Fuel Processing Technology 147 (2016) 64–70

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Insight into the intrinsic reaction of brown coal oxidation at low temperature: Differential scanning calorimetry study

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ARTICLE INFO

Article history:
Received 2 February 2015
Received in revised form 14 July 2015
Accepted 27 July 2015
Available online 26 September 2015

Keywords:
DSC
Coal
Low-temperature oxidation
Exothermic characteristic
Activation energy

ABSTRACT

The oxidation of coal at low-temperature involves a series of physical and chemical processes and many parallel reactions. But the intrinsic oxidation reaction between O_2 and coal is the main source responsible for the self-heating and spontaneous combustion of brown coal. In this research, differential scanning calorimetry (DSC) was introduced to determine the intrinsic reaction of Ximeng brown coal oxidation at low temperature. The heat evolution of the intrinsic reaction after eliminating the evaporation of water and thermal decomposition of inner oxygen-containing functional groups was obtained by subtracting the DSC curve in N_2 from the DSC curve in air. It is considered that the intrinsic reactions between coal and oxygen could be divided into three stages, including the slow oxidation, accelerated oxidation and rapid oxidation stages. Compared with DSC-air curve, the DSC-sub curve based on the subtracting results elucidated the exothermic characteristics of intrinsic oxidation reaction in each stage more clearly. In addition, DSC-sub curve reduced the experimental errors inborn from the heating rate and the sample mass, so it had more practical application value than DSC-air curves. Activation energies obtained from DSC-sub curves can better reflect intrinsic oxidation reaction and be used as important indicators for the evaluation of coal spontaneous combustion tendency.

1. Introduction

Low-temperature oxidation of coal (<300 °C) has been extensively studied by a number of investigators due to the fact that the reaction between coal and oxygen may lead to self-heating and subsequent spontaneous combustion in coal mines and stockpiles [1,2]. With the increasing utilization of coal in China, to avoid property loss and safety problems, the oxidation of coal at low temperature is becoming important research project. Coal oxidation at low temperature is a complicated process [3,4] and some macroscopic and microscopic characteristics have been found in it [5,6]. The macroscopic characteristics mainly involve the mass change, the heat release and the oxidation products formation. And the active functional groups transformation, the physical structure (pore structure and specific surface area) evolution and the element composition occurrence are contained in the microscopic characteristics. Among them, the heat release of the reactions between coal and oxygen is the main reason for coal self-heating. When the rate of the heat release is greater than the heat removal in the oxidation process, it will lead to the self-heating and eventual spontaneous combustion of coal.

Currently, some of the thermal analysis techniques viz. DTA (differential thermal analysis), TG (thermogravimetry) and DSC (differential scanning calorimetry), have been increasingly used for assessing the proneness of coal to spontaneous heating [7,8]. Garcia et al. [9] found that DSC was a useful technology to investigate the early stages of the oxidation of coal and the onset temperature was a better indicator of propensity of coal oxidation. Panigrahi et al. [10] determined the susceptibility of coal to spontaneous heating by the methods of DSC, DTA, CPT (crossing point temperature), etc. Exhaustive correlation studies between susceptibility indices and intrinsic properties had been carried out for identifying appropriate parameters used for classification of coal seams. Kok [11,12] used TG/DTG to obtain information on the temperature-controlled combustion characteristics and pyrolysis of coal, and Arrhenius-type kinetic model was used to determine the kinetic parameters. At present, the plenty of works have been published about the application of thermal analysis techniques in the combustion characteristics [13–15], while very few studies have focused on exothermic (endothermic) characteristics in the process of coal low-temperature oxidation.

The low-temperature oxidation of coal involves a series of physical and chemical processes and many parallel reactions. The oxidation reaction of O_2 and coal is typical exothermic reaction, and the dehydration and thermal decomposition of inherent oxygen-containing functional groups are endothermic. In the oxidation of coal at low temperature,

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http://dx.doi.org/10.1016/j.fuproc.2015.07.030

these processes jointly determine the heat accumulation of coal self-heating. In the present literatures on the characteristics of low temperature oxidation of coal, these parallel processes were studied as a whole and the results were comprehensively given [16,17]. However, in these processes, we might be more concerned about the change of heat caused by the reaction of coal and oxygen, after all, it is the root source of coal spontaneous heating and combustion. For the low rank coal, such as brown coal, it contains a lot of water and thermal decomposition reaction easily occurred in low-temperature oxidation. When the exothermic oxidation characteristics of reaction between coal and oxygen are studied using thermal analysis techniques (TG and DSC), it is more easily influenced by the parallel process. Therefore the exact description of intrinsic oxidation reaction of coal and oxygen become more difficult. Meanwhile, the application of thermal analytical method for studying exothermic (endothermic) characterization of samples is easily affected by experimental conditions [18–20], such as sample mass or heating rate. He. et al. [18] investigated caloric requirement of biomass pyrolysis by TG–DSC and found that DSC curve was much more insensitive to experimental conditions than TG curve. It is necessary to determine the optimal experimental conditions to study the exothermic (endothermic) characteristics of the intrinsic oxidation reaction by DSC.

In view of the above discussions, the purpose of this study is to investigate the intrinsic properties of heat release due to the coal oxidation reactions and determine the optimal experimental conditions. It is proposed that a new approach can be derived by kinetic parameters based on the heat change using the subtraction method of differential scanning calorimetry. In N_2 atmosphere, low temperature conversion of coal mainly involves water evaporation and thermal decomposition of inherent oxygen-containing functional groups. Through subtracting N_2 curve from the air curve, the influence of water evaporation and thermal decomposition can be excluded, and the intrinsic oxidation reaction of coal can be obtained. On the basis of these results, it is considered that the intrinsic reaction between coal and O_2 is used to reflect the exothermic (endothermic) characteristics of coal at low temperature.

