



Co-pyrolysis kinetics and behaviors of kitchen waste and chlorella vulgaris using thermogravimetric analyzer and fixed bed reactor

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ABSTRACT

Co-pyrolysis of CV and KW under CO₂ atmosphere were studied in this paper. The pyrolysis characteristics were investigated by thermogravimetric analysis and the kinetic parameters were calculated by Ozawa-Flynn-Wall and the Kissinger-Akahira-Sunose methods. Results showed that with the increase of mixing degree, the averaged apparent activation energy (E_{ave}) increased evidently, the 50%CV50%KW sample showed the highest E_{ave} (234.43 kJ/mol (OFW) and 228.21 kJ/mol (KAS)). Yields of liquid, solid and gas at different pyrolysis temperature and blends were obtained by a lab-scale fixed bed reactor. Both KW and CV had the highest bio-oil yield at 600 °C in the range of 500–700 °C. Mixing KW and CV deteriorated the bio-oil yield but improved higher heating value of the bio-oil product (33.9 MJ/kg at 600 °C in 5:5 ratios). The gas chromatography-mass spectrometry analysis of bio-oil product further found that co-pyrolysis of CV and KW could decrease carboxylic acids and increased hydrocarbons of bio-oil products. In brief, co-pyrolysis of CV and KW could be a potential way for improving quality and calorific value of pyrolysis oil.

1. Introduction

In current years, the research of bio-energy has attracted widespread attention. Liquefaction for renewable energy is one of the promising trends [1–3]. *Chlorella vulgaris* (CV) is a favorable feedstock for bio-oil production. Compared to the first-generation sustainable energy source made from edible oils and the second-generation from non-edible oil crops or animal fats, the third-generation sustainable energy source, derived from microalgae, possess numerous advantage: high photosynthetic efficiency, high oil content, good for CO₂ fixation, easier to cultivate, less land occupation, non-selective growth condition and exponential growth rates [4–6]. Kitchen waste (KW) is also a promising feedstock for bio-oil production. KW, taken up approximately 51% of municipal solid waste in China, usually refers to waste produced during food processing and kitchen activity, such as the leftovers, leaves, peel, flesh, eggshell and shell [7]. To cater increasingly stringent policy of garbage classification, the treatment for sole kitchen waste is developing quickly. The disposal methods, such as land-filling and discharge into water environmental system are harmful to the environment and have gradually been replaced by composting or thermal treatment. The merit of thermal treatment is that they can decompose its organic fractions into useful fuel and convert inorganic fractions into steady

cinders, with an apparent reduction of volume and quantity as well. As one of the thermal treatment, pyrolysis was defined as thermal decomposition of matters in the absence of oxygen [8]. Its pollution control is simplified, compared to direct combustion. Moreover, pyrolysis is less time-consuming and applied using smaller infrastructure footprint [9]. Hence, pyrolysis of kitchen waste can be significant.

Numerous previous researches have concentrated on the co-pyrolysis of biomass or waste, since co-pyrolysis could change pyrolysis behavior and influent the pyrolysis products easily. Tang et al. [10] found that co-pyrolysis of organic food waste and polyvinyl chloride accelerated the reaction, reduced tar, increased char and suppressed the formation of most N-containing components in tar. Fang et al. [11] investigated co-pyrolysis of combustible solid waste (CSW) and paper mill sludge (PMS), finding that 10%PMS with 90%CSW obtained the highest percentage alcohol in products, and adding 50% of PMS into CSW reduced the emission of gas pollutants. Zhang et al. [12] studied catalytic fast co-pyrolysis of corn stalk and food waste to produce aromatics, experimental results showed that there were apparent synergistic effects between biomass and food waste, which improved the production of aromatics significantly and other petrochemicals. In brief, unitary pyrolysis of biomass can merely manufacture a low yield of bio-products but a high yield of unwanted coke. Co-pyrolysis method

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can help this situation, increase quantity and quality of bio-oil, bio-char and high calorific value of gas [13]. Researches available mainly focus on co-pyrolysis of lignocellulosic biomass with food waste or biomass with plastic waste; still co-pyrolysis of CV and KW is limited in existing literature. Since both CV and KW are promising feedstock for bio-fuels and have their own typical compositions, this work tried to discuss co-pyrolysis of CV and KW in order to find out possible interactions between them.

On the other hand, the emission of carbon dioxides (CO₂) are getting aggravated due to human activities in the last several decades. Many researches had focused on carbon capture and storage (CCS) [14,15]. Less attention is paid to the utilization of CO₂. Since the power plant is the largest CO₂ emission industry at present, the utilization of CO₂ in thermal treatment process become a necessary. Compared with those using usual N₂ gas in pyrolysis process, utilizing CO₂ as carrier gas in pyrolysis process also works well [16,17]. Chen and Lin [18] found that the liquid yield of oil palm fiber pyrolysis was higher when in CO₂ atmosphere than that in N₂ atmosphere, and the impact of carrier gas type (CO₂ versus N₂) on components in bio-oils was not obvious. Zhang et al. [19] implemented microwave-induced catalytic fast pyrolysis of medicinal herb residue in different pure atmosphere, and the results showed that the hydrocarbon relative contents in bio-oil of the four reaction atmospheres follow the order of CO > CO₂ > H₂ ≈ N₂. Pyrolysis of herb residues for bio-oil formation under CO₂ atmosphere turns out to be reasonable. Other research also found that co-pyrolysis of chlorella and tire under CO₂ atmosphere could obtain more aromatic hydrocarbons in liquid products, compared to those in N₂ atmosphere [20]. As mentioned in previous literature, pyrolysis of biomass or waste under CO₂ atmosphere showed an acceptable performance. Hence co-pyrolysis of CV and KW, two promising raw feedstocks, under CO₂ atmosphere would well be worth studying.

