Effects of oxygen concentration on the macroscopic characteristic indexes of high-temperature oxidation of coal

Haitao Li, Xiaokun Chen, Chi-Min Shu, Qiuhong Wang, Teng Ma, Bin Laiwang

1 College of Safety Science and Engineering, Shaanxi Key Laboratory of Prevention and Control of Coal Fire, Engineering Research Center of the Ministry of Education, Xi’an University of Science and Technology, 58, Yanta Mid. Rd., Xi’an 710054, Shaanxi, PR China

2 Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology, 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan, ROC

A R T I C L E   I N F O

Article history:
Received 25 December 2017
Received in revised form 12 April 2018
Accepted 16 April 2018
Available online 20 April 2018

Keywords:
Oxidation
Temperature
Extreme points
Prediction
Coal mining

A B S T R A C T

To explore the macroscopic characteristic indexes for oxidation of coal under high-temperature conditions, an XKGW-1-type high-temperature-programmed heating experimental system was constructed. Tests on high-temperature oxidation of coal under high-temperature conditions at five oxygen concentrations of 21, 17, 13, 8, and 3 vol% were independently conducted. Laws of variation in high-temperature oxidation of coal indices, such as the coal temperature, gas ratios, rate of oxygen consumption, and exothermic strength from indoor temperature to 500 °C, were investigated at those oxygen concentrations. The results showed that the variation tendencies of characteristic indexes for high-temperature oxidation of coal at different oxygen concentrations were extremely intricate. At the five oxygen concentrations, the rate of oxygen consumption increased rapidly with an increase in coal temperature and eventually remained at a higher range. The rate of oxygen consumption increased with temperature with an approximate exponential trend at the five oxygen concentrations tested. For the same coal temperature, the rate of oxygen consumption decreased with the oxygen concentration. The variation tendencies of the CO and CO2 production rates were similar, both increased rapidly with an increase in coal temperature in the early stages and reached a maximum at a coal temperature of 380 °C. They decreased slightly with an increase in coal temperature at first and increased promptly thereafter. The concentrations of CH4, C2H4, and C2H6 first increased with an increase in the coal temperature and markedly decreased after the maximal value. The temperatures for the extreme points were 480, 410, and 420 °C for CH4, C2H4, and C2H6, respectively. The trends of the macroscopic characteristic indexes throughout the process of high-temperature oxidation of coal in a certain temperature range at various oxygen concentrations can be used for temperature prediction and fire prevention during coal mining.

© 2018 Energy Institute. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Coal mine fires, especially coalfield fires, which are known for their wide range, unstable and poor oxygen concentrations, high temperatures, and difficulty of control, have long posed a serious threat to coal miners, underground equipment, the natural environment, and coal mine safety, ultimately resulting in substantial losses in resources and environmental pollution. According to an incomplete statistics, coalfield fires occur frequently as a result of spontaneous combustion in coal mines in the United States, India, Russia, Australia, Indonesia, and other countries and regions. Losses in coal resources and equipment accounted for more than 50% of the gross production capacity from 2002 to 2010. Therefore, effective early prediction, pre-control, and prevention methods for spontaneous combustion in gobs are indispensable.

Various factors can affect the evolution and change of coalfield fires, including the physicochemical properties of coal, the content of coal slime, oxygen supply conditions, ambient temperature, ventilation environment, and prevention and control technologies. Among them, the oxygen concentration is vital to the oxidation and combustion of coal in coalfield fires and dangerous areas.
prone to triggering spontaneous combustion, such as gobs and closed fire zones. During the expansion of coalfield fires, the temperature of the fire center is approximately 800 °C, with the highest temperatures reaching thousands of degrees Celsius. With the development of coalfield fire areas deeply subterranean, the oxygen concentration decreases gently from the ground to the center of the fire combustion area. Oxygen concentrations in these areas are lower than that of the atmosphere, which is approximately 21 vol%.

