the test are shown in Figure 11. C_2H_4 gas started to appear when the coal temperature reached 120 °C, and the concentration was very low. Then, the concentration increased regularly with rising coal temperature and increased rapidly above 160 °C. The appearance of the C_2H_4 gas is mainly due to the breakage of the coal's molecular bonds, so once C_2H_4 gas is detected, the coal temperature has exceeded the dry-cracking temperature. Considering the uneven heat distribution in the coking coal, the risk of spontaneous combustion of the coal is already high when the dry-cracking temperature of the coal is exceeded. Therefore, effective measures must be taken to prevent fire.

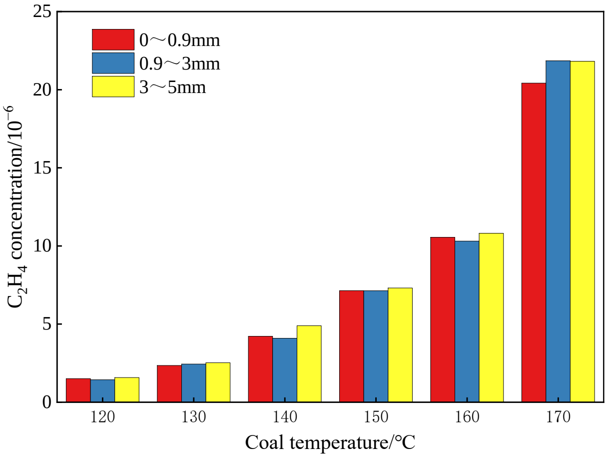


Figure 11. C_2H_4 concentrations generated by different coal particle-size ranges at different coal temperatures.

The C_2H_6 concentrations generated by the different particle-size ranges of the coking coal samples at different coal temperatures are shown in Figure 12. C_2H_6 gas is produced when the coal temperature is 30 °C; the concentration of C_2H_6 increases with rising coal temperature, and the particle size negligibly affects its concentration.

3.1.4. Chain Alkane Ratio and Olefin–Alkane Ratio

The chain alkane ratio refers to the ratio of the concentration of a single component of a long-chain alkane in the C_1–C_4 range to the concentration of methane or ethane. The C_2H_6/CH_4 ratio is one of the chain alkane ratios and is selected to analyze its correlation with the trends of the spontaneous combustion and ignition of coal. Figure 13 shows that the C_2H_6/CH_4 ratio decreases and then increases with rising coal temperature, but the regularity is poor. And because the same ratio corresponds to different temperatures, the results are easily misinterpreted; therefore, this ratio is not recommended as an indicator to analyze the stage of the spontaneous combustion of coking coal. Because the coal itself adsorbs CH_4, a high concentration of CH_4 is released from each coal sample at the beginning of the experiment. As the temperature rises, the concentration of CH_4 in the coal gradually increases and reaches an extreme value near the dry-cracking temperature, resulting in the lowest C_2H_6/CH_4 ratio. When the dry-cracking temperature is exceeded, the coal produces additional C_2H_6, and the C_2H_6/CH_4 ratio gradually increases.

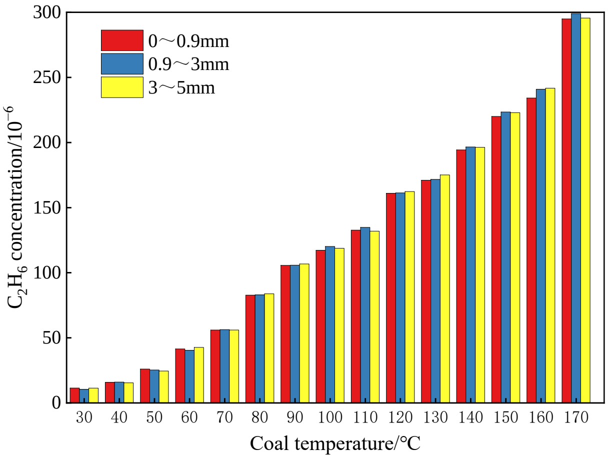


Figure 12. C_2H_6 concentrations generated by different coal particle-size ranges at different coal temperatures.

