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Pyrolysis and co-pyrolysis of lignite and plastic

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ABSTRACT

The study firstly discusses the pyrolysis characteristics and kinetics by thermogravimetric analysis (TGA), and then investigates the pyrolysis of lignite and co-pyrolysis with plastic (polyethylene or polypropylene) in tube furnace. Meanwhile, the research focuses on the co-pyrolysis products under different mixing ratios as well as pyrolysis products at different testing temperatures and heating rates. The results show that higher final testing temperature and lower heating rate contribute to bond fission in lignite pyrolysis, resulting in less char product. In co-pyrolysis, lignite acts as hydrogen donor, and the yields of char and water rise with increasing amount of plastic in the mixture, while the yields of gas and tar decrease; and a little admixture of plastic will promote the production of gas and tar. Kinetic studies indicate that in temperature range of 530–600 °C, activation energies of lignite are higher than those of lignite/plastic blends, and as plastic mass ratio increases from 0% to 10%, samples need less energy to be decomposed during co-pyrolysis.

1. Introduction

Effective recycling of waste plastics is favorable to the protection of environment and natural resources, and introducing waste plastics to blends of coals for pyrolysis may be one of the most effective methods because it provides an attractive way to dispose and convert waste plastics and coal into higher value fuel [1,2]. Co-pyrolytic techniques with coal and waste plastics have received much attention in recent years and industrial scale co-pyrolysis experience with coking coal and waste plastics has been reported; meanwhile, many studies show that mixed plastic wastes are used as minor component in coal blends without any detriment to coke quality [3,4].

The resources of lignite in China are abundant. Unfortunately, because of its low energy density and typically high moisture content, lignite is not utilized extensively compared to higher coal grades [5]. Pyrolysis, a method of upgrading for lignite, is of great significance to utilize lignite cleanly and efficiently [6,7].

At present, only little work is concerned with co-pyrolysis of lignite and waste plastics. As is known, lignite has high oxygen content, so it needs a lot of hydrogen during pyrolysis; waste plastics have high hydrogen/carbon, and it may interact with lignite during co-pyrolysis. So we may use them to provide hydrogen for lignite in co-pyrolysis, thus waste plastics can be reused and the upgrading of lignite is conducted as well [8].

Since what we care about is how much pyrolysis products can we get, our attention in this study focuses on the yields of pyrolysates, so we do not analyze the composition of collected products. Usually, TGA and fluidized bed are exercised to define the kinetic parameters in pyrolysis [9–11]. In this paper, Chi-feng, Inner Mongolia lignite, polyethylene (PE) and polypropylene (PP) are used as raw materials, and samples are tested by TGA and investigated in tube furnace [12–14]. The objective of this study is to obtain an overall understanding of the interaction mechanism of coal and plastic wastes, and how this influences the yields of pyrolysis products. This work forms part of the more comprehensive study which influences on waste plastics in coal pyrolysis.

2. Experimental

2.1. Sample preparation

Lignite sample used in this work is from Chi-feng, Inner Mongolia, and it is called CF for short in this paper. Since it tends to absorb moisture in the atmosphere, we keep it in dryer after crushing it into powders of 0.2 mm. Table 1 shows the proximate and ultimate analyses of CF, PE and PP used. CF was mixed with PE and PP (0.2 mm in size) in mass ratio of 98:2, 96:4, 94:6, 92:8, and 90:10, respectively. The mixtures obtained were prepared in sealed container.

2.2. Thermogravimetric analysis

DTA-TG (HTG-2), made in Beijing Henven Scientific Instrument Company, was adopted for TGA. Pyrolytic behaviors of CF, PE and PP and co-pyrolytic behaviors of their blends were tested by TGA, and it helped to determine the appropriate pyrolysis

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Table 1
Proximate and ultimate analyses of raw materials (%, by weight).

Sample	Proximate analysis				Ultimate analysis			
	M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf}	S_d
CF	20.89	11.77	42.50	57.50	75.64	4.78	17.98	0.9980
PE	0	0.45	99.55	0	85.63	14.45	0	0
PP	0	0.42	99.58	0	85.72	14.18	0	0

Note: M_{ad} is moisture on the air dried basis; A_d the ash content on dry basis; V_{daf} the volatile matter content on dry ash free basis; and FC_{daf} the fixed carbon content on dry ash free basis.

temperature ranges as well as to discuss the kinetic parameters [15]. In TGA, 100 ± 0.1 mg of sample was conducted under 50 mL/min N_2 flow at heating rate of 20 °C/min from room temperature to 800 °C.

2.3. Pyrolysis and co-pyrolysis in tube furnace

As shown in Fig. 1, the test units include tube furnace (GR-3–9), pyrolysis reactor, program controller, cooling system, dryer, gas collector and so on. The pyrolysis reactor is 1.2 m long, and the length of its constant temperature area is 0.2 m. In the study, the tube furnace was kept in nitrogen atmosphere with a purging flow rate of 100 mL/min for 5 min to expel air from the reactor. After that, N_2 flow rate was kept to zero, and about 20 g sample was pyrolyzed until a desired temperature reached and maintained for 30 min, with heating rates of 10, 20, 30 °C/min, respectively.

