Spontaneous Combustion Characteristics of Wetting Coal under Different Prepyrolysis Temperatures

Kai Wang,* Haohao Fan, Peng Gao, Yunzhong He, and Pan Shu

ABSTRACT: The influence of prepyrolysis temperatures on the spontaneous combustion of wetting coal remains unclear from a macroscopic perspective. To this end, a low-ash and high-volatile wetting coal sample from Western China was pretreated by a programmed heating experimental system at isothermal pyrolysis temperatures of 50, 80, 110, 140, and 170 °C under nitrogen atmosphere and then cooled to room temperature; after that, the oxidation heating experiment was carried out within the range of 30–170 °C. The results indicated that, when the wetting coal samples were subjected to isothermal pyrolysis experiments, the concentrations of CO and CO₂ gradually decreased with the prepyrolysis time, during which the cumulative value of CO increased with the prepyrolysis temperatures, while the change trend of CO₂ is first increased, then decreased, and then increased. In terms of the oxidative heating experiment, the CO concentration of prepyrolyzed coal samples was higher than that of raw coal before 70 °C and then gradually lower than that of the raw coal with the increasing temperature. The CO₂ concentration of coal samples with prepyrolysis temperature of 170 °C is significantly lower than that of other coal samples. According to the characteristic parameters of CO and CO₂ concentrations, oxygen consumption rate, and exothermic intensity, it is inferred that the coal sample with a prepyrolysis temperature of 140 °C exhibited the highest spontaneous combustibility. The experimental results have a certain guiding role for the safe mining of coal seam and the prevention and control on spontaneous combustion.

1. INTRODUCTION

Some mines in Western China have high gas and high moisture contents in the coal seam because of the influence of a unique geological environment. Under the existing technical conditions, N₂, CO₂, and moisture can be injected to displace the coal seam gas to reduce gas concentration. In order to reduce the gas adsorption capacity of coal, the coal body is usually heated to promote gas desorption. In this case, the spontaneous combustibility of wetting coal would be changed by heating treatment in an inert atmosphere.

Coal spontaneous combustion is a complex physical and chemical process, in which temperature plays a vital role. When the temperature rises, the heat accumulates continuously because of reaction between a large number of functional groups and oxygen, which provides favorable conditions for the occurrence of coal spontaneous combustion. Programmed heating experiments were used widely to determine the degree of spontaneous combustion of coal. On this basis, the preoxidized or prepyrolysis coal formed after the oxidation of raw coal was simulated by programmed heating experiments. The results show that the preoxidation temperature, oxygen concentration, and moisture are key factors affecting the spontaneous combustion of preoxidized coal. By the programmed heating experimental system, Wang and Zhang found that the preoxidation temperature has the dual effects on promoting and inhibiting the coal spontaneous combustion. Tang and Wang carried out the TG/DSC test on preoxidized lignite, the results of whose has shown that preoxidation gradually increased the self-heating risk of coal, but preoxidation at an excessively high temperature may reduce the tendency of spontaneous combustion of coal. Zhu et al. investigated pore structure, free radical concentrations, thermal behavior, and FTIR microcharacteristics of the reoxidation coal. Xiao et al. investigated the variations of mass, heat energy intensity, and gaseous products of first and second coal spontaneous combustion. All these discussions have been used to study the macroscopic and microscopic characteristics of coal from the perspective of preoxidation temperature, which is of great significance to the prevention of spontaneous combustion of preoxidized coal samples. Similarly, in the process of gas displacement, the coal body is heated in an inert atmosphere. After a series of physical–
chemical actions, the preheated decomposing coal sample is formed. Li et al.\textsuperscript{20−22} found that the coal after low-temperature pyrolysis is more prone to self-heating and spontaneous combustion and put forward the viewpoint of room-temperature oxidation of active sites, which is of great significance to the interpretation of the spontaneous combustion mechanism of coal. However, presently, there are limited research on the spontaneous combustibility of prepyrolyzed coal.

Summarizing, many studies have focused on the effect of preoxidation temperature on the spontaneous combustion of preoxidation coal, whereas there has been limited research on the spontaneous combustibility of prepyrolyzed coal. To this end, a programmed heating experimental system was setup in this study to simulate the spontaneous combustibility of wetting coal after preheating in a nitrogen atmosphere. The effect of prepyrolysis temperature on the spontaneous combustibility of wetting coal is studied from the macroscopic view, which is of great significance to prevent and control the spontaneous combustion of coal in mines with high gas and high moisture content.

