



## Research article

## Laboratory study on the inhibitory effect of free radical scavenger on coal spontaneous combustion

Jinhu Li, Zenghua Li\*, Yongliang Yang, Biao Kong, Chaojie Wang

Key Laboratory of Gas and Fire Control for Coal Mines (China University of Mining and Technology), Ministry of Education, Xuzhou 221116, China  
 School of Safety Engineering, China University of Mining and Technology, Xuzhou 221116, China

## ARTICLE INFO

## Keywords:

Coal spontaneous combustion  
 Inhibitor  
 Free radical reaction  
 Active functional group  
 Chain reaction

## ABSTRACT

In this paper, the inhibition of free radical reaction in the coal oxidation process was taken as the starting point, and free radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) which combines with free radicals very easily to generate inactive substances was regarded as the inhibitor. The occurrence of coal spontaneous combustion was suppressed by inhibiting the chain reaction of free radicals. TEMPO was compared with common halide salt inhibitors through thermogravimetry and differential scanning calorimeter (TG-DSC) thermal analysis, crossing point temperature (CPT), CO production and other data obtained from experiments. The results show that the inhibitory effect of TEMPO is stronger than that of common halide salt inhibitors and the inhibitory effect increases with the rise of TEMPO concentration. The influence of TEMPO on active functional groups in coal at different temperatures was obtained through Fourier transform infrared spectroscopy (FTIR) analysis, suggesting that the inhibitory effect of TEMPO on active functional groups (C–O, C–H, C=O and O–H) in coal gets more significant with the rise of temperature and the increase of active free radicals in coal. On this basis, five common active free radical models were constructed, and their active sites and thermodynamic parameters were calculated according to density functional theory (DFT). The calculation reveals that compared with oxygen-containing free radicals, alkyl free radicals are more active in the thermodynamic reactivity with TEMPO. The experiments prove that TEMPO has a very strong inhibitory effect on coal spontaneous combustion, because the combination between TEMPO and alkyl free radicals during coal spontaneous combustion decreases the activity of free radicals and reduces the concentration of active free radicals, thus inhibiting the chain reaction of free radicals.

## 1. Introduction

Coal is likely to combust spontaneously in various stages of mining, transportation and storage. Coal spontaneous combustion will not only lower the calorific value of coal, but also produce lots of toxic and harmful gases; in addition, it may cause casualties [1–4]. Each year, coal companies make lots of efforts to prevent and control coal spontaneous combustion, in which process numerous key techniques such as grouting and nitrogen injection have been developed to control the combustion [5–8]. Among these measures, inhibitors are widely used in the prevention of coal spontaneous combustion as they are simple and convenient to use [9–12]. At present, the commonly used inhibitors are inorganic salt inhibitors which mainly include halide salts ( $MgCl_2$  and  $CaCl_2$ ), ammonium salts, lye, etc. For these inhibitors, their own physical properties are primarily considered. In order to prevent the contact between coal and oxygen, researchers selected the inhibitors with great specific heat for endothermic cooling and chose those with large

water absorption for forming an aqueous film on the surface of coal particles [13–16]. The above methods have played a positive role in controlling coal spontaneous combustion to a certain extent, but they do not proceed from the reaction mechanism of coal spontaneous combustion. As a result, they cannot bring about an ideal inhibitory effect, and some of them even accelerate the process of spontaneous combustion with the water loss on coal surface.

Coal spontaneous combustion is caused by the accumulation of heat within the coal. The free radical theory of coal spontaneous combustion suggests that coal spontaneous combustion is resulted from a great deal of heat released by the chain reaction of active free radicals produced by the chemical bond breakage in coal [17–19]. Using electron spin resonance (ESR) technique, Wei et al. [20,21] tested the relationship between the temperature and the concentration of free radicals in coal in the heating process and proved the existence of free radical reactions in coal. Zhong et al. [22] studied the concentration changes of free radicals in coal samples with different combustion tendencies before

\* Corresponding author at: Key Laboratory of Gas and Fire Control for Coal Mines (China University of Mining and Technology), Ministry of Education, Xuzhou 221116, China.  
 E-mail address: [lzh6512@126.com](mailto:lzh6512@126.com) (Z. Li).

and after dry air was let in at room temperature, and meanwhile they analyzed the oxidation ability of coal samples at different free radical concentrations. Zhang [23] and Chen [24] proved the exothermic process of the reaction between free radicals and oxygen by adopting density functional theory (DFT) and molecular dynamics simulations, respectively. These experiments have proved the existence of free radical chain reactions in coal. Therefore, coal spontaneous combustion can definitely be suppressed to a large extent if a substance can be chosen to inhibit or reduce the generation of free radicals during coal spontaneous combustion and weaken the thermal effects of free radical chain reactions.

2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), an inert free radical, can exist stably due to the reduction of orbital energy by the electron delocalization of N atom as well as the existence of steric hindrance effect in the four methyl groups around N–O free radicals. As an electron acceptor, TEMPO is often used as a free radical scavenger to test the concentration of other free radicals because it combines with active free radicals very easily to form inactive substances. Moreover, it is also commonly used as an inhibitor for the polymerization of free radicals since it can control the reaction rate by reducing the concentration of free radicals in reaction [25].