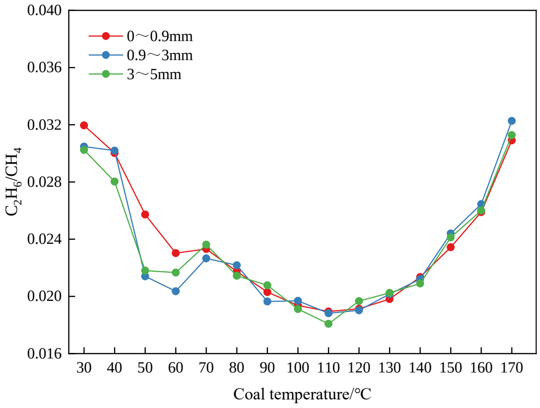


Figure 13. The C_2H_6/CH_4 ratio plotted as functions of coal temperature at different coal particle-size ranges.

The olefin–alkane ratio refers to the ratio of the concentration of an olefin gas to the concentration of the alkane in a carbon chain longer than or the same length as the olefin molecule. The C_2H_4/C_2H_6 ratio is one of the olefin–alkane ratios and is selected to analyze its correlation with the spontaneous combustion and ignition of coal. As shown in Figure 14, the C_2H_4/C_2H_6 ratio regularly and gradually increases and can be used as an indicator to assist in analyzing the stage of the spontaneous combustion of coking coal.

3.2. *Principal-Component-Analysis-Based Optimization of Marker Gas for Analyzing Spontaneous Combustion of Coal*

During the spontaneous combustion of coal, the increased temperature and concentration of precipitated gas partly unveil this process. Principal component analysis plays a vital role in selecting marker gases for the self-combustion of coal by quantitatively assessing the information contained within each gas index, which minimizes the potential human bias in the selection process.

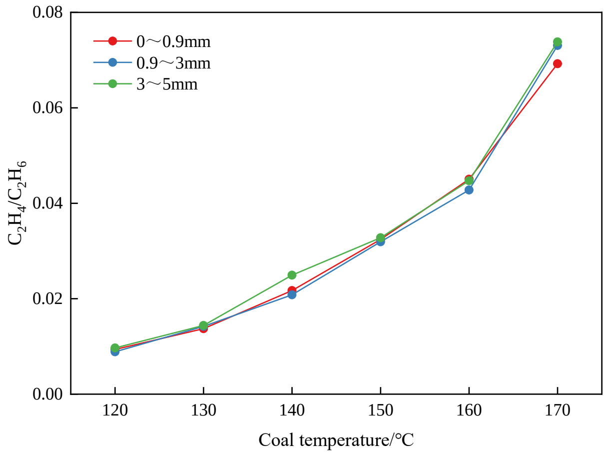


Figure 14. The C_2H_4/C_2H_6 ratio plotted as functions of coal temperature at different coal particle-size ranges.

The entropy value method is a valuable tool for assessing the dispersion of specific indicators. A lower information entropy value in an indicator signifies higher dispersion and, consequently, a more significant influence on the comprehensive evaluation process. Therefore, information entropy can be used to effectively calculate the weight of each indicator, forming the basis for selectively prioritizing marker gases in the detection of the spontaneous combustion of coal.

