Process Safety and Environmental Protection 118 (2018) 195–202

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Risk forecasting for spontaneous combustion of coals at different ranks due to free radicals and functional groups reaction

Qin Xu[a,b,c], Shengqiang Yang[a,b,c,*], Jiawen Cai[a,b,c], Buzhuang Zhou[a,b,c], Yanan Xin[a,b,c]

[a] Key Laboratory of Coal Methane and Fire Control, Ministry of Education, China University of Mining and Technology, Xuzhou, Jiangsu, 221116, China
[b] State Key Laboratory of Coal Resources and Safety Mining, Xuzhou, Jiangsu, 221116, China
[c] School of Safety Engineering, China University of Mining and Technology, Xuzhou, Jiangsu, 221116, China

ARTICLE INFO

Article history:
Received 18 March 2018
Received in revised form 27 June 2018
Accepted 29 June 2018
Available online 4 July 2018

Keywords:
Spontaneous coal combustion
Electron spin resonance
Fourier transform infrared spectroscopy
Carbon monoxide

ABSTRACT

To explore the reaction mechanism of spontaneous coal combustion and the indicators for forecasting this risk, reaction characteristics of free radicals and functional groups during low-temperature oxidation of coal with different ranks were analyzed by electron spin resonance (ESR) and Fourier transform infrared (FTIR) spectroscopy. Combined with gas chromatography of CO, other indicators besides the main indicator gas CO were researched to forecast spontaneous coal combustion. The results showed that with increasing oxidizing temperature in the range of 30 °C–230 °C, the production of free radicals changed from slow to rapid after being oxidized and heated above characteristic temperatures, depending on the coal grade. The oxygen-containing functional groups in coal of all ranks mainly include —OH, C═O, C—O and —COOH, whose reaction trends varied widely. The concentration and production rate of free radicals and the C═O functional group in coal can be regarded as the leading indicators.

1. Introduction

Risk forecasting refers to a method that can predict the occurrence of accidents and prevent them. In China, coal reservoirs in 47% of state-owned major mines are prone to spontaneous combustion, and the disasters caused by spontaneous coal combustion make up 70% of the mine fire disasters (Ren et al., 2015; Li et al., 2014). The spontaneous coal combustion disasters induced by low-temperature oxidation pose a significant threat to the safety of the mines (Lu et al., 2017; Lu and Qin, 2015; Ren et al., 2015). Coal is a macromolecular mixture that contains a variety of chemical bonds and functional groups. In the complex coal-forming process, variations in primary plant characteristics and external environmental conditions caused coal to take on different degrees of metamorphisms. Therefore, coal exhibits different ranks, predominantly lignite, bituminous coal and anthracite (Cheng et al., 2017; Li et al., 2017b; Wen et al., 2015). Coal of different ranks exhibits different spontaneous combustion tendencies and low-temperature oxidation processes due to the differences of their active groups. During spontaneous coal combustion, these active groups are first oxidized to produce new groups and release heat. The heat production is higher than the heat loss, causing that the temperature of coal masses to constantly rise to eventually trigger spontaneous combustion under appropriate heat-storage conditions (Liu et al., 2017; Qi et al., 2013; Zhou et al., 2017). Therefore, risk forecasting for spontaneous coal combustion is defined in this work as to analyze the reaction trends of active groups during the low-temperature oxidation of different coal ranks. As such, the critical temperature where coal masses start the rapid oxidation heating stages need to be obtained from the perspective of oxidation reaction mechanisms. By doing so, spontaneous coal combustion can be predicted in time and measures can be taken to inhibit coal heating before the local temperature of the coal mass reaches its critical temperature. This is of great importance to those mining the coal reservoirs prone to spontaneous combustion. Furthermore, these results are significant for the control of spontaneous combustion of left-over coal in a goaf.

Spontaneous coal combustion is simply the combined oxidation reactions of active groups, including free radicals and functional groups. Many researchers have studied these aspects. In research on free radicals, Liu et al. analyzed the nature of different free radicals in coal during the process of comminution, pyrolysis and ultraviolet irradiation by measuring ESR spectra (Liu et al., 2015). Li et al. indicated that free radicals can reveal the chemical processes of low-temperature oxidation of coal and that the fracturing process of coal masses is the key factor in the induction of free radical reactions (Li et al., 2016). For research on functional groups,

* Corresponding author at: School of Safety Engineering, China University of Mining and Technology, Xuzhou, Jiangsu, 221116, China.
E-mail address: xuqincumt@cumt.edu.cn (S. Yang).

https://doi.org/10.1016/j.psep.2018.06.040
0957-5820/

Zhou et al. analyzed the change of functional groups during oxidation reactions of coal with different ranks by Fourier transform infrared spectroscopy (FTIR), which demonstrated that the content of hydroxyl compounds has a linear relationship with the mass of coal. With an increase in oxidizing temperature, it becomes more difficult to increase the mass of coal based on oxygen-containing functional groups (Zhou et al., 2017). Xu suggested that heat is mainly produced by the decomposition of oxygen-containing functional groups, causing a slow rise in temperature (Xu, 2017). In assessing the risk of spontaneous coal combustion, Liang and Wang thought that the hidden danger of underground spontaneous coal combustion can be predicted by detecting the carbon monoxide concentration, analyzing the gas composition, monitoring the coal temperature and applying infrared radiation to detect this temperature (Liang and Wang, 2011). Peng et al. put forward the ABC-RGM (1,1) model based on the rolling-GM (1,1) and the Artificial Bee Colony (ABC) optimization algorithm to predict spontaneous combustion, which greatly improved the accuracy of forecast than the other popular grey models. The grey models are developed to forecast the change trends of uncertain systems based on a small amount of incomplete information (Peng et al., 2017).