2. RESULTS AND DISCUSSION

2.1. Evolution of CO and CO\textsubscript{2} in Isothermal Pyrolysis Process. As shown in Figure 1, the 1−5# coal samples are subjected to isothermal pyrolysis under nitrogen atmosphere, during which CO and CO\textsubscript{2} gases are continuously precipitated, which verifies the existence of an autothermal reaction between the active groups in the coal from the perspective of macroscopic products. The studies shown that these active groups are complexes composed of carbonyl, carboxyl, and other original active groups contained in coal.\textsuperscript{23−25}

With the increase of prepyrolysis time, the CO and CO\textsubscript{2} concentrations gradually decrease, indicating that the complex compounds in the coal are continuously decomposed and consumed under the action of N\textsubscript{2} purging, resulting in a gradual decrease in the concentrations of the gas products. The experimental data show that the production of CO\textsubscript{2} is significantly higher than that of CO, because the activation energy required to produce CO\textsubscript{2} is lower than that required for CO. CO\textsubscript{2} is produced in more ways than CO, and CO\textsubscript{2} as the original gas could be desorbed under the condition of heating.\textsuperscript{26−28} Under the comprehensive effect of these factors, the CO\textsubscript{2} concentration is much higher than the CO concentration.

To comprehensively characterize the influence of prepyrolysis temperature on CO and CO\textsubscript{2} production, the cumulative CO and CO\textsubscript{2} gas concentration method was used for a comparative analysis under the same experimental ventilation condition. Figure 2 shows that with the increasing prepyrolysis temperature, the accumulative value of the CO gas concentration increases nonlinearly, mainly characterized by a “jump” from 80 to 110 °C. By contrast, the change trend in the CO\textsubscript{2} concentration is more complicated. The main source of CO\textsubscript{2} gas is not only the original active-group self-heating reaction, but also the desorption effect of the original gas in the coal seam. On the one hand, with the increase in the external temperature, the molecular kinetic energy of CO\textsubscript{2} increases, and a desorption effect occurs gradually. The maximum desorption peak is reached at a temperature range of 50–80 °C, after which the desorption amount starts decreasing.\textsuperscript{29} On the other hand, as the prepyrolysis temperatures increase, the autothermal reaction between the original active groups...
becomes more intense. Under the comprehensive influence of the above factors, it is found that the 1# coal sample exhibits the lowest CO₂ production rate while the 2# coal sample exhibits the highest.

2.2. Spontaneous Combustion Characteristics of Coal Samples. The 1−5Y prepyrolyzed coal samples were obtained by preheating the wetted coal samples under the nitrogen atmosphere at different constant temperatures. These samples were subjected to secondary heating in air from 30 to 170 °C. By contrast, the raw coal 6# was directly tested under the same condition for oxidation heating. By measuring and comparing the parameters of the spontaneous combustion characteristics between the prepyrolyzed and raw coals in the oxidation process, the influence of prepyrolysis temperature on the spontaneous combustion of the wetted coal was studied.

2.2.1. Oxygen Consumption. Figure 3 shows the change trend in the O₂ concentration at the outlet of the sample vessel. In the initial stages of spontaneous combustion, the O₂ concentrations in all samples decrease slowly with temperature. During this period, the physical adsorption reaction of coal to oxygen mainly occurred. As the temperature increases, oxidation rates gradually accelerate, and more heat generates. When the temperature rises to 70 °C, more oxygen is consumed, indicating that the critical temperature of the coal has been reached, and the accelerating oxidation stage began. With increasing temperature, the decreasing rate of O₂ concentration gradually stabilizes and remains at a low level.

The oxygen fully participates in the coal−oxygen composition reaction, and the stage of intense oxidation starts. As shown in Figure 3, the O₂ concentration of the prepyrolyzed coal samples before 70 °C is lower than that of the raw coal, and the O₂ concentration is approximately proportional to the prepyrolysis temperature. During the isothermal prepyrolysis, a part of the moisture was evaporated, resulting in more pore channels or fractures in the 1−5Y coal samples, which is more conducive to the physical oxygen absorption compared to that in raw coal. When the temperature is above 70 °C, the decrease rate of O₂ concentration is accelerated, and the O₂ concentrations of the 1Y and 2Y coal samples become gradually higher than that of the raw coal. As the prepyrolysis temperatures of the 1Y and 2Y coal samples were relatively low, less water was evaporated, and the large amount of residual water owing to the higher steam pressure formed by evaporation had a significant inhibitory effect on the coal−oxygen contact reactions in the 1Y and 2Y coal samples; hence, the degree of oxygen consumption was lower than that in raw coal. As the temperature rises to 140 °C, the O₂ concentration of the coal samples in each group remains below 3%, and the O₂ concentration of 5Y is the highest in this period. Based on the entire oxidation heating process, that is, at temperatures ranging from 30 to 170 °C, it is found that the O₂ concentration of the 4Y coal samples is always at the lowest level. It can be inferred that the 4Y coal sample undergoes the highest degree of oxidation reaction.

2.2.2. Effect of Prepyrolysis Temperature on the Concentrations of CO and CO₂. As shown in Figure 4, more CO and CO₂ are produced under oxygen supply than that in the isothermal pyrolysis process, indicating the dominance of the oxidation reaction of coal. CO is one of the early indexes for predicting the spontaneous combustion coal, and CO₂ is another important oxidation product in this process. The trends in the CO and CO₂ concentrations with temperature are similar. At the initial stage of oxidation, the CO and CO₂ concentrations increase gradually with the temperature in a linear manner and, subsequently, increase rapidly in an exponential manner. Based on the release rates of CO and CO₂, the process of spontaneous combustion can be divided into three stages: slow oxidation stage (30−70 °C),
accelerated oxidation stage (70–110 °C), and rapid oxidation stage (110–170 °C).