(1) There are m samples, each described by n indicators (variables) with values of X_{ij} $(1 \le i \le m, 1 \le j \le n)$. The decision matrix, $X = (X_{ij})m \times n$, is normalized by a linearly proportional transformation to obtain the normalized matrix, $Y = (y_{ij})m \times n$, which is normalized and computed as

$$p_{ij} = \frac{y_{ij}}{\sum_{i=1}^{m} y_{ij}}(1 \ \le \ i \ \le \ m, \ 1 \ \le \ j \ \le \ n) \tag{1}$$

(2) The entropy value is calculated as

$$e_j = -k\sum_{i=1}^{m} p_{ij}\text{In}p_{ij}(1 \ \le j \le n), k > \ 0, e_j \ge \ 0 \tag{2}$$

(3) To calculate the coefficient of variation for the j indicator, we consider that a larger difference in the indicator values indicates a higher reference value in the program evaluation, leading to a lower entropy value. Conversely, a smaller difference in the indicator values suggests a lower reference value in the program evaluation, resulting in a higher entropy value. Thus, we define the difference coefficient as

$$d_j = 1 \ - \ e_j \ 1 \ \le j \le n \tag{3}$$

(4) The weights of the indicators are determined, with the j indicator weighted as

$$w_j = \frac{d_j}{\sum_{j=1}^{m} d_j} \ 1 \ \le j \le n \tag{4}$$

The weight diagrams of the single-gas index and composite-gas index are shown in Figures 15 and 16, respectively. Figures 15 and 16 provide insights into the gas index weights of the coal samples from three distinct coal seams, indicating a remarkable similarity and reinforcing the accuracy of our experimental results.

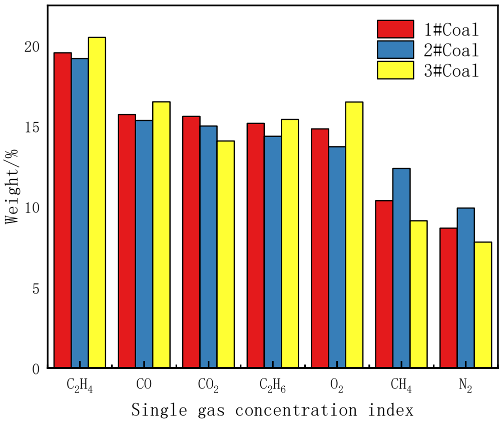


Figure 15. Single-gas index weights of three coal seams.

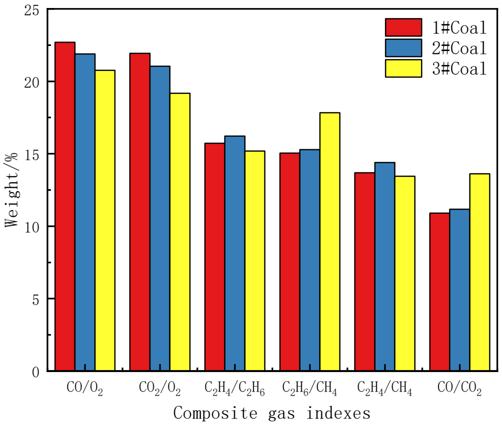


Figure 16. Composite-gas index weights of three coal seams.

3.3. Natural Ignition Period of Coal Seams

The spontaneous combustion period serves as a temporal measure of the risk of the spontaneous combustion of coal. In theory, it is defined as the time required for all the coal exposed to air to undergo spontaneous combustion, meaning the duration from coal exposure to spontaneous combustion. The shortest spontaneous combustion period for a coal seam is, therefore, the briefest period within which spontaneous combustion can occur. In the context of safety in coal mining operations, the study of the distinct characteristics and laws governing the spontaneous combustion of coal is essential for effective prevention and control. Additionally, the prediction of the shortest spontaneous combustion period of coal is a crucial aspect.

3.3.1. Thermal Property Parameters of Coal

The thermal property parameters tested during the oxidation and spontaneous combustion of coal are shown in Table 3.

3.3.2. Calculation of Natural Ignition Period of Coal Seams

When evaluating the natural ignition risk of coal, the calculation of the natural ignition period of coal seams has become a more reliable method. Before the layout of the coal mining area or working face, the natural ignition period of the coal seams within the designed mining area can accurately and intuitively reflect the probability of natural coal ignition and provide a basis for designing coal mining methods and formulating fire prevention measures. This is of great significance to the safe production of coal mines. In this study, the natural ignition period of the Hex coking coal seam at Ping Coal is calculated based on the experimental data obtained from the programmed-temperature-rise test and the thermal property parameters measured during the spontaneous combustion of coal.