Currently, a variety of bench-testing equipment for characteristic indexes of high-temperature oxidation of coal has been constructed. These benches have been widely used to simulate the process of high-temperature oxidation of coal, measure its indexes [15–20], and evaluate its degree. Wen [21,22] and Xu [23] used a large high-temperature oxidation of coal experimental platform to simulate the entire process of high-temperature oxidation of coal and obtained a dynamic change law of the rate of oxygen consumption and the high-temperature point. Using an experimental system with rising temperatures governed by an oil bath, Zhang [24] conducted low-temperature-programmed experiments to explore the effects of coal particles and temperature on high-temperature oxidation of coal characteristic indexes for a bulky coal seam. Zhu [25] found that the rate of oxygen consumption of coal in the low-temperature phase increased with the oxygen concentration. In addition, higher temperatures would lead to a greater variation amplitude. Nevertheless, the growth trend dropped off with an increase in the oxygen concentration. Using temperature-programmed experiments, Yuan [26] and Zhang [27] individually studied the characteristics of high-temperature oxidation of coal in the Cuijiazhai coal mine in China at various oxygen concentrations and found that products of spontaneous combustion increased with the initial oxygen concentration. Furthermore, the maximal amount of products was observed when the concentration of oxygen was in the range of 13–17 vol%. However, the amount of products started to decrease when the oxygen concentration exceeded this range. Zhou [28] experimentally studied the law of high-temperature oxidation of coal product generation at low oxygen concentrations. Wei [29] and Wielgosinski [30] respectively conducted experiments to probe ash deposition characteristics and the emission of some pollutants. They concluded that the overall generation of oxidation products had a negative effect with a decrease in the oxygen concentration. Adamus [31] studied factors affecting the accuracy of the determination of coal spontaneous combustion temperature on conditions of underground coal mines. The research was focused on the accuracy of interpretation of mine gases in connection with the use of laboratory verified gas characteristics of thermal oxidation of coal. However, the majority of experimental studies on coal oxidation characteristics have been limited to the low-temperature phase (under 200 °C) despite some successful predetermination and applications in coal fire control.

However, it is worth emphasizing that coalfield fires readily reach a high temperature (almost above 500 °C) and are characterized by a long burning time, a wide range and low oxygen oxidation. Furthermore, few efforts have been made to explore the laws of high-temperature oxidation characteristics and gas residues [32] of coal at various oxygen concentrations and a high temperature. Nowadays, a majority of experimental devices developed for coal oxidation can be easily influenced by numerous external and potential factors, which make it difficult to investigate coal oxidation until a rather higher temperature. Therefore, an accurate and repeatable experimental device for studying coal oxidation under high temperature needs to be developed and multiple experiments are needed.

We developed an XKGW-1 programmed heating device for high-temperature oxidation of coal at high temperatures for this study. We conducted multiple experiments with various oxygen concentrations were conducted to explore the law of change in the characteristic indexes of high-temperature oxidation of coal throughout the process. This study contributes to the prevention and risk mitigation of mine and coalfield fires. Based on the experimental results, we indicated some critical aspects of coal fire prevention providing scientific guidance for proactive measures for disaster prevention and mitigating the risk of coal fires.

2. Experimental

2.1. Experimental apparatus

Coal has a rather poor heating conductivity due to its low porosity. Nevertheless, the heat inside a coalfield from oxidation or combustion is readily stored but difficult to dissipate once the capacity of coal reaches a certain value, especially in a poor oxygen environment. To more closely reflect the actual situation and successfully achieve high-temperature oxidation of coal under high-temperature conditions, an XKGW-1-type high-temperature-programmed heating experimental system was built to simulate the process. Some auxiliary components were also implemented, namely a gas supply apparatus, a gas sample acquisition and analysis system, an exhaust gas treatment device, and a thermostatic control system. The flow chart of the high-temperature-programmed heating experimental system is illustrated in Fig. 1.

The structural diagram and physical map of the high-temperature-programmed heating experimental system are shown in Figs. 2 and 3(a), respectively. Six vertical and two lateral transverse thermistor probes were mounted inside the furnace to monitor the coal temperature. Cuvettes were inserted in the central axis of the coal oven to collect gas samples. An oil-free air compressor generated the air to be used, while the air flow rate was measured by a flowmeter, to control the humidity and temperature of the air flowing into the coal body. Gas samples were gathered manually by using beam tubes, and the gas composition and concentration were analyzed through a gas chromatograph. The core of the automatic temperature measurement and the control system was a remote data acquisition and control module. We monitored the outer-layer temperature and volume of air supply in real time.

