



Synergistic effects on thermochemical behaviors of co-pyrolysis between bio-oil distillation residue and bituminous coal



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ABSTRACT

Co-pyrolysis characteristics of bio-oil distillation residue and bituminous coal were investigated through thermogravimetric analysis coupled with Fourier transform infrared spectrophotometer (TGA-FTIR). The addition of bituminous coal changed the behaviors and kinetics of pyrolysis reaction. With temperature increasing, synergistic effects rapidly increased at relatively low temperatures, and then kept a decreasing tendency with different rates until a relatively steady state. The results of the quantitative analysis of chemical functional group by the peak area of infrared spectroscopy indicated that the addition of bituminous coal had a positive effect on the production of CO₂ and CO, and a negative effect on the functional groups containing C–H, C=C and C–O bond. The co-pyrolysis mechanism and kinetics parameters were calculated by the Coats-Redfern and Flynn-Wall-Ozawa method, suggesting that the activation energy and the reaction order of co-pyrolysis increased with mixing ratio increasing in main step. The lowest activation energy (73.17 kJ/mol by Coats-Redfern method and 71.46 kJ/mol by Flynn-Wall-Ozawa method) was obtained by blending 20 wt% bituminous coal.

1. Introduction

Recently, with energy crisis and relative environmental problems increasing, biomass, as a potential substitute of petroleum fuel, has attracted more and more public attention because it is renewable and carbon dioxide is neutral [1,2]. Biomass fast pyrolysis is an effective way to get bio-oil which is a kind of complex organic mixtures containing more than 200 compounds [3–5]. Nowadays, the major application in bio-oil utilization is to improve the physical and chemical properties of bio-oil via such refined technologies as distillation, extraction, fractionation, centrifugation, membrane separation, supercritical extraction and chromatographic separation [6,7]. Among these technologies, distillation, a feasible and effective method with simplicity and economy, has been applied to produce high-quality fuels and high-value chemicals [8]. However, approximately 30–50% of distillation residue would be remained after distillation process [9,10].

The utilization of bio-oil distillation residue is relatively difficult, due to its complicated functional groups and high volatiles. Although the bio-oil distillation residue can be directly converted into calcined coke at high temperature or used for the production of monophenols and sugars by extraction [11–13], these methods consume a lot of energy and produce a lot of pollutants, and the operation process is very complicated. The co-pyrolysis technology of low-quality solid fuels is an

interesting disposal way to produce renewable chemicals and high-quality fuels [14,15]. Recently, the co-pyrolysis characteristics of various fuels and biomass have been widely studied. Wu et al. [14] obtained positive synergistic effects from co-pyrolysis of low-rank coal and model components of microalgae biomass at all mass ratio. Wei et al. [15] also found that the inhibition effect on co-gasification reactivity from the co-pyrolysis of rice straw and coal is weakened with the increase of rice straw proportion and gasification temperature. Wang et al. [16] observed that the co-pyrolysis of seaweed polysaccharides and cellulose can increase the number of molecular fragments, conversion rate and gas production rate at middle temperature range by comparing the experimental and simulation results. Hu et al. [17] studied the co-pyrolysis of waste biomass with petroleum sludge by a response surface methodology. The results suggest that the yields of oil and char increases with the growth of the sawdust percentage in feedstock. Several researchers have found that the addition of biomass can change the atmosphere during pyrolysis process and promote tar decomposition [1,18,19]. More and more experts have focused on exposing the effect of heating rate and additives on co-pyrolysis process to improve the efficiency of pyrolysis reaction and the quality of products. The co-pyrolysis process of paper sludge and municipal solid waste at different heating rates indicates that the peak height and the temperature of maximum weight loss increase with the increase of heating

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rates [20]. The catalytic effect of additives (MgO, Al₂O₃ and ZnO) is not obvious for the co-pyrolysis process with the increase of the proportion of paper sludge [21].

In industrial applications, bituminous coal, as a low quality solid fuel, is mainly used to produce refined fuels and chemicals through pyrolysis and gasification. The utilization of bituminous coal is concerned because of the environmental impacts caused by the emission of toxic gases and the fused-ash slagging formed inside the reaction equipment. To reduce environmental impact and fossil fuel usage, bio-oil distillation residue with a little ash is a renewable energy resource as a replacement for coal [22]. Furthermore, the interaction of lower grade fuels during co-pyrolysis process has an effect on the production of refined fuels and renewable chemical compounds [1,23,24]. However, there are few reports on the co-pyrolysis synergistic effects of bio-oil distillation residue and bituminous coal. To better understand the co-pyrolysis synergistic effects which may be useful for the design and the operation of the co-pyrolysis system to improve the quality and yield of products, and the comprehensive utilization of bio-oil distillation residue and bituminous coal, it is very necessary to study thermal behavior during co-pyrolysis process.