Through the analysis of ESR and FTIR spectra, the researchers mentioned above verified that there are numerous active groups in coal and concluded that low-temperature oxidation is directly correlated with the reactions of free radicals and functional groups. The results obtained from ESR experiment were mixed concentration of all free radicals in coal, which demonstrated the reaction activity of coal oxidation but cannot distinguish the specific functional groups that easily reacted with oxygen. However, the free radicals were generated by electron gain or loss of the functional groups and the specific structure can be obtained from FTIR spectra. So spontaneous coal combustion can be analyzed by combining free radicals and functional groups, enhancing a further understanding of the oxidation reactions on the coal surface structure. However, the researchers have not investigated the reaction differences of active groups during low-temperature oxidation of coal with different ranks, analyzed the oxidation process based on free radicals and functional groups reaction, or explored the critical temperature at which oxidation develops into a runaway reaction. Therefore, using a custom simulator test rig for the low-temperature oxidation of coal, this work analyzed the reactions of free radicals and oxygen-containing functional groups of coal of various ranks (lignite, bituminous coal and anthracite) by using ESR and FTIR. Combining these with the gas chromatography results of products generated in low-temperature oxidation, the study explored the critical temperature at which spontaneous combustion transitions into an oxidation stage by analyzing the evolution of CO, the free radical concentration, and the presence of oxygen-containing functional groups. This provides theoretical guidance for forecasting spontaneous coal combustion and taking measures in time to inhibit coal heating in the coal mines prone to spontaneous combustion or under spontaneous combustion and control the oxidation of left-over coal in the goaf.

2. Materials and methods

2.1. Experimental samples

Coal at three ranks was chosen for use as specimens according to their metamorphic grades and spontaneous combustion tendency. Lignitous coal (LC) was obtained from Shengli Coalfield in Inner Mongolia, China; bituminous coal (BC) was from Hongliulin Coal Mine in Shaanxi province, China; and anthracitic coal (AC) came from Linhua Coal Mine in Guizhou province, China. The proximate and ultimate analysis of the three coal specimens are displayed in Table 1. The experimental data are standardized as the three groups of coal specimens.

Table 1
Proximate and ultimate analysis of three coal samples of different ranks.

Sample	Proximate analysis (wt%)				Ultimate analysis (wt%, ad)				
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C	H	O	S	N
LC	10.03	12.15	43.33	34.49	49.38	6.78	15.38	1.13	1.21
BC	7.40	14.16	26.72	51.72	63.77	3.60	10.01	0.20	0.86
AC	2.18	17.20	7.54	73.08	72.51	2.58	3.56	0.95	1.12

Note: M_{ad}—Moisture, A_{ad}—Ash content, V_{ad}—Volatile matter, FC_{ad}—Fixed carbon, ad—air dry basis.

2.2. Test procedure

The test procedure and experimental testing parameters of all coal samples were identical. As shown in Fig. 1, the fresh coal specimen was crushed into particles of approximately 5 mm diameter. Roughly 50 g of the particles were put into a DZF-6020-type vacuum oven for 24 h at room temperature. The dry coal samples were manually crushed in an agate mortar to obtain particles roughly 0.18–0.30 mm in size. After crushing, these specimens were put into the coal chamber in the low-temperature oxidation analyzer as shown in Fig. 1. The samples were heated separately from 30 °C to 80 °C, 130 °C, 180 °C, and 230 °C under dry air at a heating rate of 0.4 °C/min and a flow of 50 ml/min. Under this rising temperature rate, coal samples can be fully oxidized in the air atmosphere (Tang et al., 2017). During the final low-temperature oxidation, when coal specimens were heated to 230 °C, the change of CO concentration was monitored by using a gas chromatograph. The experimental parameters of the ESR are given in Table 2. The concentration of free radicals in the coal specimens was measured, using the standard Tempol with a known free radical concentration. After the coal specimens were oxidized to the required temperature, 5 mg of the samples were weighed by using a high-precision balance and immediately put into a specimen tube for ESR analysis. At the same experimental conditions, the spectrum of the standard Tempol was collected to determine the free radical concentration in coal specimens. Before the FTIR experiment, a KBr pellet was scanned to acquire a background spectrum, and then KBr and an oxidized coal specimen were uniformly ground together at the ratio of 180:1. The mixture was pressed for 10 min at 20 MPa to obtain a circular transparent pellet with 0.1 mm thickness and 0.9 mm in diameter, for FTIR analysis. Scans were taken 32 times in 1 min with the wave numbers in the range of 400–4000 cm^{-1}.

2.3. Experimental instruments

2.3.1. Simulator test rig for low-temperature oxidation

As shown in Fig. 1, the simulator test rig for the low-temperature oxidation of coal is comprised of a low-temperature oxidation analyzer, gas chromatograph, cylinder with steady voltage, coal chamber, thermocouple, gas transmission line, display, and control panel. The low-temperature oxidation analyzer produced by Starr Hengtong Technology Co., Ltd., Beijing, China is a ZRJ-2000 tester for the spontaneous combustion tendency of coal with a heating range of 20 ~ 500 °C and a minimum value for the heating rate of 0.1 °C/min. The analyzer can heat acoal specimen and monitors the coal temperature. The gas outlet is connected to the gas chromatograph, directly analyzing the gaseous products during the low-temperature oxidation. The gas chromatograph is a GC-4100manufactured by East & West Analytical Instruments, Inc., Beijing, China. The coal chamber was connected with the gas transmission line so that the gaseous products generated during the