2.2. Main indexes of the test equipment

2.2.1. Experimental device

(1) The furnace was cuboid and the corresponding internal dimensions were 650 mm × 450 mm × 400 mm. The chamber of the furnace was composed of ceramic fiber to ensure an excellent heat storage environment. Six smoke vents with a diameter of 30 mm were uniformly added to the surface of the furnace cover.

(2) Six cylindrical coal ovens composed of high-temperature-resistant carbon silicon were arranged inside the furnace. The inner diameter, outer diameter, and height of each coal oven were 20, 25, and 20 cm, respectively. The largest loading capacity of each oven was 7.5 kg.
Eight air inlets with a diameter of 1 mm were arranged at the bottom of each oven to ensure that gas flow occurred at the same horizontal level in the coal body, as shown in Fig. 3(b). The upper part of each oven body was equipped with a jar cover that could be fixed in a confined space by using nuts.

3. A steel net with strong rigidity was installed 30 mm from the bottom of the oven. The steel net was composed of two layers and 200 meshes to provide a uniform and stable heating environment for the experimental coal sample.

2.2.2. Parameters and accuracy of the automatic detection and control devices

Compared with existing experimental devices, the high-temperature-reactor used here had a thermal insulation structure for vacuum composed of high-temperature-resistant ceramic fiber. The device had the following characteristics:

Fig. 1. XKGW-1 type of high-temperature-programmed heating experimental system.

Fig. 2. Structural diagram of the high temperature programmed heating experimental furnace. (a) Front view of the experimental furnace; (b) Top view of the experimental furnace.
Table 1
Experimental conditions for oxidation under five oxygen concentrations of 21, 17, 13, 8, and 3 vol%.

<table>
<thead>
<tr>
<th>Oxygen concentration, vol%</th>
<th>Height, cm</th>
<th>Mass, g</th>
<th>Volume, m³</th>
<th>Bulk density, g/cm³</th>
<th>Flux, mL/min¹</th>
<th>Heating rate, °C/min¹</th>
<th>Initial temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>16.70</td>
<td>1000.07</td>
<td>1310.95</td>
<td>0.76</td>
<td>120</td>
<td>0.33</td>
<td>30</td>
</tr>
<tr>
<td>17</td>
<td>16.50</td>
<td>1000.12</td>
<td>1295.25</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>16.60</td>
<td>1000.00</td>
<td>1303.10</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>16.50</td>
<td>1000.15</td>
<td>1295.25</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>16.60</td>
<td>1000.21</td>
<td>1303.10</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

2.3. Coal samples and experimental conditions

Long flame coal was used in this study. The coal sample was crushed at first and then put in the furnace. The link between the rate of oxygen consumption and the particle size is \( V_o(T) = \varphi(d_{50})V_{o2}(T)_{ref} \). According to Deng et al. [8], coal samples with a mixture of particle sizes are the most suitable for studying high-temperature oxidation of coal. The extension of particle sizes and the experimental conditions are shown in Tables 1 and 2. Air (O₂ with a volume fraction of 21, 17, 13, 8, and 3 vol%) was used as the oxidant during the experiment. The airflow rate through the charged reactor was 120 mL/min. The temperature was raised from 30 to 500 °C at a rate of 0.33 °C/min; thus, it took roughly 24 h to heat up the device in each experiment. The composition and concentration of gas samples recorded at different observation points were analyzed by gas chromatography. The variations of coal temperature and gas composition and concentration were investigated throughout the process.

3. Results and discussion

The trends of the rate of oxygen consumption and the amount of CO, CO₂, CH₄, C₂H₄, and C₂H₆ gas produced with increasing coal temperature were the same despite the differences in the initial oxygen concentration. We studied characteristic indexes, such as the rate of oxygen consumption, gas production rate, and gas ratio to further clarify the influence of the oxygen concentration on high-temperature oxidation of coal in high-temperature environments.

3.1. Effects of the oxygen concentration on the rate of oxygen consumption

Recent studies have provided two methods to calculate the rate of oxygen consumption for coal oxidation under high-temperature environment. Song et al. [33] suggested calculating oxygen consumption rate of underground coal fires with lean oxygen concentration and incomplete combustion at high temperature, as air-fuel equivalence ratio and timescales of kinetic reaction and oxygen transport were involved, whereas it could be only used for estimating the oxygen consumption rate of underground coal fires which was mastered by oxygen transport at high temperature. Another approach concerning computing the oxygen consumption rate involves relative assumptions and the theory of heat and mass transfer.