As shown in Figure 5, the 1–5Y coal samples produce more CO than the raw coal in the slow oxidation stage, with 5Y exhibiting the highest CO concentration, followed by 4Y, 1Y, 3Y, 2Y, and 6#, in this order. After the isothermal pyrolysis treatment, the development of the coal fracture structure is conducive to the physical oxygen absorption reaction, whereas the production amount of CO, as the product of the oxidation and decomposition reaction, is positively correlated with the oxygen absorption. Therefore, the CO concentration of the prepyrolyzed coal samples is higher than that of raw coal.

Figure 5. Variations of CO concentrations at different oxidation stages: (a) slow oxidation stage; (b) accelerated oxidation stage; and (c) rapid oxidation stage.

Figure 6. Variations of CO$_2$ concentrations at different oxidation stages: (a) slow oxidation stage; (b) accelerated oxidation stage; and (c) rapid oxidation stage.
Generally, the higher the temperature of the isothermal prepyrolysis, the higher the evaporation of the water in the wetting coal and the higher the degree of coal looseness, which are more conducive to the oxidation and decomposition reaction of coal. However, the CO concentration of 1Y is higher than those of 3Y, 2Y, and 6#. This is because the prepyrolysis temperature of 1Y is the lowest, and the resulting large amount of residual water would generate more wetting heat in the initial stage of oxidation, which promotes the generation of CO gas to a certain extent. Therefore, the CO concentration of the 1Y coal sample is higher than those of the 3Y, 2Y, and 6# coal samples.

As the temperature increases, the coal samples enter the accelerated oxidation stage, as shown in Figure 5b; the CO concentrations of 5Y and 4Y coal samples are still higher than those of the other coal samples, and the CO concentration of 6# raw coal gradually exceeds those of the 3Y, 1Y, and 2Y coal samples, whereas the CO concentration growth rate of 1Y decreases. In the accelerated oxidation stage, the large number of original active groups in the raw coal promotes the coal—oxygen composite reaction with the accumulation of heat, thereby significantly increasing the CO concentration of the 6# coal sample. Moreover, the maximum residual water in the 1Y coal sample would lose a lot of heat under evaporation, and the steam pressure thus generated would hinder the coal—oxygen contact and heat transfer.31,32 Under the influence of these comprehensive factors, the coal—oxygen composite reaction of the 1Y coal sample is inhibited, thereby gradually decreasing the CO concentration to the lowest value. When the coal samples enter the rapid oxidation stage, as shown in Figure 5c, the CO concentration of 6# coal sample gradually increases to the highest level, whereas the 1–5Y coal samples exhibit a short crossover above 150 °C, that is, the CO concentrations of 3Y, 4Y, and 5Y become gradually lower than those of 1Y and 2Y. Without any treatment, raw coal retains the most original active structure, which significantly promotes the generation of CO gas. In addition, the prepyrolysis temperatures of 1Y and 2Y coal samples are lower; this makes the original active structure to be less consumed during the isothermal pyrolysis process compared to the 3–5Y coal samples, and the residual water in the 1Y and 2Y coal samples would generate more peroxyl complexes in the evaporation stage. These peroxyl complexes are thermally decomposed to accelerate the oxidation process of coal; therefore, the CO concentrations of 1Y and 2Y gradually increase compared to the 3–5Y coal samples.

Compared with the generation of CO, more factors affect the generation of CO₂ from coal under the condition of oxygen supply. In addition to the pore structure of the coal and the degree of coal metamorphism, factors such as the original gas in the coal and the type and number of active groups affect the generation of CO₂.33 These factors lead to the change rule of CO₂ concentration more complicated than that of CO. Figure 6 shows the curve of the CO₂ concentration with temperature at different oxidation stages. In the slow oxidation stage, that is, in the temperature range of 30–70 °C, the CO₂ concentrations of the prepyrolyzed coal samples are lower than that of 6# raw coal except for 1Y. The CO₂ stored in the raw coal itself is desorbed by heating, which has a significant impact on the CO₂ concentration in the slow oxidation stage. By contrast, the residual water in the 1Y coal sample generates more wetting heat, which is more conducive to the generation of CO₂ than that in raw coal to some extent. With the increase in the temperature, the coal samples enter the accelerated oxidation stage, and the CO₂ concentrations of 2Y and 6# increase faster and exceed that of the 1Y coal sample, whereas the CO₂ concentrations of the 3–5Y coal samples remain relatively low. When the rapid oxidation stage starts, as shown in Figure 6c, the CO₂ concentration growth rates of 3Y and 4Y are significantly accelerated, and there is a brief crossover with those of the coal samples of 1Y, 2Y, and 6# at approximately 140 °C; thereafter, the CO₂ concentration difference between the 1Y, 3Y, 4Y, and 6# samples gradually narrows. In this stage, the growth rate of the CO₂ concentration of the 2Y coal sample gradually slows down and is only higher than that of 5Y above 150 °C, and the CO₂ concentration of the 5Y coal sample is always at the lowest level. Considering that the prepyrolysis temperature of 5Y is the highest, more original active groups would be decomposed and consumed at a constant temperature of 170 °C, which makes the active structure retain in the oxidation process less than that in the other coal samples. The active structure in the rapid oxidation stage has a particularly significant impact on CO₂ production, bringing about the difference between the CO₂ concentration of 5Y and the other experimental coal samples more obvious.