Table 3. Experimental results for thermal property parameters of coal.

Number	Coal Temperature (°C)	Specific Heat Capacity (J/(g·°C))	Thermal Diffusion Coefficient (mm^2/s)	Thermal Conductivity (W/(m·°C))
1	20	1.089	0.102	0.127
2	30	1.078	0.098	0.12
3	40	1.187	0.091	0.124
4	50	1.192	0.089	0.121
5	60	1.205	0.087	0.12
6	70	1.241	0.085	0.121
7	80	1.271	0.082	0.119
8	90	1.309	0.08	0.12
9	100	1.325	0.078	0.119
10	110	1.358	0.078	0.12
11	120	1.391	0.076	0.121
12	130	1.428	0.075	0.122
13	140	1.462	0.074	0.123
14	150	1.487	0.073	0.124
15	160	1.507	0.072	0.123
16	170	1.521	0.071	0.124
17	180	1.594	0.07	0.128

И. B. Karin [29,30] conducted a comprehensive analysis of the thermal effects during the process of the spontaneous combustion of coal and subsequently developed a calculation model tailored to determine the spontaneous combustion period of coal. This model postulates that under ideal adiabatic environmental conditions, all the heat generated from oxygen adsorption by coal samples is employed for heating the samples, along with physical effects, such as water evaporation, that exhibit endothermic properties during the heating process. The calculated heating time represents the shortest natural ignition period for coal. The calculation model is expressed by the following formula:

$$\tau = \sum_{i=1}^{n} \frac{\left(C_{pi} + C_{pi+1}\right)\Delta T_i + 2\left(\frac{W_p \lambda}{100} + \Delta\mu_p Q'\right)}{1440\left[q(t_i) + q(t_{i+1})\right]} \tag{5}$$

where τ is the minimum natural ignition period of the coal seam; C_{pi} is the specific heat of the coal measured at temperature T_i, J/(g·°C); C_{pi+1} is the specific heat of the coal measured at temperature T_{i+1}, J/(g·°C); ΔT_i is the time required for the coal temperature to rise from T_i to T_{i+1}, min; W_p is the amount of water evaporation from the coal from T_i to T_{i+1}, %; λ is the heat of water evaporation and desorption, taking the average value of 2.26 kJ/g; $\Delta\mu_p$ is the amount of gas desorption in the coal from T_i to T_{i+1}; Q' is the heat of gas desorption, taking the average value of 12.6 J/mL; and $q(t_i)$ and $q(t_{i+1})$ are the exothermic rates of the coal sample at temperatures T_i and T_{i+1}, respectively.

Niu [31] enhanced the accuracy of the coal's oxygen absorption rate (K_c) by implementing a test method that involved temperature-based assessments and segmented calculations for the coal's oxygen absorption rate. This approach improved the reliability of the ignition period calculations to a considerable extent.

Nevertheless, Karin's model is primarily applicable for calculating the duration of the low-temperature oxidation stage. As the coal oxidation temperature increases, the model fails to account for the subsequent accelerated oxidation and thermal-cracking stages that occur during the later stages of the process. In these later stages, the heat generated by the oxidation reaction becomes the primary source of heat, and the adsorption heat is comparatively low. This oversight can lead to significant errors, rendering the model unsuitable for calculating the shortest spontaneous combustion period of coal during violent reactions.

Additionally, Yu [32] further advanced the field by deriving a mathematical model for calculating the shortest spontaneous combustion period in the enhanced И. B. Karin coal seam. This model aligned more accurately with real-world conditions. In this model, the heat released for surface oxidation at each temperature segment was determined using the differential scanning calorimetry (DSC) method. The temperature denoted as T_{kp} was identified as the ignition temperature. Subsequently, heat released owing to the coal's oxygen absorption was calculated across different temperature segments from the ambient temperature to the ignition temperature. This, combined with the released oxidation heat, provided a comprehensive assessment of heat released during coal's oxidation process. Remarkably, the model achieved a prediction accuracy ranging from 74% to 90% and has been widely applied in the study of the shortest spontaneous combustion period in coal seams.