Under the experimental conditions of a low heating rate in the cylindrical coal oven, the air flows inside the loose coal body along the vertical z-axis direction uniformly and steadily within a certain time. Based on the theory of heat and mass transfer, the one-dimensional steady-state equilibrium equation of oxygen concentration migration inside the loose coal body can be described as below:

\[
-QdC_{O2}^{\infty} = (1 - n)R_{O2}Sdx
\]

(1)
where $Q$ represents the experimental supply air volume \([\text{mm}^3/\text{s}]\), $C_{x_o2}$ is the oxygen concentration \([\%]\), $n$ is the coal porosity \([\%]\), $R_{x_o2}$ is the rate of oxygen consumption of loose coal at the temperature $T$ \([\text{mol}/(\text{mm}^3 \cdot \text{s})]\), and $dC_{x_o2}$ is the oxygen concentration change in the range of $dx$ \([\text{mol}/\text{mm}^3]\).

On the basis of chemical kinetics and chemical equilibrium, the rate of oxygen consumption is proportional to the oxygen concentration, and the rate of oxygen consumption per unit volume of coal in fresh air flow can be expressed as follows:

$$ R_{o2} = R_{x_o2} \frac{C_{0_o2}^0}{C_{0_o2}} $$

(2)

where $R_{o2}$ is the rate of oxygen consumption of coal in fresh air at the temperature $T$ \([\text{mol}/(\text{mm}^3 \cdot \text{s})]\), $C_{0_o2}^0$ is the oxygen concentration in the air inlet, and $C_{x_o2}$ is the oxygen concentration at any point inside the coal oven \([\%]\). By integrating both sides of Eq. (2):

$$ R_{o2} = \frac{QC_{0_o2}}{(1 - n)SL} \ln \left( \frac{C_{0_o2}^0}{C_{x_o2}} \right) $$

(3)

where $S$ is the bottom area of the coal oven \([\text{mm}^2]\) and $L$ denotes the height of the coal \([\text{mm}]\).

Fig. 4 shows the relation between the rate of oxygen consumption and the temperature. The rate of oxygen consumption increased with temperature in an approximate exponential trend at the five oxygen concentrations tested. For the same coal temperature, the rate of oxygen consumption decreased with the oxygen concentration. As the oxygen concentration was 21 vol%, the outlet oxygen concentration was less than 3 vol% at 130°C, and it decreased to below 1 vol% at 150°C. Above 150°C, the rate of oxygen consumption reached a stable value aside from fluctuations of some individual points. Similar trends were found when the oxygen concentration decreased to 17, 13, 8, and 3 vol%. This indicated that less oxygen is required at the early stage of the reaction due to the low temperature of the coal. Therefore, a lower oxygen concentration has a suppressive effect on high-temperature oxidation of coal. Influenced by some intrinsic chemical kinetic factors, the number of reactive functional groups increased with temperature. Therefore, oxygen consumption increased as well, accelerating the coal oxidation process. However, the amount of oxygen supplied was unable to maintain the oxidation reaction once the temperature rose to a certain value. The oxygen reaction was extremely slow and was affected by the rate of oxygen supply. Furthermore, oxygen can be exhausted in a short time when the coal is at a high temperature. Therefore, a number of fluctuation points appeared as the outlet oxygen concentration reached its minimum.

### 3.2. Effects of the oxygen concentration on the gas production rate

The oxygen concentration decreased gradually along the airflow direction when oxygen was consumed through coal oxidation. Accordingly, the concentrations of both CO and CO$_2$ increased. The rates of CO and CO$_2$ production are directly proportional to the oxygen concentration; therefore, Eq. (4) can be described as follows:

![Fig. 4. Variation law of rate of oxygen consumption against coal temperature under various oxygen concentrations.](image-url)

Table 2

<table>
<thead>
<tr>
<th>Proximate analysis, %</th>
<th>Elemental analysis, %, daf</th>
<th>Forming period</th>
<th>Categories of coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mad</td>
<td>A_d</td>
<td>Vdaf</td>
<td>Fdaf</td>
</tr>
<tr>
<td>14.9</td>
<td>8.38</td>
<td>69.67</td>
<td>7.06</td>
</tr>
</tbody>
</table>
$V_{\text{co}} = \frac{C_{\text{co}}}{u}$

where $V_{\text{co}}$ is defined as the rate of CO production [$\text{mol}/(\text{mm}^3 \cdot \text{s})$] and $V_{\text{co}}^0(T)$ is defined as the rate of CO production in fresh air [$\text{mol}/(\text{mm}^3 \cdot \text{s})$].

