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Effectiveness of catechin and poly(ethylene glycol) at inhibiting the spontaneous combustion of coal

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ABSTRACT

The effects of various combinations of catechin and poly(ethylene glycol) (PEG) concentrations on the inhibition of coal oxidation were studied. The oxidation behaviors of coal samples both with and without the additives were examined, based on measurements of cross point temperature, oxygen consumption during low temperature oxidation and carbon monoxide emission rates. The results demonstrate that an additive consisting of a combination of both catechin and PEG 200 is capable of inhibiting the oxidation process. *In situ* monitoring of the surfaces of coal samples during oxidation also indicated that these additives suppress coal oxidation by accelerating the formation of ether bonds. Accordingly, a suppression mechanism is proposed.

1. Introduction

Coal is a reactive organic material; when exposed to air, it reacts with oxygen and generates heat, a process that sometimes results in spontaneous combustion with the release of hazardous gases and attendant risks to health and the environment [1–3]. For this reason, the inhibition of the spontaneous combustion of coal is highly desirable and of high value.

The use of a chemical inhibitor is widely applied in coal mines for the prevention and extinguishing of fires and has been demonstrated to work effectively [4,5]. There are two main roles of an inhibitor in retarding coal oxidation: preventing oxygen from reaching active centers on the coal surfaces and adsorbing water. Three-phase foam, water glass, gels and some suction salts such as NaCl, $MgCl_2$ and $CaCl_2$ function in this manner [6–8]. These inhibitors are therefore all physical inhibitors and typically exhibit both low efficiency and short active lifetimes. A second type of chemical inhibitor reacts with active functional groups on the coal surface so as to decrease the formation of active groups or inhibit free radical reactions. Oxidizing agents [9], such as permanganate, perchlorate and peroxide, as well as ionic liquids [10], such as 1-acetoxyetyl-methylimidazolium tetrafluoroborate ([AOEmim][BF_4]), 1-hydroxylethyl-3-methylimidazolium tetrafluoroborate ([HOEmim][BF_4]), 1-allyl-3-methylimidazolium chloride ([Amim][Cl]), 1-ethyl-3-methylimidazolium acetate ([Emim][AC]), 1-butyl-3-methylimidazolium ([Bmim][AC]) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][OTf]), and several inorganic salts [11], including Na_3PO_4 and $Mg(Ac)_2$, work on this principle. These substances are based on chemical reactions and are highly efficient, although some of the chemical inhibitors exhibit disadvantages such as an unstable inhibitory effect when combined with certain types of coal. As a result, there is a need for new inhibitors that are both highly efficient and environmentally friendly.

It is generally believed that catechins, the principal biomolecules in tea plants, can function as protective agents against cardiovascular disease and cancer [12–14]. Catechins also have a variety of pharmacological effects, such as diuretic and hypotensive actions [15], and have been investigated as antioxidants by food scientists as a result of their ability to scavenge reactive oxygen species [16–18]. Any potential abilities of catechins with regard to retarding the spontaneous combustion of coal, however, remain to be discovered. Poly(ethylene glycol) (PEG) is a hydrophilic ethylene oxide polymer that has a number of desirable characteristics, including low cost, low toxicity, biodegradability, thermal stability and water solubility. Although these characteristics have led to the use of PEG as a helpful phase transfer catalyst in chemical synthesis [19–22], its usefulness as an inhibitor of coal oxidation is unknown. In this study, various combinations of catechin and PEG concentrations were selected and their inhibiting effects on coal oxidation were studied.

2. Material and methods

2.1. Experimental materials and coal samples

(+)-Catechin and poly(ethylene glycol) (PEG) 200 (99% purity) were selected as the additive for the experiment trials. The samples were purchased from a local medical station and used without further

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purification. Three different coal samples were collected from the Liangbaosi (LBS) Colliery of Shandong Province, the Pansan (PS) Colliery of Anhui Province and the Bulianta (BLT) Colliery of Neimeng Province. Table 1 summarizes the basic characteristics of these coals. During sample preparation, lumps of these coals were milled and sieved, and fragments 0.25–0.80 mm in size were used for the experimental investigations.

2.2. Methods

The coal samples were crushed and ground into particles, and the 0.25–0.80 mm sized fraction was retained for further preparation. Coal specimens thus prepared were subsequently dried in a vacuum oven overnight at 40 °C, the moisture contents were then measured by a coal proximate analyzer (shown in Table 2), and the pure additives were then blended with the raw coal particles in a beaker with mechanical stirring to produce samples containing varying proportions of additives. The additive-treated coal samples were dried in a vacuum oven until the moisture contents of them are similar to those of dried raw coals. All samples were stored in desiccators prior to measurements. The cross point temperature (CPT), the oxygen consumption at low temperature and the emitted CO of raw coal samples and additive-treated coal samples were then measured. Finally, changes in the functional groups of both the additive-treated and -untreated coals were determined by *in situ* analysis using a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer.