The free radicals contain unpaired electrons, and the activation energy of the reaction between the radicals is zero, and the bond-forming reactions can happen rapidly in a very short time. In this paper, the inert free radical TEMPO which combines with free radicals very easily was chosen as the inhibitor to study its effect on coal spontaneous combustion. The inhibitory performance of TEMPO was compared with that of common halide salt inhibitors by means of thermogravimetry and differential scanning calorimeter (TG-DSC) thermal analysis and low-temperature oxidation experiments. Next, the changes of functional groups on coal surface before and after TEMPO inhibition under different temperature conditions were analyzed through (Fourier transform infrared spectroscopy) FTIR experiments. Finally, five active free radical models were constructed, through which the combination process and reactivity of TEMPO and active free radicals existing in the coal oxidation process were studied according to quantum chemical methods, revealing the inhibitory reaction mechanism of TEMPO.

## 2. Experimental

### 2.1. Coal samples and inhibitor preparation

The coal used in this paper was taken from No. 6 coal seam in Shengli coal mine, Inner Mongolia. The coal is lignite with low metamorphic grade. The coal seam is easy to spontaneous combustion. The newly exposed coal was collected and vacuum-sealed to prevent it from being oxidized before the experiments. The industrial analysis is shown in Table 1.

Bond breakage during the crushing process of coal sample will lead to the formation of a large number of active free radicals. Therefore, the coal sample collected was smashed and ground under the protection of nitrogen atmosphere within a sealed coal sample tank after it was taken to the laboratory, so as to protect it from being pre-oxidized in the crushing process. The grinded sample was sieved, and those with a particle size of 0.180–0.250 mm were selected. Since the organic matter

TEMPO is insoluble in water, a mixed solvent was made by mixing the organic solvent acetone with water at the ratio of 1:1, and 50 g of TEMPO solutions was prepared respectively at mass fractions of 2 wt%, 3 wt% and 4 wt%. Next, 50 g of coal sample was added to each prepared inhibitor solution to be inhibited for 24 h. Then, the samples were vacuum dried at 40 °C until the acetone and excess water were both completely evaporated. The coal samples inhibited by inorganic inhibitors MgCl<sub>2</sub> and CaCl<sub>2</sub> at the concentration of 2 wt% were prepared in the same way for comparison tests.

### 2.2. TG-DSC experiment

Simultaneous thermal analysis technique is often applied to the comparative analysis of heat and reaction process of coal sample before and after inhibition [26]. In this experiment, the thermal analysis was conducted respectively on four groups of coal samples including the raw coal sample and the inhibited coal samples. The experimental instrument was STA-449-F5 (NETZSCH, Bavaria, Germany) which can measure both TG and DSC. Before the experiment, parameters such as the temperature, quality and sensitivity of the instrument were calibrated, with the quality sensitivity controlled at 0.1 µg and the temperature accuracy at ± 0.1 °C. 6 mg of the dried raw coal sample and inhibited coal samples with a particle size of smaller than 200 µm was loosely put into the alumina crucible on the automatic sampling tray, and then the thermal analysis experiment was performed with the dry air flow rate controlled to 50 ml/min, the coal heating rate to 5 K/min and the heating temperature range to from room temperature to 800 °C.

### 2.3. Inhibitory performance experiment

#### 2.3.1. CO concentration experiment

As an important indicator to determine the spontaneous combustion degree of coal, the amount of CO produced in the low-temperature oxidation process can be tested by combining a programmed-temperature experimental device with a chromatographic analysis device [27]. The experimental setup can be divided into two parts, namely, the programmed-temperature part and the chromatographic analysis part. First, the sample was put into a self-made coal sample tank whose top and bottom were filled with asbestos to prevent the pulverized coal particles from entering and blocking the airway. With the flow rate of dry air taken into the tank set as 50 ml/min and the heating rate controlled as 1.2 °C/min, the programmed-temperature experiment was carried out from 30 °C to 180 °C, and CO concentration at the outlet was measured through the GC-9790 gas chromatograph (Fuli Company, China) every 10 °C temperature rise. The experimental setup is shown in Fig. 1.

#### 2.3.2. Crossing point temperature test

Crossing point temperature (CPT) is another important index for determining the spontaneous combustion tendency of coal. In the experiment, the CPTs of samples before and after the inhibition were determined in accordance with the metal basket method [28]. The metal basket consists of a 5 × 5 × 5 cm cubic metal bracket and 300 metal meshes. The samples were kept in the oven under the protection of nitrogen at constant temperature of 105 °C for 10 h, and then transferred into the metal basket after it cooled down to room temperature under the protection of nitrogen. In this way, the programmed-temperature test was carried out. In order to monitor the CPT during the heating process accurately, two K-type thermocouples with a precision of 0.1 °C were arranged. One of them was located at the geometric center of coal sample, and the other was arranged at a point which was at the same horizontal level with the geometric center and was 1 cm away from the geometric center. With the heating rate controlled to 8 °C/min, the data acquisition system was turned on to automatically record the temperature data measured by the two sensors every 10 s.

**Table 1**  
Industrial analysis and elemental analysis.

Industrial analysis				Elemental analysis			
Moisture	Ash content	Volatiles	Fixed carbon	O <sub>daf</sub>	C <sub>daf</sub>	H <sub>daf</sub>	N <sub>daf</sub>
M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	FC <sub>d</sub>				
%	%	%	%	%	%	%	%
18.29	7.83	33.46	40.42	10.21	82.24	5.18	1.63

Download English Version:

<https://daneshyari.com/en/article/6656534>

Download Persian Version:

<https://daneshyari.com/article/6656534>

[Daneshyari.com](https://daneshyari.com)