The oxygen concentration at any point inside the coal oven Eq. (5) is inferred from Eq. (4) as below:

$C_{\text{O}_2} = C_{\text{O}_2}^0 \cdot e^{-\frac{V_{\text{co}}^0}{C_0} u z}$

where $z$ is the distance to the gas supply point [mm].

$\frac{d CO}{n} = \frac{V_{\text{co}} S}{n} \frac{dz}{u}$, $u = \frac{Q}{s^* n}$

Assume that $C_1$ and $C$ are the oxygen concentrations at a high temperature point and an adjacent point, respectively. Then, $z_1$ and $z_2$ represent the distance from this point to the gas supply point and to the adjacent point, respectively:

$C_{\text{co}2}^2 - C_{\text{co}2}^1 = \int_{z_1}^{z_2} \frac{V_{\text{co}}^0}{C_0} \frac{dz}{u}$

The rate of CO production in fresh air Eq. (8) can be determined as follows:

$V_{\text{co}}^0 = \frac{V_0 (C_{\text{co}2}^2 - C_{\text{co}2}^1)}{C_0 \* \left[ 1 - e^{-\frac{V_{\text{co}}^0}{C_0} u z} \right]} \left( z - z_1 \right)$

Similarly, the rate of CO$_2$ production in fresh air Eq. (9) is:

$V_{\text{co}2}^0 = \frac{V_0 (C_{\text{co}2}^2 - C_{\text{co}2}^1)}{C_0 \* \left[ 1 - e^{-\frac{V_{\text{co}}^0}{C_0} u z} \right]} \left( z - z_1 \right)$

where $V_{\text{co}}^0$ and $V_{\text{co}2}^0$ are the rate of CO and CO$_2$ production by coal in unit mass, respectively. $C_{\text{co}2}^1$ and $C_{\text{co}2}^2$ are the volume concentrations of CO at the inlet and outlet, respectively, and $C_{\text{co}2}^1$ and $C_{\text{co}2}^2$ are the volume concentration on the corresponding values for CO$_2$. $V_0$ is the volume of the coal sample in the oven.

### 3.2.1. Rate of CO production

An analogous experiment on coal oxidation at a 21 vol% oxygen concentration as coal temperature increased from 30 to 650 °C was conducted by Deng and Song [34], they determined that CO concentration increased as the exponential function in general despite undergoing a fall at 600 °C. Figs. 5 and 6 show the concentration and production rate of CO at different oxygen concentrations, respectively.
The rate of CO production initially increased rapidly as the coal temperature increased to 150 °C. When the coal temperature increased to 300 °C, the rate of CO production and its acceleration at a 21 vol% oxygen concentration was the highest among the five oxygen concentrations tested, whereas it was the lowest at a 3 vol% oxygen concentration. As the coal temperature continued to increase, the rate of CO production at the five oxygen concentrations tested decreased sharply above 400 °C, whereas the concentration of CO decreased markedly after reaching a maximum at a coal temperature of 380 °C.

Previous studies [35–38] suggested that CO mainly comes from coal oxidation, thermal decomposition of stable coal–oxygen complexes containing carbonyl groups, oxygen chemisorption, and the self-reaction of the active groups in coal molecules. The rate of CO production was low due to the low temperature of the coal at this stage. CO was mainly produced by chemical oxygen adsorption on the coal and the chemical reaction, leading to a low reaction rate of the coal. When the coal temperature increased, the CO concentration and rate of CO production began to increase and accelerated to a certain extent. As the coal temperature surpassed 400 °C, the CO concentration and production rate first decreased and then increased rapidly to a greater extent. This indicates that as the coal temperature increases, the mechanism of CO generation varies. The CO concentration and production rate may have increased again after reaching a minimum because of the direct combustion reaction of the fixed carbon in the oxygen atmosphere (burn-off reaction). Because the oxygen concentration is crucial for the direct combustion of coal, the CO concentration and rate of CO production did not vary substantially at oxygen concentrations of 17, 13, 8, and 3 vol%.

