



Investigation on the co-combustion of low calorific oil shale and its semi-coke by using thermogravimetric analysis



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ARTICLE INFO

Article history:

Received 8 November 2016

Received in revised form 29 December 2016

Accepted 4 January 2017

Keywords:

Thermogravimetric analysis
Co-combustion
Oil shale
Semi-coke
Kinetics

ABSTRACT

In the present work, thermogravimetric analysis was employed to investigate co-combustion behaviors of Fushun low calorific oil shale and its semi-coke. The synergy effect was estimated by using the interaction coefficient and the relative error of mean square root. In addition, activation energy was also calculated by means of Coats-Redfern, distributed activation energy model and Flynn-Wall-Ozawa methods. Results indicated that with the increase of oil shale mass fraction and oxygen concentration, combustion characteristics of the samples were improved. And some little interaction did occur during the co-combustion process, but it was relatively slight. Consequently, the co-combustion of oil shale and semi-coke still could be expressed roughly by the addition of individual components of the mixtures. Furthermore, activation energy of the samples decreased slowly at the initial stage attributed to the minerals' catalytic effects, and in the final stage, it jumped to a high value, suggesting that the burnout of the samples was difficult. Besides, the mix proportion of oil shale which was added to stabilize the combustion in the circulating fluidized bed was also theoretically calculated.

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1. Introduction

In China, abundant oil shale (OS) resources are mainly used by retorting for the production of shale oil to alleviate the shortage of petroleum [1–3]. Currently, its prevailing method is still using Fushun-type retorts, thus resulting in a portion of fine OS particles being unable to meet the demand of retorting technique and discarding as the tailings [4]. Meantime, around 10–30 tons of oil shale semi-coke (SC) per ton of shale oil is left after production [5]. Owing to the absence of available techniques, landfill is always adopted to dispose of SC. However, this method occupies a lot of land, but also causes great hazards to the environment [6–9].

In order to dispose of SC harmlessly and make full use of OS resources, it is considered that SC combusts with fine OS particles in the fluidized bed combustor at a certain proportion. And the key to carry out this scheme is confirming combustion characteristics of OS and SC accurately. Until now, the co-combustion of OS and SC has attracted interest of many researchers. Arro et al. [10] compared with different combustion technologies and proposed that SC and OS should be burnt together in the circulating fluidized bed boiler. Wang et al. [11–13] studied combustion behaviors of Huadian OS and its SC in a thermogravimetric analyzer (TGA)

and the results indicated that the whole combustion process could be divided into several low temperature sections, a transition section and a high temperature section. And the addition of OS improved combustion characteristics of the samples. Furthermore, some interactions occurred during the co-combustion process, and the combustion behavior of the blends went away from the calculated one. Sun et al. [14] found that the ignition characteristic was greatly improved when SC was mixed with OS.

Fushun Basin hosts the largest opencast OS mine in Asia [15], and its OS is featured in high ash content, low heating value and relatively low oil yield. Presently, with the update of retorting technique and the application of low grade OS, calorific values of fine OS particles and its SC generated from the Fushun OS retorting process both have already dropped to below 4000 kJ/kg. However, above-mentioned literatures mainly focus on co-combustion behaviors of SC whose calorific value is above 4000 kJ/kg and much higher calorific OS, and there has been little work in the literature regarding co-combustion behaviors of such low calorific OS and SC. As is known, different fuel properties exhibit different combustion behaviors, including ignition and burnout characteristics, as well as the interaction. And then, previous results may not be completely appropriate. Moreover, there are also no literatures or engineering applications for co-combustion of such low calorific fuels for references. Hence, it is imperative to carry out studies on combustion performances of Fushun low calorific OS and SC in detail, as well

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as the optimal blending ratio, because these parameters are vital for the subsequent industrial application.

This paper mainly focuses on thermal characteristics of Fushun low calorific OS, its SC and their blends with different mass ratios at different heating rates and oxygen concentrations, trying to comprehensively reveal the combustion behaviors. What's more, activation energy was obtained by means of Coats-Redfern, activation energy model (DAEM) and Flynn-Wall-Ozawa (FWO) methods. And finally, on the basis of thermal balance theory, the mix proportion of OS which was added to stabilize the combustion in the circulating fluidized bed combustor was theoretically calculated. Thus, this paper will offer the reference for further application of Fushun low calorific OS and SC co-combustion in the fluidized bed combustor.

2. Experimental study

2.1. Materials

The low calorific fine OS particles and its SC adopted in this work were sourced from the Fushun OS retort factory located in Liaoning Province, China, and the ultimate and proximate analyses are given in Table 1. Before experiments, the samples were ground and sieved in accordance with national standards to a particle size, ranging from 0 to 0.21 mm. The samples in different blending ratios (SC/OS) of 1:0, 3:1, 1:1, 1:3 and 0:1 were labeled as S1, S2, S3, S4 and S5, respectively.