Nevertheless, advancements in the characterization and testing of coal oxidation and spontaneous combustion's thermal effects allow for error reduction through more precise measurements of the intensity of the actual heat released during coal's heating process. In this study, the mathematical model for the shortest spontaneous combustion period of the И. B. Karin coal seam, as improved by Yu [30], is employed in combination with a programmed-temperature test device and the LFA457 laser thermal conductivity analyzer. This approach reduces measurement errors during the later stages of the temperature rise in the coal samples, enabling the accurate calculation of the shortest spontaneous combustion period for the Hex coal seam at Ping Coal.

(1) Specific heat capacity of coal

The specific heat capacity of the Hex coking coal seam at Ping Coal was evaluated based on the coal's thermal property parameters, and the thermal diffusion coefficient and thermal conductivity of the coal were also evaluated.

(2) Water evaporation from coal

Because the amount of water evaporation from the coal is small in the temperature range from 20 to 100 °C, the water evaporation is mainly approximated in the temperature range from 100 to 120 °C. Usually, 5% of the water evaporates from room temperature to 100 °C, and 95% of the water evaporates from 100 °C to 120 °C.

(3) Gas desorption of coal

The amount of gas desorption from the coal sample at different temperatures is calculated using the following equation:

$$\mu_p^{t_i} = \mu_p^{t_0} \exp[n(t_0 - t_i)] \tag{6}$$

where ${\mu_p}^{t0}$ is the gas adsorption of the coal sample at temperature t_0, m^3/kg; and ${\mu_p}^{ti}$ is the gas adsorption of the coal sample at temperature t_i, m^3/kg.

(4) Exothermic rates of coal

For the coal sample, $q(t_i)$ and $q(t_{i+1})$ are the exothermic rates at temperatures T_i and T_{i+1}, respectively, which can be calculated as follows:

$$q(t) = q_a[n_{o_2}(t) - n_{co}(t) - n_{co_2}(t)] + n_{co}(t)[h^0_{co}(298) + \Delta h^0_{co}] + n_{co_2}(t)[h^0_{co_2}(298) + \Delta h^0_{co_2}] \tag{7}$$

where $n_{CO}(t)$ is the rate of CO production under a given condition, mol/(kg·min); $n_{CO_2}(t)$ is the rate of CO_2 production under a given condition, mol/(kg·min); $n_{O_2}(t)$ is the rate of O_2 consumption under a given condition, mol/(kg·min); q_a is the chemical adsorption heat of the coal and oxidation, taken as 58.8 kJ/mol; $h^0_{CO}(298)$ is the standard enthalpy of CO generation, taken as 110.59 kJ/mol; and $h^0_{CO_2}(298)$ is the standard enthalpy of CO_2 generation, taken as 393.77 kJ/mol. The above calculation model and experimental results were used to calculate the natural ignition period of the three coal samples, and the specific calculation results are shown in Tables A1–A3.

4. Discussion

4.1. Analysis of the Spontaneous Combustion Characteristics of Coking Coal

Figures 4 and 5 show that at oxygen concentrations of 21%, 18%, 15%, and 10%, coal oxidation enters an intense stage marked by coal temperatures that are significantly higher than furnace temperatures, leading to steep peaks in the graph. During this phase, the coal releases a substantial amount of heat, causing rapid temperature increases. As the coal oxidation intensifies, the oxygen consumption also rises. As a result, the oxygen concentration in the coal oxidation environment significantly decreases, which hinders oxidation owing to hypoxia and consequently lowers the coal temperature. When the oxygen concentration increases again, another round of intense oxidation occurs, leading to the observed multi-peak phenomenon. At an oxygen concentration of 8%, although the coal temperature remains higher than the furnace temperature, the steep peak of the significant temperature increase disappears. This suggests that fierce oxidation combustion during the spontaneous combustion of coal at an oxygen concentration of 8% is essentially impossible. Consequently, we conclude that the lowest critical oxygen concentration required for spontaneous combustion in the hexagonal coking of flat coal is 8%.

