Full Length Article

Effects of oxygen supply on low-temperature oxidation of coal: A case study of Jurassic coal in Yima, China

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HIGHLIGHTS

- Characteristics and gas-release trends of coal oxidation at low temperatures ($\leq$190 °C) under different oxygen concentrations.
- Ratios of gaseous products under different oxygen concentrations.
- Effects of oxygen supply on risk determination of coal self-ignition which uses representative indicators.
- Accurate risk determination of coal self-ignition in situ.

ARTICLE INFO

ABSTRACT

Low-temperature oxidation of coal is the fundamental process for self-heating and self-ignition in the mining, storage, and transportation of coal, and mostly occurs in oxygen-depleted air. However, little is known about the effects of oxygen supply on risk determination of coal self-ignition using the representative indicators. Four Jurassic coal samples from Yima were selected, and experiments on low-temperature oxidation of coal with different oxygen concentrations ranging from 6% to 21% were conducted to determine the characteristics and gas-release trends of coal oxidation at low temperatures ($\leq$190 °C). It was shown that the direct burn-off reaction began to play a major role at a temperature above 80 °C regardless of oxygen concentration; the changes in the oxygen consumption rate with temperature at oxygen concentrations of 16% and 11.7% were not significantly different; and when the temperature reached 95 °C, there was a visible increase in the CO production with increasing oxygen concentration and C_2H_4 was detected. The ratios of gaseous products were studied to determine the effects of oxygen supply on risk determination. They showed that the same logarithmic growth trend existed for the CO/CO_2 ratio under different oxygen concentrations; the C_2H_4/C_2H_6 ratio rose steadily at temperatures above 130 °C, and there may be a decreasing linear trend for the C_3H_8/C_2H_6 ratio with a threshold temperature between 110 and 130 °C. Finally, an improved method was proposed for accurate risk determination of coal self-ignition in situ.

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1. Introduction

Coal self-heating leading to self-ignition incidents continues to be a serious problem in collieries, especially in underground longwall gobs (a semi-enclosed space) and stockpiles, as well as in coal related industries [1–7]. Low-temperature oxidation of coal, a reaction between coal and oxygen at a low temperature (i.e. <200 °C), is the fundamental process for self-heating and self-ignition in the

mining, storage, and transportation of coal [8,9], and causes fires which produce large amounts of toxic and harmful gases, which are serious threats to staff safety, and gas explosions [10]. It occurs because the reaction is an irreversible exothermic reaction between coal and oxygen which can generate heat, which accumulates to promote coal self-ignition [11]. Therefore, it is important to study the characteristics of coal oxidation at low temperature for the evaluation of self-ignition propensity.

The low-temperature oxidation of coal is a complicated process, involving a reaction sequence which consists of several steps [1,12–14]. These steps include physical adsorption of oxygen, chemisorption of oxygen on the internal surfaces of coal pores

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producing unstable carbon-oxygen complexes, decomposition of the unstable complexes into gaseous products and stable solid complexes, degradation and decomposition of the stable complexes and generation of new active sites, the direct burn-off reaction, and the formation of gaseous hydrocarbon products. Many scholars have used some representative parameters, such as the kinetics (activation energy and pre-exponential factor), oxygen consumption rate, and formation rate of carbon-containing gaseous products, to characterise the low-temperature oxidation of coal [8,10,15–17]. The activation energy and pre-exponential factor determine the reaction rate, and are the main parameters for the evaluation of thermal hazards of substances [18]. According to the conventional Arrhenius equation, the reaction rate of coal oxidation based on oxygen consumption can be expressed by Eq. (1):

$$\frac{d\rho_{ox}}{dt} = \rho_{ox}^0 \cdot A \exp(-E/RT) \tag{1}$$

where ρ_{ox} is the oxygen density in the gas phase, A is the pre-exponential factor, and E is the activation energy. However, it has been shown that the Arrhenius equation does not completely reflect the low-temperature oxidation of coal because of the complexity of the latter. Arisoy and Beamish [1] found that the reaction rate at temperatures from 20 to 57 °C was predominantly non-Arrhenius, but converged to Arrhenius at temperatures above 70 °C.