Taking 170 °C as an example, the CO and CO₂ concentrations of prepyrolyzed 1–5Y samples during the oxidation heating process were compared, as shown in Figure 7. According to Figure 7a, it can be found that when the oxidation temperature rises to 170 °C, the CO concentration is inversely proportional to the prepyrolysis temperature, which is contrary to the law that the cumulative value of CO concentration increases with the increase of prepyrolysis temperature described in Figure 2a. It can be inferred that the CO concentration of 1–5Y coal samples are related to the isothermal prepyrolysis process.
According to Figure 7b, it can be found that the CO₂ concentration of prepyrolyzed 1–SY samples decrease first, then increase, and then decrease with the increase of prepyrolysis temperature. This is roughly opposite to the change trend of cumulative CO₂ concentration of 1–5Y coal samples with prepyrolysis temperature in Figure 2b. In addition, combined with Figures 2b and 7b, it can be found that there are significant differences in the variation range of cumulative CO₂ concentration, which also indirectly indicates that the influence factors of producing CO₂ are more than that of CO.

2.2.3. Effect of Prepyrolysis Temperature on Oxygen Consumption Rate. According to the difference of O₂ concentration between the inlet and outlet of the furnace, the total oxygen consumption rate of coal sample can be calculated. The calculation formula is as follows:

\[ V_{O_2}^0(T) = \frac{Q \cdot O_2^0}{S \cdot L} \ln \left( \frac{C_{O_2}^1}{C_{O_2}^2} \right) \]

(1)

where \( V_{O_2}^0(T) \) is the oxygen consumption rate, mol/(cm³ s); \( C_{O_2}^1 \) is the oxygen concentration in fresh air, 21%; \( C_{O_2}^1 \) and \( C_{O_2}^2 \) are the inlet and outlet O₂ concentrations, mol/m³; \( S \) is the furnace cross-sectional area, cm²; \( L \) is the height of the coal sample in the furnace, cm; \( Q \) is the air flow rate volume, cm³/s.

By substituting the relevant data of the experimental measurement into the above formula, the oxygen consumption rate and temperature change curve of the coal sample can be drawn from the calculation, as shown in Figure 8:

**Figure 8.** Variation of the oxygen consumption rate of each coal sample during the oxidative heating process.

In Figure 8, the oxygen consumption rate of coal at the initial oxidation stage is low and increases slowly. With the increase of temperature, the coal–oxygen composite reaction accelerates, and the oxygen consumption rate also increases rapidly. The higher the temperature, the greater the effect of oxygen concentration on the oxygen consumption rate. Moreover, by comparing with the O₂ concentration, it is found that the change rule of the oxygen consumption rate is opposite to that of the O₂ concentration, which can be used to characterize the composite ability of coal oxygen, that is, oxygen consumption ability.

Within 70 °C, the oxygen consumption rates of the 1–SY coal samples are roughly proportional to the prepyrolysis temperature. Specifically, the oxygen consumption rate of 5Y is the highest, followed by 4Y, 3Y, 2Y, 1Y, and of the raw coal 6# is the lowest. After the wetting coal is treated with isothermal prepyrolysis, many micropore structures are formed owing to partial water evaporation, and these structures promote the physical oxygen adsorption effect of the 1–SY coal samples. With the increase in the temperature, the formation of secondary active groups is accelerated, and a chain reaction takes place rapidly, thus sharply increasing the rate of oxygen consumption and gradually increasing the difference in the oxygen consumption rate between the groups; the oxygen consumption rate of the 4Y coal sample is significantly higher than that of the other coal samples. When the temperature reaches 140 °C, the oxygen consumption rate of SY coal sample decreases to the lowest, and the difference between the oxygen consumption rate of the SY coal sample and those of the other coal samples is significant.

