Kinetics of coffee industrial residue pyrolysis using distributed activation energy model and components separation of bio-oil by sequencing temperature-raising pyrolysis

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HIGHLIGHTS

- DAEM is used to study the kinetics of coffee industrial residue.
- Sequencing temperature-raising pyrolysis (new method) is used.
- A solution of components separation of bio-oil was put forward.

ARTICLE INFO

ABSTRACT

This study was carried out to investigate the kinetics of coffee industrial residue (CIR) pyrolysis, the effect of pyrolysis factors on yield of bio-oil component and components separation of bio-oil. The kinetics of CIR pyrolysis was analyzed using distributed activation energy model (DAEM), based on the experiments in thermogravimetric analyzer (TGA), and it indicated that the average of activation energy (E) is 187.86 kJ·mol^{-1}. The bio-oils were prepared from CIR pyrolysis in vacuum tube furnace, and its components were determined by gas chromatography/mass spectrometry (GC–MS). Among pyrolysis factors, pyrolysis temperature is the most influential factor on components yield of bio-oil, directly concerned with the volatilization and yield of components (palmitic acid, linoleic acid, oleic acid, octadecanoic acid and caffeine). Furthermore, a new method (sequencing temperature-raising pyrolysis) was put forward and applied to the components separation of bio-oil. Based on experiments, a solution of components separation of bio-oil was come out.

1. Introduction

Biomass is a clean and renewable energy source leading to environmental, technical and economical benefits. With the concern of environmental protection, the energetic recovery of biomass via pyrolysis, gasification or combustion has attracted increasing worldwide interest. The pyrolysis is a thermal decomposition process producing char with ash content, volatiles and low molecular weight gases. Without char and volatiles oxidation or less, it's the better way to recycle energy from biomass (e.g. microalgae, wood, straw and coffee waste) (White et al., 2011; Bridgwater, 2012; Collard and Blin, 2014).

Coffee is considered as the second largest traded commodity in the world. Coffee plants are cultivated in over 70 countries with an average annual production of 8 million tons in the world (ICO, 2014). Coffee industrial residue (CIR) is the by-product from instant coffee manufacturing process, left behind at the factory. By the statistics, instant coffee production consumes around 20% of the global production of green coffee beans (Gonzalez et al., 2013) and for each kilogram of instant coffee produced 0.91 kg of CIR (Silva et al., 1998). In addition, the CIR contains great amounts of organic compounds (i.e. fatty acids, lignin, cellulose, hemicellulose and other polysaccharides) (Pujol et al., 2013), while its comprehensive utilization has become a new study in recent years. For example, CIR has been investigated for biodiesel production (Gonzalez et al., 2013; Kwon et al., 2013), as production of activated carbon (Tsai et al., 2012; Ma and Ouyang, 2013; Tehrani et al., 2015), as source of sugars (Passos et al., 2014) or raw material of fatty acids (Cruz et al., 2014).

Thermogravimetric analysis is one of the most common techniques used to investigate the thermal behavior of small samples

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(Zhao et al., 2012). Thermogravimetry of CIR pyrolysis has been studied by several researchers (Skreiberg et al., 2011; Bok et al., 2012; Li et al., 2014), but the kinetics of CIR pyrolysis has not been investigated. Kinetics is a theoretical analysis to obtain reaction laws (e.g. activation energy and frequency factor), based on thermogravimetric analysis. Numerous kinetic models have been developed, such as single-step global reaction model, multiple-step model, semi-global model, and distributed activation energy model (DAEM) (Soria-Verdugo et al., 2013). Among these models, DAEM is considered as an accurate and versatile approach to model the pyrolysis process (Cai et al., 2014). Therefore, DAEM was used to study the kinetics of CIR pyrolysis.

Bio-oil is one of products from biomass pyrolysis, and its yield and components are influenced by pyrolysis condition (Bridgwater, 2012). The conventional separation technology of bio-oil components includes solvent extraction, column chromatography and distillation. Solvent extraction is a method which uses specific solvent to dissolve target components of a mixture of components. Column chromatography commonly utilizes silica gel and aluminum oxide as the stationary phase, where the mobile phase is selected according to the polarity of bio-oil components. Distillation separates bio-oil components according to their different volatilities (Kim, 2015). In this study, a new method of bio-oil components separation (sequencing temperature-raising pyrolysis) is put forward and used.

This paper presents a study about kinetics of CIR pyrolysis and components separation of bio-oil. First of all, the pyrolysis of grounded CIR was carried out in thermogravimetric analyzer at nitrogen atmosphere, with different heating rates. The thermogravimetric analysis and kinetic analysis using DAEM of CIR pyrolysis were studied. Moreover, the bio-oils were prepared from CIR pyrolysis in vacuum tube furnace on different pyrolysis conditions. The effects of pyrolysis factor (pyrolysis temperature, time, pressure and heating rate) on yield of bio-oil component were researched by gas chromatography/mass spectrometry (GC–MS). Finally, the bio-oil components were separated by sequencing temperature-raising pyrolysis, and the absolute yield of components in separation liquid were estimated. Those results would make a contribution on the understanding of CIR pyrolysis, especially the utilization of bio-oil.

