Study on thermochemical kinetic characteristics and interaction during low temperature oxidation of blended coals

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ABSTRACT

The low temperature oxidation characteristics of individual coals and blended coals were studied via thermogravimetric analysis. Blends 50% on dosage ratio were prepared to investigate their thermo-chemical behavior and kinetic. The low temperature oxidation process of coal could be roughly divided into two interval stages, corresponding temperature ranges of which were 30–140 °C and 150–260 °C, respectively. A synergistic interaction between blending coals was observed within the temperature range of 45–180 °C during the low temperature oxidation process. A certain addition of high volatile bituminous coal to the blended coals would help to relieve low temperature oxidation of coal, which could be attributed to the low moisture and some potential minerals that could increase the chemical inertness. Third-order reaction mechanism model and three-way transport diffusion mechanism model could be used to depict stage 1 and stage 2, respectively. And the apparent activation energy of stage 1 was smaller than stage 2.

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1. Introduction

Coal is the main fossil fuel of primary energy in China which cannot be replaced for a long time in the future, and the capacity of thermal power generation units accounts for over 70% of the national total generation capacity [1,2]. Due to the rising price of coal and the imbalance between supply and demand for the past few years, the types of coal used in power generation has been diversified and the quality has been further reduced, even on account of long-term coal deficiency, especially for many of the power plants that import most of their coal [3].

In recent years, blending of different types is becoming common and promising in power plants [3]. Coal-blend combustion technology is one of the co-combustion technologies. Several merits of coal-blended combustion technology has been proved in improving combustion behavior, enhancing fuel flexibility, meeting emission regulations, controlling ash deposition and reducing costs [1,2,4].

On the other hand, self-ignition of stockpiled coals results in not only property losses and safety problems but also pollutant gas emissions [5]. Spontaneous combustion of coals is an oxidation of the coals at low temperatures [6]. This process spans a wide range of temperature from room temperature to nearly 300 °C (ignition occurring) and it causes deterioration in the technological properties of coal such as coking and caking [7]. Thorough researches on the oxidation mechanism of coal at low temperature and analysis about the influence of variable parameters such as temperature, particle size, surface area, moisture content, and mineral substance on this process have been done in past studies [8–10]. Different reaction models were applied to calculate activation energy, which was an important index to describe the low temperature oxidation process [9,11]. Besides, various methods based on different principles have been developed to estimate the self-ignition tendency [5,6].

Since the coal-blend combustion technology is still in development, and most of the current investigations are focusing on individual coals during low temperature oxidation, the low temperature oxidation of blended coals has seldom been investigated. As the blending of coals is a popular way which is widely used in power plants in nowadays, further understanding about low temperature oxidation of blended coals, chemical reaction kinetics as well as the interaction between the constituents, for instance, is of paramount importance. Thus,

the aim of this article is to study thermal behavior during coal-blend low temperature oxidation under air atmosphere by thermogravimetric analyzer. And based on the TGA, the low temperature oxidation process of blended coals is presented to analyze the interaction. Reaction mechanism function and kinetic parameters were obtained by TGA. The results could provide a detailed observation on low temperature oxidation of blended coals, thus offering referential information for designing effective methods for suppressing the self-ignition tendency of blended coals and perfecting co-combustion technology.

2. Methods

2.1. Materials

Study samples were selected as three coals widely used in power plants of Guangdong Province in China, two sub-bituminous coals (Coal A and Coal B) and a high volatile bituminous coal (Coal C). Their ultimate analyses and proximate analyses are given in Table 1, exhibiting quite large differences in composition. The ultimate analysis and proximate analysis of the samples were based on ASTM D5373 criterion and GB212-91/GB212-84 criterion, respectively. After quartering sampling and sealing, the samples were sent to the laboratory. The raw materials were finely pulverized and sieved with a mesh size 178 μm. For blended coals, they were mixed at weight ratios of 50%, namely 50A50B, 50A50C and 50B50C, respectively. Furthermore, to study the effect of blending ratio on the low temperature oxidation of blended coal. Another four different blending ratios of coal A and coal C were taken in to consideration. The coal C content of the blended ratios were set by mass as 10%, 30%, 70% and 90%, 90A10C, 70A30C, 30A70C and 10A90C, respectively. The samples were mixed a total amount of 100 g by a micro rotary mixer for 2 h to ensure the uniformity of the blends, and then 10 g of the blends were performed by quartering for tests. The final samples were stored in gas-tight desiccators before experiment.

2.2. Experimental facility

The thermochemical kinetic characteristics and interaction during low temperature oxidation of blended coals were studied by using an METTLER TGA thermogravimetric simultaneous thermal analyzer. Its microbalance sensitivity was less than ±0.1 μg and temperature precision was ±0.5 °C. The samples for low temperature oxidation investigations were heated from 30 °C to 300 °C in air atmosphere with a flow rate of 50 ml/min, at heating rate of 3 °C/min. To make sure that the heating transfer limitations can be ignored, the initial weights of all samples were 10 ± 0.5 mg which were loaded into an Al_2O_3 ceramic crucible for each run. Several blank experiments without samples were carried out to obtain the baselines, in order to calibrate the effects of the buoyancy and the weight of crucible with samples. All experiments were repeated to eliminate risks of test error, and the reproducibility turned out to be quite good.

2.3. Kinetic modeling

Sample mass was proved a function of temperature in thermo balance experiments. In another word, the rate of degradation or conversion, $d\alpha/dt$, is the linear function of a temperature-dependent rate constant, $k(T)$, and the temperature-independent function of conversion, $f(\alpha)$,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the conversion degree, $t(s)$ is time, T (K) is the absolute temperature, k (T) usually described by the Arrhenius equation [12]:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A (s^{-1}) is pre-exponential or frequency, E (kJ mol^{-1}) is the activation energy, R (kJ mol^{-1} K^{-1}) is the universal gas constant.

The degree of conversion of the reduction process is expressed as [12]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{3}$$

where m_0 is the initial mass of the sample, m_t is the mass of the sample at the time t and m_f is the final mass of the sample.

Table 1
The ultimate analyses and proximate analyses of the coal samples (on an air dried basis).

Properties	Coal A	Coal B	Coal C
Ultimate analysis (wt%)			
C	68.07	59.86	79.24
H	4.64	4.25	5.67
N	0.82	0.79	1.3
S	0.62	0.56	1.31
O	8.95	9.62	4.17
Proximate analysis (wt%)			
Moisture	8.45	10.3	4.56
Ash	8.44	14.62	3.75
Volatile matter	38.7	41.26	33.14
Fixed carbon	44.41	33.83	58.55
Lower heating value (MJ/kg)	25.75	23.6	27.85