2.2.4. Effect of Prepyrolysis Temperature on Exothermic Intensity. The exothermic intensity of coal is one of the main indicators to evaluate coal spontaneous combustion; it can reflect the thermal capacity of coal from a macroscopic perspective. In this study, the exothermic intensity curve of each coal sample was calculated and drawn based on the chemical bond energy estimation method (Figure 10). The calculation formula is as follows:

\[ q_{max}(T) = \frac{v_{CO}(T)}{v_{CO}(T) + v_{CO_2}(T)} v_{O_2}(T) \Delta H_{CO} \]

\[ + \frac{v_{CO_2}(T)}{v_{CO}(T) + v_{CO_2}(T)} v_{O_2}(T) \Delta H_{CO_2} \]

(2)

where \( q_{max}(T) \) is the maximum exothermic intensity of coal, J/(cm³ s); \( v_{CO}(T) \) and \( v_{CO_2}(T) \) are the production rates of CO and CO₂, mol/(cm³ s); \( \Delta H_{CO} \) and \( \Delta H_{CO_2} \) are the average reaction heat of 1 mol CO and CO₂ produced by coal–oxygen composite reaction, \( \Delta H_{CO} = 311.9 \text{ kJ/mol} \), \( \Delta H_{CO_2} = 446.7 \text{ kJ/mol} \).

**Figure 9.** Variation of exothermic intensity of each coal sample during the oxidative heating process.
oxidative heat release of the coal and ultimately leading to a sharp increase in the heat release intensity.

In the prepyrolyzed coal samples, the 1−5Y, owing to the influence of micropore structures formed by water evaporation and the wetting heat released by residual water, the exothermic heat is promoted in the initial stage of oxidation; hence, the exothermic intensity of 1−5Y is always higher than that of 6# raw coal below 70 °C. As the temperature increases, the exothermic intensity of the 4Y coal sample is gradually higher than that of other coal samples. As the exothermic intensity of coal mainly depends on its oxygen consumption rate, the highest oxygen consumption rate of 4Y indicates that the coal sample would release the most heat under the coal−oxygen composite reaction. When the temperature rises to 140 °C, the coal samples have already entered the stage of rapid oxidation, and the value of exothermic intensity is closely related to the number of active structures. Owing to the influence of the prepyrolysis treatment, the active complexes that participated in the oxidative reaction of 5Y coal sample are fewer during the later stage of oxidation; hence, the exothermal intensity of 5Y is lower than those of other coal samples. Moreover, based on the exothermic intensity curve of the oxidation heating experiment, it can be found that the exothermic intensity of the 4Y coal sample is the highest overall, whereas the exothermic intensity of the 1Y coal sample is higher than that of the raw coal above 140 °C, and the exothermic intensity of the 5Y coal sample is the lowest at the later oxidation period.

To comprehensively discuss the changes in the spontaneous combustion characteristic parameters of the prepyrolyzed coal samples during the oxidative heating process, taking the exothermic intensity as an example, the quantitative analysis method was used to compare the exothermic intensity values of 1−6# and 6Y coal samples at 30−170 °C, and it was found that the exothermic intensity of the six groups of coal samples changed significantly when the oxidation temperature was increased to 80, 110, 140, and 170 °C. Therefore, the exothermic intensity at these four temperature points was selected for analysis in this paper.

As shown in Figure 10, at 80 °C, the exothermic intensity of 6# raw coal exceeds that of 1Y and 2Y coal samples, which is explained as the temperature reached the critical temperature point of coal, the original active groups in 6# accelerate to participate in the coal−oxygen composite reaction, whereas the spontaneous combustion of the 1Y and 2Y samples is restrained to some extent by the evaporation of water. When the temperature is 110 °C, which is close to the boiling point of water, a large amount of heat is absorbed, and a high steam pressure is formed after the rapid evaporation of residual water. As the residual water of the 1Y coal sample is the highest, making the inhibition effect of water evaporation is also the most obvious and the exothermic intensity of 1Y coal sample is decreased to the lowest. When the temperature rises to 140 °C, the residual water in coal is basically evaporated. At this time, the exothermic intensity of coal is influenced by the type and quantity of active groups, whereas the residual original active groups of the 5Y coal sample after isothermal prepyrolysis are fewer, and the formation rate of secondary active groups cannot meet the rapid consumption of active groups in the rapid oxidation stage. The exothermic intensity of 5Y would be decreased to the minimum owing to the weakening of the strength of the coal−oxygen composite reaction. When the temperature is 170 °C, the coal-oxygen composite reaction is particularly intense, and the exothermic intensity is influenced by the active group quantity, coal−oxygen contact area, and porosity of coal. Because of the large amount of residual water in 1Y and 2Y, more pore structures and fracture channels would be formed after the complete evaporation of water evaporation, which promotes the oxidation heat release of 1Y and 2Y; hence, its exothermic intensity increases significantly. Moreover, the residual water of 1Y coal sample is more than that of the 2Y coal sample. After water evaporation, the pore structure and fracture channel of 1Y are better developed;
hence, the exothermic strength of the 1Y coal sample is higher than that of the 2Y coal sample.

3. CONCLUSIONS

In this paper, the programmed heating experimental system was used to study the effect of prepyrolysis temperature on the spontaneous combustion of wetting coal. The following conclusions are drawn:

1. Wetting coal samples are subjected to different isothermal pyrolysis experiments in nitrogen atmosphere, during which the production of CO₂ is much higher than that of CO, and the concentration of CO and CO₂ decreases with the extension of the isothermal prepyrolysis time. The higher the prepyrolysis temperature, the higher the cumulative value of the CO concentration during the isothermal prepyrolysis process, while the cumulative value of CO₂ concentration increases first, then decreases, and then increases.