In this work, the co-pyrolysis behaviors of bio-oil distillation residue and bituminous coal were investigated via thermogravimetric analysis under N₂ atmosphere. Gas volatiles were quantitatively analyzed by FTIR peak area. At the same time, kinetics parameters were calculated by Flynn-Wall-Ozawa method and Coats-Redfern integration method with non-integer reaction order. What's more, relevant pyrolysis mechanisms were also analyzed on basis of the above. The results discussed in this paper would provide valuable information for the modelling, design, and operation of thermochemical conversion processes of bio-oil distillation residue and bituminous coal.

2. Methods

2.1. Materials

The bio-oil distillation residue (R100C0) used in this study was obtained from Anhui Province Key Laboratory of Biomass Clean Energy, University of Science and Technology of China. Moreover, the bituminous coal (R0C100) in this study was collected from Shenfu coal mine (Shannxi Province, China). Prior to use, the raw materials were dried at 80 °C for 48 h, and then milled and sieved to obtain the desired particle size less than 178 μm. Several binary mixtures were prepared by adding bituminous coal to bio-oil distillation residue at weight ratios of 20%, 40%, 60% and 80%, so corresponding samples were named as R80C20, R60C40, R40C60 and R20C80, respectively.

2.2. Analytical method

In this paper, the ultimate analysis and the heating values of raw materials in Table 1 were carried out by respectively using the Vario EL III cube elemental analyzer and the bomb calorimeter (XRY-1B). What's more, the proximate analysis (GB/T 28731–2012) was listed in Table 1. R100C0 showed higher volatiles than R0C100 but possessed the lower content of fixed carbon and ash.

Pyrolysis experiments took advantage of thermogravimetric

analyzer (TGA Q500) coupled with FTIR spectrophotometer (Nicolet 6700) in the range of 400–4000 cm⁻¹ (wavenumber) with the resolution factor 4 cm⁻¹. The samples were performed from room temperature to 750 °C under nitrogen atmosphere with a flow rate of 60 ml/min at the heating rate of 10, 20 and 30 °C/min. FTIR was connected to TGA by gas transmission pipelines and gas cell which were preheated to 200 °C. For each test, the initial weight of all samples was about 5 mg. All experiments were carried out and analyzed three times to ensure the reproducibility of results. By analyzing the experimental data, the standard error was about 0.2%.

2.3. Kinetic method

The activation energy involving the thermal degradation mechanism is considered as the minimum energy of chemical reaction. The Coats-Redfern (C-R) method [25,26] and Flynn-Wall-Ozawa (FWO) method [20,21] were concerned to calculate the values of activation energy during the pyrolysis process. The Coats-Redfern formula can be generally described as follows:

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad n \neq 1 \quad (1)$$

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad n = 1 \quad (2)$$

The FWO method is expressed as:

$$\ln(\beta) = \ln \left[\frac{AE\alpha}{Rg(\alpha)} \right] - 5.331 - \frac{E\alpha}{RT} \quad (3)$$

Where β means heating rate (K/min); E is activation energy (kJ/mol); A implies frequency factor (s⁻¹); T represents absolute temperature (K); R is universal gas constant [J/(mol*K)]. α can be calculated by the following equation on basis of thermogravimetric curve.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (4)$$

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

The mentioned equations of (1), (2) and (3) can result in a straight line with a slope E/R and an intercept. Activation energy E and frequency factor A can be calculated from the slope and intercept of line, respectively.

3. Results and discussion

3.1. Thermogravimetric analysis

3.1.1. Individual samples

Thermogravimetric data (TG) curves and first derivative data (DTG) curves in Fig. 1 showed the distinct difference between the thermal behaviors of R100C0 and R0C100. A noteworthy mass loss in a narrow temperature range distinguished R100C0 and R0C100 into three individual stages through TG tangent method. From the two TG curves, the first mass loss peak below 150 °C corresponded with the release of moisture and a very low quantity of volatiles. For R100C0, the main

Table 1
Proximate and ultimate analyses of bio-oil distillation residue and bituminous coal.

Samples	Proximate analysis $w_{ad}/\%$				Ultimate analysis $w_{ad}/\%$					HHV/MJ kg ⁻¹
	M	A	V	FC ^a	C	H	O	N	S	
R100C0	1.00	0.50	72.90	25.60	74.00	6.21	18.25	1.45	0.48	29.12
R0C100	2.06	9.34	34.08	54.52	64.99	3.97	24.70	0.89	1.46	29.30

^a Calculated by difference; M: moisture; A: ash; V: volatiles; FC: fixed carbon.

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