In contrast to the decomposition reaction of coal and oxygen, the direct combustion of coal can be less affected by the oxygen concentration. This information can be used to explain why the concentration and production rate at an oxygen concentration of 21 vol% were higher than those at oxygen concentrations of 17, 13, 8, and 3 vol% when the coal temperature was less than 400 °C, but close to those at oxygen concentrations of 17 and 13 vol% when the coal temperature exceeded 400 °C. When the coal temperature was higher than 400 °C, the CO concentration and production rate at an oxygen concentration of 13 vol% were higher than those at oxygen concentrations of 21 and 17 vol% due to the incomplete oxidation of the coal in low-oxygen-concentration conditions.

### 3.2.2. Rate of CO₂ production

Figs. 7 and 8 show the concentration and production rate of CO₂ at different oxygen concentrations. Both the CO₂ concentration and production rate were first rather low as the temperature increased to 150 °C. When the coal temperature increased from 150 to 300 °C, the increase of the oxygen concentration accelerated the coal oxidation process. Furthermore, with a given oxygen concentration and a continuous increase of the coal temperature, the number of active groups in the coal that participated in the oxidation reaction gradually increased. Therefore, the CO₂ concentration and production rate increased. A higher rate of the coal oxidation reaction requires much more oxygen, whereas a lower concentration of oxygen limits the chemical reaction process. Therefore, the CO₂ concentration and production rate decreased with a decreasing oxygen concentration.

As the coal temperature increased to 400 °C, the CO₂ concentration and production rate increased again and reached the maximum at the same time, regardless of the oxygen concentration. This occurred because a large number of inactive functional groups began to participate in the coal oxidation reaction due to the increase of the apparent activation energy of the system provided by the temperature increase. As the coal temperature increased above 400 °C, the CO₂ concentration and production rate at different oxygen concentrations decreased when the temperature increased and reached a minimum because the active groups were consumed in the early stage. Additionally, more CO₂ was produced by incomplete oxidation at lower oxygen concentrations. After the coal temperature exceeded 460 °C, the CO₂ concentration and production rate increased again after reaching a minimum, potentially because of the direct combustion reaction of the fixed carbon in the oxygen atmosphere (burn-off reaction) [34]. Since the oxygen concentration plays a crucial role in the direct combustion of coal, the CO₂ concentration and production rate were similar for oxygen concentrations of 17, 13, 8, and 3 vol%.
3. Effects of the oxygen concentration on hydrocarbons generation

3.3. CH₄ concentration

The generation of CH₄ inside a loose coal body mainly occurs through desorption, the release of free CH₄ in coal cracks, oxidation of the active groups in coal, and the self-reaction of active groups in coal molecules. As shown in Fig. 9, CH₄ was detected at the beginning of the reaction and decreased to a minimum at 50 °C with increasing coal temperature. When the coal temperature further increased, the concentration of CH₄ increased slowly, and then decreased with decreasing oxygen concentration for a given coal temperature. At this stage, CH₄ mainly came from the oxidation reaction of the active groups because adsorbed CH₄ was completely detached. The concentration of CH₄ showed a fluctuating but growing trend at different oxygen concentrations for temperatures ranging from 280 to 480 °C. The concentration of CH₄ decreased as the coal temperature increased to 500 °C. This indicates that the oxidation of active groups in the coal and self-reaction of active groups resulted in a decrease in the CH₄ concentration.

3.3.2. C₂H₄ concentration

Deng and his associates [8] suggested that the aliphatic hydrocarbons in the free phase of coal and the rich side chain in the aromatic ring are gradually cleaved to form C₂H₄ gas through the splitting of free radicals. As shown in Fig. 10, C₂H₄ was detected at 60 °C at different oxygen concentrations and slowly increased until the coal temperature reached 150 °C because of the weak coal oxidation reaction at low temperatures. The concentration of C₂H₄ began to decrease with decreasing oxygen concentration at a given coal temperature before the coal temperature reached 290 °C. The concentration of C₂H₄ increased sharply at different oxygen concentrations when the temperature continuously increased because of the cleavage of a large amount of aliphatic hydrocarbons in the coal molecules and the rich side chains on the aromatic rings in this stage. The temperatures at which the concentrations of C₂H₄ reached their maxima were 420, 410, 410, 420, and

Fig. 7. Variation laws of CO₂ concentration against coal temperature under various oxygen concentrations.