The volatile compounds from the reactor entered into the liquid collector which was immerged in an ice-water bath unit. The tar and vapor with lower boiling point condensed in this liquid collector, and gases with higher boiling point were collected by the rubber bag collector after eliminating moisture and low molecular tar in the dryer. The moisture could be separated from tar by means of distillation, and then was to be measured.

3. Results and discussion

3.1. Kinetics calculation

The kinetic parameters, activation energy and pre-exponential factor, of pyrolysis and co-pyrolysis can be determined by Coats-Redfern method. It is assumed that solid fuel pyrolysis is a first-order reaction [4,16]. So the coal and plastic pyrolysis reaction equation may simply be expressed as Eq. (1):

$$\frac{d\alpha}{dt} = kf(\alpha) = A\ \exp\left(-\frac{E}{RT}\right)(1-\alpha) \tag{1}$$

where A is the pre-exponential factor; E the activation energy; T the temperature; t the time; and α the carbon conversion. α can be calculated by Eq. (2)

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \tag{2}$$

where W_0 is the original mass of the test sample; W_t the mass at time t; and W_f final mass at the end of test.

For a constant heating rate β during pyrolysis, $\beta = dT/dt$, rearranging Eq. (1) and integrating give Eq. (3):

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{3}$$

The expression $\ln[AR/\beta E(1 - 2RT/E)]$ in Eq. (3) can be taken as $\ln(AR/\beta E)$. If the left side of Eq. (3) is plotted versus $1/T$, a straight line may be obtained if the process can be assumed as a first-order reaction. From the slope, $-E/R$, the activation energy E can be determined, and then the pre-exponential factor A can also be determined.

3.2. Thermogravimetric analysis

Fig. 2 demonstrates that CF pyrolysis occurs at 350–550 °C, while PE and PP pyrolyze at 420–560 and 380–530 °C, respectively. Considering the overlap of their pyrolysis temperature ranges, pyrolysis and co-pyrolysis could be conducted in temperature range of 400–600 °C.

PE and PP show similar pyrolysis characteristics due to the similar chemical bonds in their molecular structures. According to TG/DTG curves in Figs. 3 and 4, this study gets the kinetic parameters in three temperature ranges (350–450, 450–530 and 530–600 °C) determined by Coats-Redfern method, as shown in Table 2. The good correlation coefficient indicates that the corresponding independent first-order reaction model fits the experimental data very well.

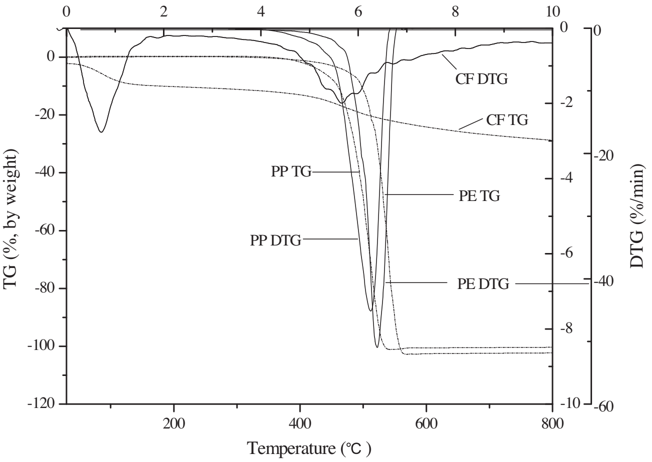

Fig. 2. TG/DTG curves of CF, PE and PP at heating rate of 20 °C/min from room temperature to 800 °C.

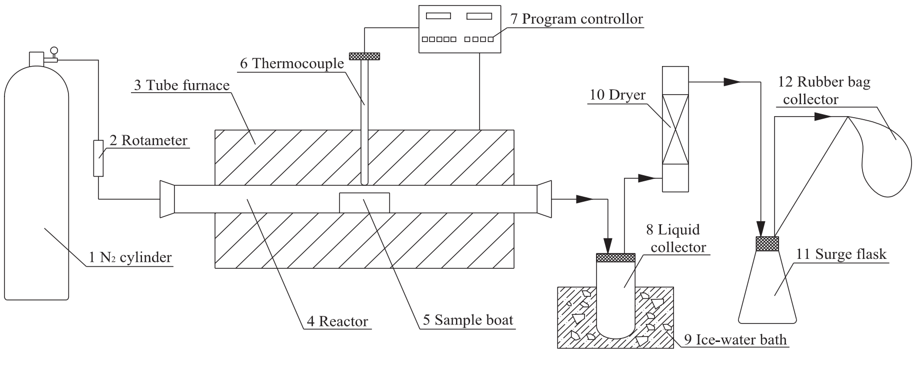

Fig. 1. Scheme of the experimental apparatus with a tube furnace.