Figure 6 shows that the accumulation of oxidation heat in coal samples is positively correlated with the O_2 concentration and that the higher the O_2 concentration, the more significant the heat accumulation. At about 220 min, the coal sample in the high-oxygen-content atmosphere oxidized violently and released a large amount of heat, which increased the coal temperature above the environmental temperature, while the temperature of the coal sample in the low-oxygen-content environment basically changed with the environmental temperature, and violent oxidation was not obvious. At about 260 min, the curves representing the temperatures of the coal under different O_2 concentration conditions all showed an inflection point and decreased. This is mainly because the programmed temperature rise ended, the environmental oxygen had been consumed to support the violent oxidation of the coal sample, and the coal temperature then continued to be consistent with the environmental temperature.

From Figure 7, the O_2 concentration has a substantial influence on the CO production rate. When the O_2 concentration is greater than 10%, the CO production rate is influenced by the environmental temperature. When the O_2 concentration is less than 8%, the CO production rate increases slowly. An inflection point appears after a certain value, and the CO production rate starts to decrease. This indicates that when the environmental oxygen concentration is lower than 8%, the oxidation rate of the coal is low, and very little heat is generated, which has a negligible effect on the environmental temperature. Owing to the heat-transfer diffusion effect of the rock, the overall ambient temperature is low, and it is difficult to produce the conditions required for heat accumulation. Therefore, it can be considered that there is no possibility of the spontaneous combustion of the coal, and the coal seam enters the asphyxiated state.

Figures 5–7 show that the exothermic oxidation reaction of the coal will accelerate rapidly when the environmental temperature of the coking coal is above 200 °C, and the coal can ignite and burn rapidly if no preventive and control measures are taken. Therefore, the study of the spontaneous combustion and ignition of coking coal should focus on the changes in the indicator gases below 200 °C.

4.2. Optimization of Marker Gas for Analyzing Spontaneous Combustion of Coal

From Figures 15 and 16, when we focus on individual gas indicators, it becomes evident that compared with the other gases, CH_4 and N_2 carry significantly lower weights, rendering them unsuitable as indicators for the initial stage of the spontaneous combustion of coal. On the contrary, among C_2H_4, CO, CO_2, and C_2H_6, C_2H_6 bears notably less weight than the other three gases.

In conventional mining processes, coal layers tend to adsorb a certain amount of CO_2. However, during coal seam mining, the desorption of coal leads to the release of CO_2 and CH_4 in the working area. Owing to these dynamic processes, CO_2 and CH_4 are unsuitable as direct marker gases for predicting the spontaneous combustion of coal. Consequently, we have chosen CO, C_2H_4, and C_2H_6 as the marker gases for forecasting the initial stage of spontaneous combustion in coal seams. Concerning the composite-gas indicators, the three most significant weight ratios include CO/O_2, CO_2/O_2, and C_2H_4/C_2H_6, wherein O_2 serves as a negative indicator variable. During the spontaneous combustion of coal, O_2 is swiftly consumed and undergoes a complex reaction process such that the O_2 content lacks a reference value. Consequently, chain-to-alkane and olefin-to-alkane ratios are typically favored as primary indicators. In experiments on the spontaneous combustion of coal, the C_2H_4/C_2H_6 ratio exhibits the highest weight, rendering it a valuable auxiliary warning indicator for predicting the spontaneous combustion of coal.