Fig. 8. Variation laws of CO₂ production rate against coal temperature under various oxygen concentrations.
410 °C for oxygen concentrations of 21, 17, 13, 8, and 3 vol%, respectively. However, the concentration of C₂H₄ decreased rapidly with increasing coal temperature after reaching the maximum. This can be attributed to the complete reaction of aliphatic hydrocarbons in the free basic fatty side chain and the aromatic ring at high temperatures [34].

3.3.3. C₂H₆ concentration

The generation of C₂H₆ inside a loose coal body mainly occurs through desorption, oxidation of the active groups in coal, and the self-reaction of the active groups in coal molecules. Fig. 11 illustrates the laws of C₂H₆ production at different oxygen concentrations. C₂H₆ was detected at 30 °C and then reached its maximal production. This indicates that a quantity of C₂H₆ exists in the coal body itself and detaches from the coal body when the temperature increases. Furthermore, the concentration of C₂H₆ increased slowly due to the slow chemical reaction at the initial stage of the temperature increase. The concentration of C₂H₆ decreased with the oxygen concentration until the coal temperature reached 340 °C. This was because C₂H₆ mainly came from the oxidation of the active groups in the coal molecules, while the self-reaction of the active groups played only a minor role at this stage.

The concentration of C₂H₆ increased rapidly as the coal temperature increased further and reached its maximum at 420 °C. When the coal temperature was approximately 350 °C, the concentration of C₂H₆ at an oxygen concentration of 3 vol% was higher than that at an oxygen concentration of 8 vol%. When the coal temperature increased to 380 °C, the concentrations of C₂H₆ at oxygen concentrations of 17 and 3 vol% were higher than that at an oxygen concentration of 8 vol% and the initial C₂H₆ concentrations at 21 and 13 vol%. However, when the coal temperature was approximately 390 °C, the concentration of C₂H₆ at an oxygen concentration of 3 vol% was higher than that at oxygen concentrations of 18 and 21 vol%. Such a phenomenon could be due to the contribution of the self-reaction of the active groups in the coal molecules at high temperatures. However, under sustained hypoxia, the reaction of the active groups became more intense with increasing coal temperature at low oxygen concentrations [34].
3.4. Effects of the oxygen concentration on the gas ratio

3.4.1. CO2/CO ratio

Fig. 12 demonstrates that the CO2/CO ratio increased at the beginning of the heating cycle and then decreased gradually with increasing temperature. At oxygen concentrations of 13, 8, and 3 vol%, it reached its maximal value between 0 and 50 °C, whereas at concentrations of 21 and 17 vol%, the ratio reached its maximal value between 50 and 100 °C. However, when the oxygen concentration increased, the maximal values showed a downward trend in all cases due to the inadequate oxidation and combustion of coal at lower oxygen concentrations. For a certain independent condition, the CO2/CO ratio of increased at the beginning of the heating cycle and then decreased gently with the increase in coal temperature. This shows that during the natural rise period of coal temperature, the heat provided by an external heating source could promote the oxidation and combustion of coal even in a poor oxygen environment.

3.4.2. CH4/C2H6 ratio

Fig. 13 shows that during the heating cycle, a slight growth in the CH4/C2H6 ratio occurred below 280 °C apart from the fluctuations of some independent points. From 280 to 500 °C, the CH4/C2H6 ratio first decreased slightly and then increased markedly with increasing temperature. This makes clear that when the CH4/C2H6 ratio observably increased, a high-temperature point existed at 280 °C during the natural rise in coal temperature.

3.4.3. C2H4/C2H6 ratio

Fig. 14 shows that at the beginning of heating process, the C2H4/C2H6 ratio first increased slowly to a peak when the temperature was below 64 °C, and then rose sharply when the temperature ranged from 64 to 280 °C. As the coal temperature increased to 280 °C, the ratio at each oxygen concentration reached its respective maximal value. Above 280 °C, the C2H4/C2H6 ratio decreased substantially. This indicated...
that during the heating process, when the C2H4/C2H6 ratio clearly increased, a high-temperature point appeared at 64 °C. When the C2H4/C2H6 ratio reached the maximum, a high-temperature point appeared from 280 to 500 °C.