2. The concentrations of CO and CO₂ in the oxidation heating process are significantly higher than that in the isothermal prepyrolysis process. During the oxidation heating experiment, before 70 °C, the CO concentration of the prepyrolyzed coal samples is higher than that of raw coal, then become gradually lower than that of raw coal with increasing temperature. For the change of CO₂ concentration, it is found that the CO₂ concentration of coal samples with prepyrolysis temperature of 170 °C is significantly lower than that of other coal samples.

3. According to the characteristic parameters of CO and CO₂ concentrations, oxygen consumption rate, and exothermic intensity, it can be inferred that the spontaneous combustion of the coal samples with a prepyrolysis temperature of 140 °C is the highest. The spontaneous combustion of the coal sample with a prepyrolysis temperature of 50 °C is significantly enhanced during the rapid oxidation stage, while the coal sample with a prepyrolysis temperature of 170 °C decreased to the weakest.

4. EXPERIMENTS AND METHODS

4.1. Preparation of Coal Samples. In this paper, a low-ash and high-volatile bituminous coal from Western China was taken as the research object. The coal sample was crushed and sifted in atmospheric air, screened, and divided into ash and high-volatile of bituminous coal from Western China.

Table 1. Proximate Analysis of Coal Sample

| Sample          | Proximate Analysis/% |
|-----------------|----------------------|
|                 | M₄₀   | V₄₀   | A₀₀   | FC₀₀ |
| Bituminous coal | 2.85  | 29.55 | 9.63  | 57.97 |
| Shaanxi         |        |       |       |       |

4.2. Experimental Device. Figure 11 shows the programmed heating experimental system, including a programmed heating box, a sample chamber, a gas supplying system, and a gas chromatograph. The temperature monitoring device located outside the programmed heating box is used to monitor and adjust the temperature in real time. On the inside are two sample chambers with a diameter of 9.5 cm and a height of 25 cm. The loading limit of coal is 1 kg. The gas source is provided by the air generator and nitrogen cylinder, which are introduced from the bottom of the chamber through a flowmeter and a gas path, respectively. The gas generated during the experiment is discharged through the gas path at the top of the sample chamber and sampled and analyzed using a gas chromatograph.

4.3. Experimental Methodology. To simulate the spontaneous combustibility of wetting coal after preheating in a nitrogen atmosphere, 1–5# coal samples were heated to 50, 80, 110, 140, and 170 °C, respectively, in the programmed heating experimental system in a nitrogen atmosphere. In the process of the isothermal prepyrolysis experiment, the gas was extracted every 0.5 h for chromatographic analysis, totally 10 times; after the experiment was completed, the coal samples were cooled to room temperature, thereby obtaining five groups of prepyrolyzed coal samples denoted by 1Y, 2Y, 3Y, 4Y, and 5Y, respectively. Then, the 1–5Y prepyrolyzed coal samples and 6# raw coal sample were carried out to an oxidative heating experiment in an air atmosphere, and the temperature range was from 30 to 170 °C. During the process of oxidation heating, output gases were analyzed per 10 °C. The gas flow rate of nitrogen and air were 120 ml/min throughout the experiment. The experimental conditions of all the prepyrolyzed coal samples are listed in Table 2.

Table 2. Experimental Conditions of Prepyrolyzed Coal Samples

| Sample Number | Raw Coal with Mixed Particle Sizes |
|---------------|-----------------------------------|
|               | 1#  | 2#  | 3#  | 4#  | 5#  | 6#  |
| Water Addition/g | 100 | 100 | 100 | 100 | 100 | 100 |
| Prepyrolysis Temperature/°C | 50  | 80  | 110 | 140 | 170 |
| Prepyrolyzed Coal Number | 1Y  | 2Y  | 3Y  | 4Y  | 5Y  | 6#  |

AUTHOR INFORMATION

Corresponding Author
Kai Wang — School of Safety Science and Engineering and Shaanxi Key Laboratory of Prevention and Control of Coal Fire, Xi’an University of Science and Technology, Xi’an 710054, China; orcid.org/0000-0001-5667-9073; Email: wangk912@xust.edu.cn
Complete contact information is available at:

https://pubs.acs.org/10.1021/acsomega.0c05172

Notes

The authors declare no competing financial interest.