2. Materials and methods

2.1. Materials

The coffee industrial residue (CIR) used for this study was collected from a coffee processing plant in Dongguan, Guangdong province, China. The original sample was oven-dried at 105 °C for 24 h and then became the sample of experiments in vacuum tube furnace. Dried CIR was grounded with a micromill (Yili QE-300, China) to pass through a 150 μm sieve, taken as the sample for characterization and thermalgravimetric analyzer. According to proximate analysis, CIR (dry basis) includes 6.98 wt.% of moisture, 64.94 wt.% of volatile, 21.03 wt.% of fixed carbon and 7.05 wt.% of ash. The result of ultimate analysis showed that CIR (dry basis) includes 46.62 wt.% of C, 8.87 wt.% of H, 23.90 wt.% of O, 5.64 wt.% of N and 0.94 wt.% of S. And the higher heating value of CIR (dry basis) is 21.3 MJ kg^{-1}.

2.2. Characterization of materials

2.2.1. Proximate analysis

The moisture analysis was conducted according to DD CEN/TS 14774-3: 2004, which heats solid samples at 150 ± 2 °C in air dry oven for determination of moisture content. The ash content was determined according to DD CEN/TS 14775: 2004, which heats solid samples to 550 ± 10 °C in muffle furnace with temperature programming for determination of ash content. The volatile content was analyzed according to DD CEN/TS 15148: 2005, which heats solid samples at 900 ± 10 °C for 7 min in muffle furnace for determination of volatile content. The fixed carbon was calculated using Eq. (1).

$$FC = 100\% - V - A - M \tag{1}$$

where FC, V, A and M are the content (wt.%) of fixed carbon, volatile, ash and moisture, respectively.

2.2.2. Ultimate analysis

The C, H, N and S contents in the sample were measured using an elemental analyzer (Perkin Elmer Series II 2400, USA). The O content was calculated using Eq. (2).

$$O = 100\% - C - H - N - S - A - M \tag{2}$$

where O, C, H, N, S, A and M are the content (wt.%) of O, C, H, N, S, ash and moisture, respectively.

2.2.3. Heating value

The higher heating value (HHV) was determined by an isothermal-jacket bomb calorimeter (SHR-15, China).

2.3. Thermogravimetric analysis

The experiments were carried out in a thermalgravimetric analyzer (Henven HCT-3, China). Pyrolysis was performed under a carrier gas flow (nitrogen) of 30 mL min^{-1}, with a sample mass of approximately 10 mg, which was heated up to 800 °C at heating rates of 5, 10, 15, 20, 25 and 30 °C·min^{-1}.

2.4. Kinetic analysis using DAEM

The distributed activation energy model (DAEM) is originally developed by Vand (1943). It has been widely applied to analyze the complex reactions in the pyrolysis of biomass (Wang et al., 2008; Shen et al., 2011), which assumes that a number of parallel, irreversible and first-order reactions with different energies occur simultaneously.

When the model is used to analyze biomass, the DAEM is expressed as (Sonobe and Worasuwannarak, 2008):

$$1 - \frac{V}{V^*} = \int_0^\infty \exp\left(-k_0 \int_0^t e^{-\frac{E}{RT}} dt\right) f(E) dE \tag{3}$$

where V is the total volatile content at temperature T, V^* is the effective volatile content of the biomass, t is against time, E is the activation energy, $f(E)$ is the normalized distribution curve of the activation energy of many reactions, and k_0 is the frequency factor corresponding to the E value, R is gas constant (8.314 J mol^{-1} K^{-1}). Eq. (3) was simplified to Eq. (4) (Miura, 1995; Miura and Maki, 1998).

$$\frac{V}{V^*} = 1 - \int_{E_S}^\infty f(E) dE = \int_0^{E_S} f(E) dE \tag{4}$$

In this simplified model, the Arrhenius equation can be described as follows (Andon et al., 2002; Munir et al., 2009):

$$\ln\left(\frac{\alpha}{T^2}\right) = \ln\left(\frac{k_0 R}{E}\right) + 0.6075 - \frac{E}{R} \cdot \frac{1}{T} \tag{5}$$

where α is the heating rate of pyrolysis, k_0 is the frequency factor. Using Eq. (5), we can estimate both E and k_0 from the Arrhenius plot of $\ln(\alpha/T^2)$ vs. $1/T$ at the selected V/V^* values for different α values.