2. Experimental

The brown coal sample (denoted as XM coal) used in this study was collected from Ximeng mine in China. Coal sample was crushed in N_2 atmosphere after stripping the surface oxide layer, and then sieved to the particle sizes of 0.125–0.250 mm and stored in sealed container before the experiments. Table 1 shows the proximate and ultimate analyses of the coal sample used in this study.

The experiments were performed with DSC 204 HP. An aluminum crucible with the lid with a pinhole was used as the sample holder. An empty aluminum crucible with a lid was used as reference. To reduce the experimental error, calibration test was also carried out before the experiments. Coal sample used in the experiments should be kept in clean and dry crucible evenly. Differential scanning calorimetry experiments were performed with 3 mg, 5 mg, 10 mg, and 20 mg samples at the heating rate of 0.5 °C min^{-1}, 1.0 °C min^{-1}, 2.5 °C min^{-1} and 5.0 °C min^{-1} in the temperature range of 30–230 °C. Experiments were respectively carried out in nitrogen and air atmosphere with the gas flow rate of 50 mL min^{-1}. Each experiment was performed twice for reproducibility. The DSC curve of the intrinsic reaction between coal and molecular O_2 was obtained by subtracting the DSC–N_2 curve from the DSC-air curve [4].

Table 1
Proximate and ultimate analyses of coal sample used in experiments.

Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
M_{ad}	A_d	V_{daf}	C	H	O^a	S	N
27.99	11.08	47.45	68.16	3.95	24.95	1.41	1.53

Note: ad, air dry basis; d, dry basis; daf, dry ash-free basis.
[a] Determined by difference.

3. Results and discussion

3.1. Heat change of low-temperature oxidation of coal

DSC curve mainly reflects the relationship between heat flow and temperature. The DDSC is the first derivative of DSC, which can reflect the relationship between heat flow rate and temperature. Fig. 1 shows the curves of DSC-air, DDSC-air, DSC-N_2, DDSC-N_2, DSC-sub (subtracting the DSC–N_2 curve from the DSC-air curve), DDSC-sub of 5 mg XM coal at the heating rate of 1 °C min^{-1}, within the temperature of 30–230 °C, which are taken as examples to describe the exothermic (endothermic) characteristics of low-temperature oxidation of coal.

From Fig. 1, it is observed that the heat change in the process of low-temperature oxidation can be divided into several stages. For the sake of analysis, the DSC curves in air atmosphere, nitrogen atmosphere and subtractive spectra were segmented as Fig. 2(a), (b) and (c), respectively.

From Fig. 2(a), it can be observed that the DSC-air curve of XM coal contains three regions. The first region, from the ambient temperature to 93.5 °C, is an obvious endothermic peak, in which the moisture in coal evaporates, and physically adsorbs and desorbs to the particle surface continually [21]. Therefore, this region is called dehydration stage. The second stage, from 93.5 °C to 134.5 °C, is the uniform oxidation stage, in which heat release rate does not change obviously. In the third region, from 134.5 to 230 °C, the rate of heat release increases rapidly with the temperature increase. It means that the oxidation process turns into the advanced oxidation stage.

In Fig. 2(b), the whole DSC-N_2 curve of XM coal is negative, which means that the whole process is endothermic. The first region is from the ambient temperature to 91.0 °C. In this region, the evaporation water from coal sample is the major reason for the appearance of an endothermic peak. It is similar with the first region of DSC-air curve, but the area of endothermic peak is greater. This result suggests that quite a little heat from the reaction between coal and O_2 in air atmosphere is released. The second stage is from 91.0 °C to 136.5 °C, in which the remaining inner water continues to be evaporated and a small amount of heat is absorbed. The third stage, from 136.5 to 230 °C, is called as the thermal decomposition stage. With the temperature rising, the DSC value decreases and the curve shows a slowly declined trend. It shows that endothermic heat increases constantly, which is associated with the intensity of coal pyrolysis. The higher the temperature, the greater the intensity and endothermic heat of thermal decomposition.

In Fig. 2(c), the DSC–sub curve of XM coal is positive in the whole process, which indicates that the low-temperature oxidation of coal is an exothermic process. The DSC-sub curve can also be divided into three stages. The first stage, from ambient temperature to 91.5 °C, is denoted as the slow oxidation stage. A small exothermic peak is presented in this stage, which may be caused by some oxygen-containing complex formation [22]. The main processes at this stage are the chemisorption of oxygen and the formation of intermediate complexes, which can be

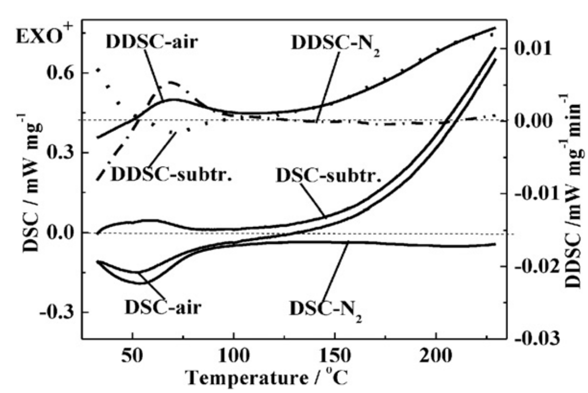

Fig. 1. Typical heat change of XM coal sample heated under different atmosphere conditions.