ACS Omega http://pubs.acs.org/journal/acsodf

Article

Authors

Haohao Fan — School of Safety Science and Engineering and Shaanxi Key Laboratory of Prevention and Control of Coal Fire, Xi’an University of Science and Technology, Xi’an 710054, China

Peng Gao — School of Safety Science and Engineering and Shaanxi Key Laboratory of Prevention and Control of Coal Fire, Xi’an University of Science and Technology, Xi’an 710054, China

Yunzhong He — School of Safety Science and Engineering and Shaanxi Key Laboratory of Prevention and Control of Coal Fire, Xi’an University of Science and Technology, Xi’an 710054, China

Pan Shu — School of Safety Science and Engineering and Shaanxi Key Laboratory of Prevention and Control of Coal Fire, Xi’an University of Science and Technology, Xi’an 710054, China

References

(1) Guo, C.; Xia, Y.; Ma, D.; Sun, X.; Dai, G.; Shen, J.; Chen, Y.; Lu, L. Geological conditions of coaled methane accumulation in the Hancheng area, southeastern Ordos Basin, China: Implications for coaled methane high-yield potential. Energy Explor. Exploit. 2019, 37, 922–944.

(2) Zheng, X. Z.; Lu, J. H.; Xiao, Y.; Zhao, Y. H.; Li, Q. W. Experimental study over the effect of high moisture on the coal spontaneous combustion characteristic parameters. J. Saf. Environ. 2014, 14, 71–75.

(3) Yang, H.; Zhang, T. G.; Wang, Z. F.; Zhao, C. C. Experimental study on technology of accelerating methane release by nitrogen injection in coaled. J. China Coal Soc. 2010, 35, 792–796.

(4) Zhao, D.; Zhao, Y. S.; Feng, Z. C.; Liu, Z. X.; Liu, T. Experiments of methane adsorption on raw coal at 30–270 °C. Energy Sources, Part A 2012, 34, 324–331.

(5) He, M. C.; Wang, C. G.; Feng, J. L.; Li, D. J.; Zhang, G. Y. Experimental investigations on gas desorption and transport in stressed coal under isothermal conditions. Int. J. Coal Geol. 2010, 83, 377–386.

(6) Wang, H.; Fu, X.; Jian, K.; Li, T.; Luo, P. Changes in coal pore structure and permeability during N 2 injection. J. Nat. Gas Sci. Eng. 2015, 27, 1234–1241.

(7) Tang, Y. Sources of underground CO: Crushing and ambient temperature oxidation of coal. J. Loss Prev. Process Ind. 2015, 38, 50–57.

(8) Zhu, J.; He, N.; Li, D. The relationship between oxygen consumption rate and temperature during coal spontaneous combustion. Saf. Sci. 2012, 50, 842–845.

(9) Zhao, J.; Deng, J.; Chen, L.; Wang, T.; Song, J.; Zhang, Y.; Shu, C.-M.; Zeng, Q. Correlation analysis of the functional groups and exothermic characteristics of bituminous coal molecules during high-temperature oxidation. Energy 2019, 181, 136–147.

(10) Tang, Y.; Xue, S. Laboratory study on the spontaneous combustion propensity of lignite undergone heating treatment at low temperature in inert and low-oxygen environments. Energy Fuels 2015, 29, 4683–4689.

(11) Wang, H.; Dlugogorski, B. Z.; Kennedy, E. M. Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modelling. Prog. Energy Combust. Sci. 2003, 29, 487–513.

(12) Lee, D.-G.; Isworo, Y. Y.; Park, K.-H.; Kim, G.-M.; Kim, S.-M.; Jeon, C.-H. Low-Temperature Oxidation Reactivity of Low-Rank Coals and Their Petrographic Properties. ACS Omega 2020, 5, 18594–18601.

(13) Jo, W.; Choi, H.; Kim, S.; Yoo, J.; Chun, D.; Rhim, Y.; Lim, J.; Lee, S. Changes in spontaneous combustion characteristics of low-rank coal through preoxidation at low temperatures. Korean J. Chem. Eng. 2015, 32, 255–260.

(14) Wang, G.; Liu, Q.; Sun, L. L.; Song, X.; Du, W. Z.; Yan, D. C.; Wang, Y. Secondary Spontaneous Combustion Characteristics of Coal Based on Programmed Temperature Experiments. J. Energy Resour. Technol. 2018, 140, 082204.

(15) Wang, K.; Liu, X.; Deng, J.; Zhang, Y.; Jiang, S. Effects of preoxidation temperature on coal secondary spontaneous combustion. J. Therm. Anal. Calorim. 2019, 138, 1363–1370.

(16) Zhang, X. H.; Li, Q. W. Experiment Study on Spontaneous Combustion Characteristics of Pre-oxidized Coal. Coal Sci. Technol. 2014, 42, 37–40.

(17) Tang, Y.; Wang, H. Experimental investigation on micro-structure evolution and spontaneous combustion properties of secondary oxidation of lignite. Process Saf. Environ. Prot. 2019, 124, 143–150.

(18) Zhu, H.-q.; Zhao, H.-r.; Wei, H.-y.; Wang, W.; Wang, H.-r.; Li, K.; Lu, X.-x.; Tan, B. Investigation into the thermal behavior and FTIR micro-characteristics of re-oxidation coal. Combust. Flame 2020, 216, 354–368.