In this work, we fundamentally investigated the co-pyrolysis of CV and KW under CO₂ atmosphere. Pyrolysis behaviors and kinetics analysis of CV, KW and their blends, and the quality of its bio-oil were discussed. In the future work, the interactions between CV and KW by using catalytic pyrolysis, flash pyrolysis and different pyrolytic atmosphere will be inquired.

2. Materials and methods

2.1. Materials

The chlorella vulgaris (CV) was purchased from Shaanxi SCIPHAR Natural Products Co. Ltd (China) online in powder form (particle size < 178 μm). After air-forced dried at 90 °C until the weight was steady, the chlorella powder was stored in desiccator. The kitchen waste (KW) was collected from cafeterias in South China University of Technology (Guangdong province, China). It was air-dried at 105 °C for 24 h to deprive moisture, next crushed and ground to powder of 80 meshes, keeping in a desiccator for further use.

The moisture, ash and volatile content of samples were obtained using a muffle furnace according to GB/T 28731-2012. The elemental proportion (C, N, H, S) of samples was measured by Vario El Cube Elemental Analyzer (Elementar Co., Ltd, German). The higher heating value (HHV) was measured by Oxygen bomb calorimeter. All the tests were done in triplicate. The sample characteristics are listed in Table 1.

2.2. Experimental apparatus and methods

The decomposition behavior of samples was studied by the thermogravimetric simultaneous thermal analyzer (METTLER TOLEDO TGA/DSC1), whose temperature precision is ± 0.5 °C and microbalance sensitivity is less than ± 0.1 μg. The samples were mixture of CV and KW in 5 different degrees. The CV mass proportion was 0%, 20%, 50%, 80% and 100%, respectively. 5 ± 0.1 mg of each sample was placed in a quartz crucible heated from room temperature (22 ± 1 °C) to 105 °C

Table 1
Ultimate and proximate analyses, HHV, H/C and O/C of CV and KW.

Samples		CV	KW
Ultimate analyses (wt.%, dry basis)	C	46.82 ± 0.34	45.15 ± 0.03
	H	8.63 ± 0.07	8.57 ± 0.03
	O ^a	32.03 ± 0.35	36.31 ± 0.07
	N	11.05 ± 0.08	1.53 ± 0.03
	S	0.29 ± 0.03	0.00 ± 0.00
Proximate analyses (wt.%, dry basis)	Moisture	1.98 ± 0.13	2.47 ± 0.12
	Volatiles	77.23 ± 0.14	80.27 ± 0.22
	Fixed Carbon ^b	12.35 ± 0.19	16.07 ± 0.22
	Ash	8.44 ± 0.02	1.19 ± 0.12
	HHV(MJ/kg)	22.82 ± 0.044	18.74 ± 0.040
	H/C ^c	2.21	2.28
	O/C ^c	0.51	0.60

^a Calculated by difference (O = 100-C-H-N-S-Ash).

^b Calculated by difference (fixed carbon = 100-moisture-ash-volatiles).

^c Molar ratio.

and kept at 105 °C for 10 min to deprive its moisture; after that, it was heated to 800 °C under different heating rates. The heating rate of 30, 40, 50 °C/min were carried out in this study. High purity carbon dioxide atmosphere (purity > 99.9 vol%) at a flow rate of 80 ml/min was used.

Another co-pyrolysis experiment was carried out in a lab scale fixed bed reactor, whose apparatus was connected as shown in Fig. 1. The experimental process was as following: the chamber was replenished with carbon dioxide (purity > 99.9 vol%) continuously at a flow rate of 666.7 ml/min for 30 min beforehand, in order to vent original gas inside the chamber. When the tube reactor was heated to the desired temperature (500 °C, 550 °C, 600 °C, 650 °C and 700 °C), a sample of 5 ± 0.01 g in a quartz boat was pushed into the reactor instantly. After reactions for 25 min, the fixed bed reactor was turned off and air-cooled with uninterrupted carrier gas until the entire units reached room temperature. The collected bio-oil product was kept in a refrigerator for further use. The solid residue, bio-oil and gas yield were calculated by using Eqs. (1)–(3):

$$Y_{res} \text{ (wt. \%)} = \frac{\text{weight of residual (g)}}{5 \text{ (g)}} \times 100\% \quad (1)$$

$$Y_{liq} \text{ (wt. \%)} = \frac{\text{weight of liquid (g)}}{5 \text{ (g)}} \times 100\% \quad (2)$$

$$Y_{gas} \text{ (wt. \%)} = \frac{5 \text{ (g)} - \text{weight of residual (g)} - \text{weight of liquid (g)}}{5 \text{ (g)}} \times 100\% \quad (3)$$

where Y_{res} , Y_{liq} and Y_{gas} represent the yield of residue, bio-oil and gas products, respectively.

HHV of bio-oils was estimated by oxygen bomb calorimeter with thermostat control (TE-C610, Changsha Titen Electronic Co., Ltd, China), whose heat capacity repeatability was less than 0.15% and calorific value error was below 50 J/g.

The organic components of bio-oils were analyzed by the Gas Chromatography-Mass Spectrometry (GC-MS) (Agilent 7890B&5977A). The metal capillary column (type: HP-5 ms, 30 m × 0.25 mm ID × 0.25 μm) temperature was set from 50 °C (kept for 1 min) to 290 °C (kept for 5 min), at a heating rate of 10 °C/min. The scan range of the quadrupole mass spectrometer was between 33 and 500. The compounds were identified by NIST library and relevant literature.

2.3. Kinetic models

In this work, the Ozawa-Flynn-Wall (OFW) method and the Kissinger-Akahira-Sunose (KAS) method were used to calculate the apparent activation energy with three different heating rates, as

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