4.3. Analysis of the Natural Ignition Period of the Coal Seam

As shown in Tables A1–A3, the natural ignition time of the Hex coking coal seam at Ping Coal from 30 °C to 170 °C is calculated at about 59.69 days. According to the coking coal spontaneous combustion and ignition simulation experiments, the time required to reach the ignition point for the spontaneous combustion of coal starting from 170 °C is generally less than one day under the condition of sufficient oxygen. From this, it can be inferred that the natural ignition period of the Hex coking coal seam at Ping Coal is about 60 days, which is a short time, and the coal seam has a high risk of spontaneous combustion.

5. Conclusions

The conclusions can be summarized as follows:

(1) Coking coal violently and spontaneously oxidizes near the ignition point of the coal when the environmental temperature is above 200 °C, and fire prevention measures for controlling coking coal should be implemented below 200 °C. The starting temperature at which CO appears in the oxidation process of coking coal rises with decreasing O_2 concentration. The temperature at which CO is first detected rises by 10–15 °C for each reduction in the O_2 concentration. The minimum critical oxygen concentration required for the spontaneous ignition of the Hex coking coal seam at Ping Coal is identified as 8%;

(2) During the programmed-temperature-rise test, the oxygen consumption rate of the Hex coking coal seam at Ping Coal increased with rising coal temperature. The critical temperature range for accelerated oxidation is 50–60 °C, where the CO and CO_2 productions accelerated. The dry-cracking temperature of the coking coal is in the range 100–120 °C, and this stage is accompanied by the production of C_2H_4 gas. The coking coal particle size has a negligible effect on the generation of CO, CO_2, CH_4, C_2H_4, and C_2H_6 gases;

(3) We quantitatively analyzed and comprehensively evaluated the experimental data for the oxidation heat by constructing a multi-index weight model. CO and C_2H_4 were identified as the primary indicator gases for determining the spontaneous combustion stage of the Hex coking coal seam at Ping Coal. Additionally, C_2H_6 and the C_2H_4/C_2H_6 ratio were used as secondary indicators for the auxiliary analysis. That is, when the CO concentration increases slowly, the coal temperature is below 50–60 °C. When the CO concentration increases significantly faster, the coal temperature exceeds 50–60 °C. When the CO concentration increases extremely fast and C_2H_4 and C_2H_6 gases are detected while the C_2H_4/C_2H_6 ratio is not 0, the coal temperature in the mining area exceeds 120 °C. Then, the risk of spontaneous combustion is already very high, and it is necessary to take fire prevention measures;

(4) The concentration of each gas during the temperature rise of the coal samples was measured using the programmed-temperature-rise test, and the thermal property parameters from the oxidation of the coal samples to the occurrence of spontaneous combustion were obtained by measuring the thermal property parameters of the coal during spontaneous combustion. Utilizing the enhanced mathematical model for determining the shortest spontaneous combustion period of coal seams, in conjunc-

tion with a programmed-temperature test device, experimental calculations were conducted to ascertain the adiabatic spontaneous combustion period. Additionally, the intensity of the exothermic reaction during the later stages of coal-sample heating was calculated quantitatively, resulting in a substantial reduction in the error of the calculation model. The results indicate that the natural ignition period for the Hex coking coal seam at Ping Coal is approximately 60 days, representing a brief timeframe, and the coal seam is characterized by a high risk of spontaneous combustion.

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Appendix A

Table A1. Experimentally measured natural ignition period of coal sample #1.