3.5. Analysis of indices for predicting high-temperature oxidation of coal

According to the analyses in sections 3.1–3.4, the influence of the oxygen concentration on the characteristic indexes of high-temperature oxidation of coal varies. Thus, the following points merit extra attention for coal fire prevention [39,40].

Since the temperature, instead of the oxygen concentration, mainly affects the production of hydrocarbons, various temperature stages of high-temperature oxidation of coal could be determined by analyzing the trends of hydrocarbon production. Moreover, the peaks of C2H4 and C2H6 production appeared at approximately 410 and 420 °C, respectively.

The oxygen concentration had a substantial impact on the production of COx. The actual oxygen concentration in the spontaneous combustion area should be considered when COx production is employed as an indicator. The previous analyses indicated that a low oxygen concentration inhibits the spontaneous combustion of coal. Consequently, air leakage should be minimized for coal fire prevention. Furthermore, the oxygen concentration in the spontaneous combustion area should be reduced.

The effect of the oxygen concentration on high-temperature oxidation of coal showed various features at different stages. Below 330 °C, the oxygen concentration was the main factor influencing spontaneous combustion of coal. However, the temperature of the coal sample, instead of the oxygen concentration, became the main factor when the temperature exceeded that point. Therefore, from an economic efficiency standpoint, comprehensive measures should be taken to prioritize cooling the fire area for coal fire prevention in the high-temperature phase. Accordingly, comprehensive measures to lower the oxygen concentration should be taken in the low-temperature range.

---

Fig. 13. Relationship between ratio of CH4/C2H6 and temperature under various oxygen concentrations.

Fig. 14. Relationship between ratio of C2H4/C2H6 and temperature under various oxygen concentrations.
4. Conclusions

We designed and applied a high-temperature-programmable experimental system to investigate the characteristic indexes of high-temperature oxidation of coal. The new system was used to perform experiments on the characteristics of high-temperature oxidation of coal at five oxygen concentrations in the high-temperature phase. The variation laws and indexes determined are detailed as follows.

When the oxygen concentration increased, the rate of oxygen consumption continuously increased, but the dependence on the oxygen concentration varied for different temperatures. However, the rate of oxygen consumption increased with an approximate exponential trend as the temperature increased at all five oxygen concentrations tested, despite a few fluctuation points. For the same coal temperature, the rate of oxygen consumption decreased with a decreasing oxygen concentration. A lower oxygen concentration has a prominent inhibitory effect on high-temperature oxidation of coal.

The laws of variation in the rates of CO and CO2 production were similar at different oxygen concentrations. The rates initially increased promptly with increasing coal temperature and then reached their respective maxima when the coal temperature reached 380 °C. The two indexes decreased with a decreasing oxygen concentration and strongly depended on the oxygen concentration.

The concentrations of CH4, C2H4, and C2H6 increased first to a maximal value and then decreased with increasing coal temperature at various oxygen concentrations. The temperatures corresponding to the extreme points of CH4, C2H4, and C2H6 production were approximately 480, 410, and 420 °C, respectively. Furthermore, a certain anti-correlation existed between the concentrations of CH4, C2H4, and oxygen, probably because of the oxidation and self-reaction of the active groups in the coal molecules at higher oxygen concentrations, leading to the formation of active groups in C2H4 and C2H6.

The variation of the CO2/CO, CH4/C2H4, and C2H4/C2H6 ratios shows the intricate laws of coal oxidation at high temperatures under various oxygen concentrations. In addition to the index gases, these ratios could be applied for coal fire prediction and control.

Acknowledgments

This work was supported by National Natural Science Foundation (Grant Nos. 51504190 and 51604215), National Key R&D Program of China (2016YFC0800100), Cultivation Fund for Excellent Doctoral Dissertation of the XUST, General Program of National Natural Science Foundation (Grant Nos. 51674191 and 51674193), the International Science and Technology Cooperation and Exchange of Shaanxi Province (Grant No. 2016KW-070).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.joei.2018.04.003.

References

[24] L Yuan, Experimental Study on Coal Spontaneous Combustion Characteristics under Varying Ambient Oxygen Concentration, Master thesis, Xi’an University of Science and Technology, Xi’an, China, 2015.