2.3. Examination of the cross point temperature (CPT) and CO-temperature evolution

The point at which the temperature of the coal bed exceeds the temperature of the heating bath is referred to as the CPT and marks the onset of self-heating. The CPT values of samples were determined using an experimental apparatus of our own design consisting of a spontaneous combustion simulation system and a temperature data acquisition system. Each 50-g coal sample was positioned in the apparatus reactor in such a way as to ensure that there was sufficient airflow within the sample. Dry air with an oxygen concentration of 20.96% was then passed through the sample for half an hour while the reactor was heated to a predetermined initial temperature to stabilize the test specimen. The temperature enclosure was then set to increase at a programmed rate of 0.8 °C/min, and dry air was permitted to flow into the reactor at a rate of 8 mL/min for 160 min. During this process, the temperature was recorded by a data logging system for later analysis. Meanwhile, the CO gases emitted from the outlet were analyzed by gas chromatography. The experimental procedure was as follows. First, at the initial of the measurement of CPT, the coal sample was put in the reactor, and the rise rate of temperature was also set up. At the same time, CO gas collection temperature was set up, the first gas collection temperature was 40 °C, and gas sample was collected at intervals of 10 °C.

2.4. Examination of oxygen consumption during low temperature coal oxidation

The oxygen consumption of samples between 40 °C and 70 °C was also ascertained using the same spontaneous combustion simulation system in conjunction with gas chromatography. During this process, the enclosure was set to a constant temperature of 40 °C and dry air with an oxygen concentration of 20.96% was permitted to flow into the reactor at 50 mL/min for half an hour, following which the temperature was set to increase at a rate of 0.8 °C/min and the dry air flow into the reactor was decreased to 8 mL/min. During this process, the temperature was monitored continuously and, when the temperature reached 70 °C, the oxygen concentration of the gas exiting the reactor outlet was sampled and analyzed; therefore, the oxygen consumption at 70 °C can be calculated based on initial O_2 concentration (20.96%) and concentration measured at the outlet.

Table 1
Properties of the coal samples.

Sample	Proximate analysis (air dried basis) (%)			
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}
LBS coal	3.24	9.40	33.24	54.14
BLT coal	11.86	3.28	28.56	56.30
PS coal	1.62	24.86	27.45	46.18

Table 2
The moisture content of dried raw coal samples.

Sample	Moisture content (%)
LBS coal	2.55
BLT coal	5.90
PS coal	1.49

2.5. Variations in active functional groups of samples with and without catechin

As noted, changes in the functional groups of treated and untreated coals were determined by *in situ* FTIR. A KBr powder background was first collected as a reference, after which a ground coal sample was placed into the reaction chamber and the dome was installed. Dry air flowed into the reaction chamber from its base (below the coal sample) and exited out from the top. A temperature controller was connected to the reaction chamber and the chamber was heated to 220 °C at a heating rate of 1 °C/min. The region from 650 to 4000 cm^{-1} was scanned using 4 cm^{-1} resolution, 64 scans were summed to produce each spectrum and a Kubelka–Munk conversion was applied to the data. Spectra collected in series were acquired at 30-second intervals.

3. Results and discussion

3.1. Impact of (+)-catechin on the coal oxidation process

3.1.1. CPT measurements

CPT has been widely used as a means of categorizing the propensity of coals for self-ignition. The CPT data obtained from the air oxidation measurements of LBS coal samples containing various weight percentages of (+)-catechin are shown in Fig. 1.

When the CPT data for the (+)-catechin-treated LBS coal are compared with the value obtained for raw coal, there is obviously a significant increase in the CPT values. It is evident that the CPT increases owing to the addition of (+)-catechin to the coal samples and that the application of 10 wt.% (+)-catechin results in the highest CPT. These results demonstrate that mixing (+)-catechin with coal sample results in a raised critical self-heating temperature and thus improves the thermal stability of the coal.

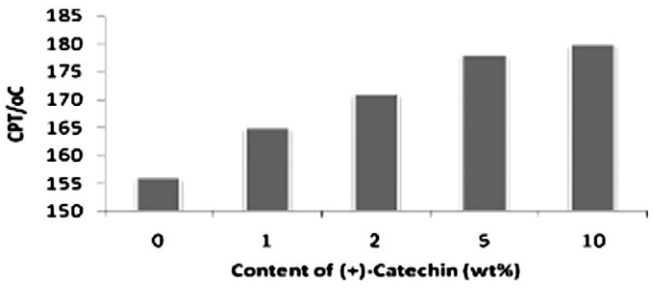

Fig. 1. CPT data obtained for LBS coal samples containing various amounts of (+)-catechin (0, 1, 2, 5 and 10 wt.%).