Coal Temperature (°C)	C_P	λ	W_P	q(t)	$q(t_1)$	μ	τ (s)	τ (d)
30	1140	1200	0.00	62,599	0.010	6.10	2,405,999	27.85
40	1249	1240	0.16	1,316,839	0.025	9.02	991,353	11.47
50	1254	1210	0.46	2,191,457	0.047	17.33	537,435	6.22
60	1267	1200	0.62	4,329,587	0.070	30.90	365,282	4.23
70	1303	1210	1.14	5,457,058	0.107	41.17	246,915	2.86
80	1333	1190	1.82	9,401,904	0.162	65.31	167,284	1.94
90	1371	1200	2.76	13,121,998	0.218	89.24	127,105	1.47
100	1387	1190	2.08	17,151,520	0.298	103.82	94,521	1.09
110	1420	1200	0.80	24,287,484	0.380	120.15	76,054	0.88
120	1453	1210	0.37	28,422,203	0.455	144.25	65,083	0.75
130	1490	1220	0.14	34,708,331	0.599	148.05	50,607	0.59
140	1524	1230	0.00	48,432,512	0.905	156.11	34,144	0.40
150	1549	1240	0.00	77,221,549	1.326	161.01	23,641	0.27
160	1569	1230	0.00	106,933,209	1.748	155.15	18,126	0.21
170	1583	1240	0.00	135,809,171	1.123	163.66	14,247	0.16
Total natural ignition period (days):								60.39

Table A2. Experimentally measured natural ignition period of coal sample #2.

Coal Temperature (°C)	**C_P**	**λ**	**W_P**	**q(t)**	**$q(t_1)$**	**μ**	**τ (s)**	**τ (d)**
30	1140	1200	0.00	124,789	0.010	5.83	2,412,688	26.96
40	1249	1240	0.16	1,250,808	0.023	9.07	1,069,079	12.37
50	1254	1210	0.46	2,002,431	0.042	20.23	601,848	6.97
60	1267	1200	0.62	3,821,391	0.062	34.00	417,085	4.83
70	1303	1210	1.14	4,750,798	0.105	42.61	251,033	2.91
80	1333	1190	1.82	9,865,272	0.173	64.19	156,956	1.82
90	1371	1200	2.76	14,139,775	0.231	92.38	120,080	1.39
100	1387	1190	2.08	17,908,566	0.296	104.66	95,161	1.10
110	1420	1200	0.80	23,253,017	0.379	122.86	76,201	0.88
120	1453	1210	0.37	29,359,646	0.464	145.44	63,715	0.74
130	1490	1220	0.14	35,128,737	0.624	146.11	48,578	0.56
140	1524	1230	0.00	51,479,097	0.944	159.02	32,723	0.38
150	1549	1240	0.00	79,646,017	1.307	157.07	23,972	0.28
160	1569	1230	0.00	101,944,069	1.645	156.23	19,258	0.22
170	1583	1240	0.00	126,537,061	1.056	158.96	15,143	0.18
Total natural ignition period (days):								61.58

Table A3. Experimentally measured natural ignition period of coal sample #3.

Coal Temperature (°C)	**C_P**	**λ**	**W_P**	**q(t)**	**$q(t_1)$**	**μ**	**τ (s)**	**τ (d)**
30	1140	1200	0.00	124,804	0.010	6.42	2,306,654	26.70
40	1249	1240	0.16	1,314,065	0.026	9.42	957,429	11.08
50	1254	1210	0.46	2,318,600	0.046	19.25	553,901	6.41
60	1267	1200	0.62	4,009,094	0.079	33.75	326,646	3.78
70	1303	1210	1.14	6,936,384	0.129	40.66	205,465	2.38
80	1333	1190	1.82	10,919,864	0.181	67.02	150,033	1.74
90	1371	1200	2.76	14,195,463	0.228	88.09	121,735	1.41
100	1387	1190	2.08	17,412,007	0.295	106.58	95,471	1.10
110	1420	1200	0.80	23,619,084	0.380	125.13	76,041	0.88
120	1453	1210	0.37	29,109,057	0.447	141.56	66,129	0.77
130	1490	1220	0.14	33,017,323	0.587	148.37	51,576	0.60
140	1524	1230	0.00	48,562,573	0.901	161.10	34,284	0.40
150	1549	1240	0.00	76,600,534	1.309	158.53	23,946	0.28
160	1569	1230	0.00	105,192,463	1.669	159.47	18,982	0.22
170	1583	1240	0.00	126,632,361	1.057	162.11	15,136	0.18
Total natural ignition period (days):								57.91

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