The concentrations of CO, O_2, N_2 and CO_2 are the most commonly used indicators of heating. However, there are many problems with using absolute gas concentrations; the gases can be diluted with other gas streams, indicator gases can come from other sources (e.g. vehicle emissions and seam gases), and no indication of heating intensity would be given if a gas with the same concentration was produced by heating at a higher or lower temperature [19]. To overcome these problems, the oxygen consumption rate, the formation rate of carbon-containing gaseous products, and indicators which use combinations of gas concentrations are used to predict coal self-heating status. The most famous indicators include the Trichett indicator, Graham indicator, indicator WP1, and oxide indicator.The Trichett indicator [20,21], TR, is calculated using Eq. (2):

$$TR = \frac{C_{CO_2} + 0.75 \times C_{CO} - 0.25 \times C_{H_2}}{0.265 \times C_{N_2} - C_{O_2}} \tag{2}$$

where C_{CO_2}, C_{CO}, C_{H_2}, C_{N_2}, C_{O_2} are respectively the percentages of CO_2, CO, H_2, N_2 and O_2.The Graham indicator (G) and indicator WP1 [22] are expressed by Eqs. (3) and (4) respectively:

$$G = \frac{100 \times C_{CO}}{C_{iO_2} - C_{fO_2}} \tag{3}$$

where i denotes the initial state and f denotes the final state.

$$WP1 = \frac{C_{CO}}{C_{H_2}} \tag{4}$$

The oxide indicator [23] is expressed as follows:

$$\frac{C_{CO}}{C_{CO_2}} \tag{5}$$

The above indicators are mostly based on the concentration of CO, which high values of are necessary to indicate a fire risk, but they are not accurate enough to assess the fire risk because the concentration of CO may be affected by various factors, such as high colliery air thinness and the inerting process [24]. With the development of gas chromatography, risk determination on the basis of low-concentration hydrocarbons, such as C_2H_2, C_2H_4,

C_2H_6, and C_3H_8, was proposed to predict the maximum temperature of coal heating and improve the determination of fire risk levels. The main indicators are shown below:

$$C_{CO}/C_{C_2H_2}; C_{CH_4}/C_{C_2H_6}; C_{C_2H_4}/C_{C_2H_6}; C_{C_3H_8}/C_{C_2H_6}; C_{C_2H_4}/C_{C_2H_2}; C_{C_2H_4}/C_{H_2} \tag{6}$$

where $C_{C_2H_2}$, $C_{C_2H_4}$, $C_{C_2H_6}$, and $C_{C_3H_8}$ are the gas concentrations of C_2H_2, C_2H_4, C_2H_6, and C_3H_8, respectively.

Because of the oxygen consumption in coal oxidation, inadequate supply of fresh air, dilution effect of gas produced by coal oxidation, and injection of nitrogen for the prevention of low-temperature oxidation of coal, in longwall gobs and stockpiles, coal oxidation mainly occurs under oxygen-depleted conditions [10]. Zhou et al. [25] conducted model experiments simulating coal oxidation under reduced oxygen concentrations to study the formations of CO, C_2H_4 and CO_2, and a hysteresis effect was shown; the temperature for initial production was lowered and the amount of products was decreased at reduced oxygen contents. Su et al. [26] analysed the correlation between oxygen concentration and dynamic parameters of low-temperature oxidation of coal, and showed that the rapid oxidation stage was gradually postponed as oxygen concentration decreased and that the apparent activation energy was unaffected by oxygen concentration during this stage. Tang and Xue [27] investigated the self-ignition propensity of coal at low temperature (<200 °C) in N_2, O_2, and 10% O_2 environments. Qi et al. [10] determined the kinetics parameters of low-temperature oxidation of coal in oxygen-depleted air by evaluating the heat generation in atmospheres with different oxygen concentrations, and revealed that the difference in the kinetics parameters in different oxidation stages was smaller when the oxygen concentration was lower. Generally, the indicators are important for the prediction of coal self-ignition, which may occur under different oxygen concentrations owing to the changes in fresh air supply and oxygen consumption. However, little is known about the effects of oxygen concentration on the above representative indicators.

In this work, four coal samples were selected for oxidation experiments with different oxygen concentrations. The gaseous products were detected by a gas chromatograph in order to obtain values for the representative indicators. The effects of oxygen concentration on the oxygen consumption rate, release trends of gaseous products, and representative indicators were analysed to enable us to propose an accurate method to estimate the risk of coal self-ignition.

2. Materials and methods

2.1. Coal samples

Four samples, taken from the Yuejin, Changcun, Yangcun, and Gengcun collieries were selected for this work. These collieries are located in the Yima mining area in Henan Province, and the coal samples were from the Jurassic age. The results of proximate analysis of the four coal samples are given in Table 1. In the pre-oxidation treatment process, a large coal particle from each colliery was selected as the sample. The oxide layer on the coat surface was removed, and the sample was broken and sieved to a particle size of 0.25–0.42 mm for experiments.

2.2. Experimental setup

2.2.1. Apparatus

Fig. 1 shows a schematic diagram of the apparatus applied for the low-temperature oxidation of coal. The experimental apparatus consisted of a programmable temperature-control box, a gas