(19) Xiao, Y.; Ren, S.-J.; Deng, J.; Shu, C.-M. Comparative analysis of thermokinetic behavior and gaseous products between first and second coal spontaneous combustion. Fuel 2018, 227, 325–333.

(20) Li, J.; Li, Z.; Yang, Y.; Zhang, X. Study on the generation of active sites during low-temperature pyrolysis of coal and its influence on coal spontaneous combustion. Fuel 2019, 241, 283–296.

(21) Li, J.; Li, Z.; Yang, Y.; Wang, C. Study on oxidation and gas release of active sites after low-temperature pyrolysis of coal. Fuel 2018, 233, 237–246.

(22) Li, J.; Li, Z.; Yang, Y.; Niu, J.; Meng, Q. Room temperature oxidation of active sites in coal under multi-factor conditions and corresponding reaction mechanism. Fuel 2019, 256, 115901.

(23) Wang, H.; Dlugogorski, B. Z. Thermal decomposition of solid oxygenated complexes formed by coal oxidation at low temperatures. Fuel 2002, 81, 1912–1923.

(24) Zhang, Y.; Dong, J.; Guo, F.; Chen, X.; Wu, J.; Miao, Z.; Xiao, L. Effects of the evolutions of coal properties during nitrogen and MTE drying processes on the spontaneous combustion behavior of Zhaotong lignite. Fuel 2018, 232, 299–307.

(25) Li, J.; Li, Z.; Yang, Y.; Duan, Y.; Xu, J.; Gao, R. Examination of CO, CO2 and active sites formation during isothermal pyrolysis of coal at low temperatures. Energy 2019, 188, 28–38.

(26) Zhang, Y.; Wang, J.; Wu, J.; Xue, S.; Li, Z.; Chang, L. Modes and kinetics of CO2 and CO production from low-temperature oxidation of coal. Int. J. Coal Geol. 2015, 140, 1–8.

(27) Qi, X.; Li, Y.; Chen, L.; Tang, J.; Xin, H.; Liang, Z. Reaction mechanism of aldehyde groups during coal self-heating. ACS Omega 2020, 5, 23184–23192.

(28) Wang, C.; He, M.; Zhang, X.; Liu, Z.; Zhao, T. Temperature influence on macro-mechanics parameter of intact coal sample containing original gas from Baijiao Coal Mine in China. Int. J. Min. Sci. Technol. 2013, 23, 597–602.

(29) Buzek, F.; Lnenickova, Z. Temperature programmed desorption of coal gases - Chemical and carbon isotope composition. Fuel 2010, 89, 1514–1524.
(30) Wang, K.; Deng, J.; Zhang, Y.-n.; Wang, C.-p. Kinetics and mechanisms of coal oxidation mass gain phenomenon by TG-FTIR and in situ IR analysis. *J. Therm. Anal. Calorim.* 2018, **132**, 591–598.

(31) Huang, Z.; Tian, Y.; Gao, Y.; Shao, Z.; Zhang, Y.; Liu, X. Study on the Oxidation Kinetics and Microreactivity of Water-Immersed Coal. *ACS Omega* 2020, **5**, 17287–17303.

(32) Wang, K.; Fan, H.; Gao, P.; He, Y.; Yang, C. Influence of water content on the coal spontaneous combustion behavior during low-temperature prepyrolysis processes. *Combust. Sci. Technol.* 2020, DOI: 10.1080/00102202.2020.1727456.

(33) Li, J.-l.; Lu, W.; Kong, B.; Cao, Y.-j.; Qi, G.-s.; Qin, C.-r. Mechanism of Gas Generation during Low-Temperature Oxidation of Coal and Model Compounds. *Energy Fuels* 2019, **33**, 1527–1539.

(34) Liu, W.; Qin, Y. P.; Qiao, T.; Ma, B. C. Experimental demonstration on calculation of oxygen consumption rate and CO generation rate in coal spontaneous combustion. *J. China Univ. Min. Technol.* 2016, **45**, 1141–1147.

(35) Li, Y.; Zhao, H.; Song, Q.; Wang, X.; Shu, X. Influence of critical moisture content in lignite dried by two methods on its physicochemical properties during oxidation at low temperature. *Fuel* 2018, **211**, 27–37.

(36) Wang, D.-m.; Xin, H.-h.; Qi, X.-y.; Dou, G.-l.; Qi, G.-s.; Ma, L.-y. Reaction pathway of coal oxidation at low temperatures: A model of cyclic chain reactions and kinetic characteristics. *Combust. Flame* 2016, **163**, 447–460.

(37) Wang, K.; He, Y.; Fan, H.; Shang, B. Study of the coal secondary spontaneous combustion behavior under different pre-heating oxygen concentrations. *J. Therm. Anal. Calorim.* 2020, DOI: 10.1007/s10973-020-10036-y.

(38) Deng, J.; Zhao, J. Y.; Zhang, Y. N.; Geng, R. L. Study on coal spontaneous combustion characteristic temperature of growth rate analysis. *Procedia Eng.* 2014, **88**, 796–805.