2.2. Experimental facility and method

Thermogravimetric experiments were carried out in artificial air using an STA409PC TGA (NETZSCH, German). This analyzer has a temperature precision of ± 0.1 °C and the microbalance sensitivity is less than ± 0.2 μ g, and its temperature and mass accuracy are respectively calibrated periodically using Curie temperature and standard material. For combustion experiments, about 10 mg of each sample was spread evenly in an alumina crucible and heated at a rate of 20, 30, 40 and 50 °C/min, respectively from room temperature to 1000 °C until no further mass change was detected. High-purity nitrogen and oxygen in a 79/21 ratio was fed with the constant flow rate of 100 ml/min, and the mix proportion of nitrogen and oxygen was also changed to conduct different oxygen concentration combustion experiments. A separate blank run was conducted using an empty pan under each heating rate and this was used for baseline correction during the combustion of samples. The same experiments were repeated at least twice to ensure the reproducibility of the experiments and accuracy of the data.

2.3. Combustion parameters

Combustion performance was analyzed by combustion parameters which were derived from combustion curves. Extrapolation of TG-DTG data was used to determine ignition temperature (T_i) [16]. Burnout temperature (T_h) was defined as the temperature where 98% of the combustible material had already been burnt [17]. Comprehensive combustion characteristic index (S) reflected the burning ability of sample [18]. A higher value of S meant the

sample had a better burning ability. Combustion stability index (R_w) evaluated the burning stability of sample [19]. A higher value of R_w meant the sample had a better burning stability.

$$S = \frac{(dw/dt)_{\max} \times (dw/dt)_{\text{mean}}}{T_i^2 \times T_h} \quad (1)$$

$$R_w = 8.5875 \times 10^7 \times \frac{(dw/dt)_{\max}}{T_i \times T_{\max}} \quad (2)$$

where $(dw/dt)_{\max}$ and $(dw/dt)_{\text{mean}}$ are respectively the maximum combustion rate and the average combustion rate. T_{\max} is the temperature of maximum mass loss rate.

2.4. Estimation methods of synergy

In order to verify whether there were the interactions between OS and SC during the co-combustion, the theoretical thermogravimetry (TG) and differential thermogravimetry (DTG) curves were calculated using Eqs. (3) and (4) [20].

$$M_{\text{cal}} = x_{\text{os}}M_{\text{os}} + x_{\text{sc}}M_{\text{sc}} \quad (3)$$

$$\left(\frac{dW}{dt}\right)_{\text{cal}} = x_{\text{os}}\left(\frac{dW}{dt}\right)_{\text{os}} + x_{\text{sc}}\left(\frac{dW}{dt}\right)_{\text{sc}} \quad (4)$$

where x_{os} and x_{sc} are respectively the mass fraction of OS and SC in the blends. M_{os} and M_{sc} are separately the residual mass of OS and SC. $(dW/dt)_{\text{os}}$ and $(dW/dt)_{\text{sc}}$ represent the mass loss rate of OS and SC, respectively. M_{cal} and $(dW/dt)_{\text{cal}}$ are respectively the calculative residual mass and the calculative mass loss rate of blended samples.

Moreover, the synergy was also quantitatively determined by the interaction coefficient (f) and the relative error of mean square root (rms) [21]. And these two indexes were defined by the following equation.

$$f = \frac{R_{\text{exp}}\Delta T_{1/2,\text{exp}}/T_{\text{max,exp}}}{R_{\text{cal}}\Delta T_{1/2,\text{cal}}/T_{\text{max,cal}}} \quad (5)$$

$$\text{rms} = \sqrt{\frac{\sum_{i=1}^n \left(\frac{x_{\text{exp}}^i - x_{\text{cal}}^i}{x_{\text{cal}}^i}\right)^2}{n}} \quad (6)$$

where R is the value of DTG peak point. $\Delta T_{1/2}$ is the peak half-width. x^i is the mass loss rate of NO. i , and n is the number of points selected in the experiment. f is used to distinguish whether the mixture of OS and SC is beneficial for the co-combustion by judging if it is larger than 1 or not. The value of rms characterizes the level of interaction between OS and SC.

2.5. Reactivity analysis

Thermogravimetric analysis is commonly used to measure the reactivity of fuels. In this work, the specific reactivity (R) reported in the literature [22] was calculated as follow.

$$R = -\frac{dm}{dt} \left(\frac{1}{m - m_{\text{ash}}} \right) = -\frac{m_2 - m_1}{(t_2 - t_1)(m_1 - m_{\text{ash}})} \quad (7)$$

Table 1

The ultimate analyses and proximate analyses of OS and SC.

Samples	Ultimate analyses (wt.%)					Proximate analyses (wt.%)				$Q_{\text{ar,net}}$ kJ/kg
	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	M_{ar}	V_{ar}	A_{ar}	FC_{ar}	
OS	9.51	1.64	5.67	0.55	0.4	6.01	15.93	76.22	1.84	3530
SC	6.29	0.78	3.72	0.6	0.45	1	7.68	87.16	4.16	2384

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