Energy Conversion and Management 168 (2018) 178–187

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

# Comprehensive study on pyrolysis and co-pyrolysis of walnut shell and bio-oil distillation residue

Xiefei Zhu, Yiming Zhang, Haozhi Ding, Lingrui Huang, Xifeng Zhu*

*University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China*

ARTICLE INFO

*Keywords:*
Co-pyrolysis
Synergistic effect
Gaseous products
Reaction model
Kinetics

ABSTRACT

In this study, the pyrolysis and co-pyrolysis characteristics of walnut shell and bio-oil distillation residue were investigated by means of thermogravimetric analysis followed by Fourier transform infrared spectrophotometer (TGA-FTIR). Multiple reaction models were employed to fit individual pyrolysis experiment of walnut shell and bio-oil distillation residue to find the optimal model for further analysis of co-pyrolysis. The results showed that the pyrolysis behavior of bio-oil distillation residue was different from that of walnut shell. Compared to the pyrolysis of walnut shell, bio-oil distillation residue retained more biochar and a relatively lower rate of mass loss. However, the best fitting models for walnut shell and bio-oil distillation residue were all five-reaction model through comparing the fitting effect and the component complexity. Moreover, five-reaction model was introduced to analyze the co-pyrolysis of walnut shell and bio-oil distillation residue, indicating that the co-pyrolysis had good adaptability to five-reaction model. The thermal degradation of the co-pyrolysis shoulder and spike peaks could be accurately predicted. In addition, the gas products of bio-oil distillation residue and walnut shell had the same absorption band by infrared spectroscopy, indicating that the pyrolysis of two raw materials had similar products while the different absorption intensities represented different concentrations of gas products. Based on Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods, as the proportion of walnut shell in blend sample increased, the average activation energy gradually increased except for the pure walnut shell.

## 1. Introduction

In order to cope with environmental pollution and achieve the goal of sustainable development, the production of renewable energy has attracted more and more attention. Among them, solid biomass, a very important renewable resource, can be used to produce energy products and chemicals (bio-oil, biochar and syngas) through rapid pyrolysis technology [1–3]. However, crude bio-oil, as the main product of biomass pyrolysis, is a typical low-quality fuel which cannot be directly applied to automobiles [4–6]. Thereby, bio-oil atmospheric distillation, one of the technologies to improve the quality of bio-oil, is often employed to upgrade bio-oil due to its economy and easy operation [7,8]. Simultaneously, about 20–50% of bio-oil distillation residue would be retained at the bottom of instrument [9,10].

Bio-oil distillation residue is a by-product produced during the process of upgrading bio-oil, which cannot be used directly. Simultaneously, particulate bio-oil distillation residue has an unpleasant odor which causes environmental pollution. Therefore, the rational processing of bio-oil distillation residue could effectively reduce environmental problem and improve the comprehensive utilization of bio-oil and the efficiency of biomass pyrolysis. At present, many scholars take advantage of bio-oil distillation residue as raw materials to extract chemical components such as pyrolysis lignin, phenols and sugars [11,12]. Although methanol-water, water extraction, and the combination of extraction, heat treatment and column chromatography, etc., can reach the purpose of extracting chemicals, these methods also bring some pollution and waste of chemical reagents. In addition, since bio-oil distillation residue contains a large amount of carbon components, bio-oil distillation residue could be directly converted to biochar by heating under different atmospheres [13,14].

In comparison to these methods, the solid co-pyrolysis technique may be one of the more promising ways for dealing with bio-oil distillation residue because it is almost the same as pyrolysis. Presently, co-pyrolysis technology has been applied to the treatment of scrap tire [15–17], municipal solid waste [18], paper sludge [19,20] and petroleum sludge [21]. Meanwhile, Jin et al. [22] studied the effect of plastics on pyrolysis products through the co-pyrolysis of lignin and

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* Corresponding author at: Department of Thermal Science and Energy Engineering, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China.
*E-mail address:* xfzhu@ustc.edu.cn (X. Zhu).

https://doi.org/10.1016/j.enconman.2018.05.012
Received 26 March 2018; Received in revised form 24 April 2018; Accepted 4 May 2018

three different plastics (low density polyethylene, polycarbonate and polystyrene). The results revealed that the strong interaction affecting product distribution existed between lignin and plastics, while the water produced by lignin decomposition at low temperature could promote the hydrolytic reaction of plastic and the release of carbon dioxide. Wang et al. [23] investigated the co-pyrolysis mechanism between seaweed polysaccharides and cellulose through macroscopic experiments and molecular simulations, indicating that co-pyrolysis was conductive to increase molecular fragments, conversion rate and the rate of gas production. Hua et al. [24] found obvious positive effects during the co-pyrolysis of sugarcane bagasse and Enteromorpha prolifera. Compared to the individual pyrolysis of the raw materials, the co-pyrolysis could reduce the acidity of bio-oil while increasing the calorific value of bio-oil. Co-pyrolysis technology is beneficial to improve the distribution and quality of pyrolysis products.

What's more, the co-pyrolysis of biomass and various fuels has also been widely studied. Typically, the co-pyrolysis of pine sawdust and lignite was explored using a thermogravimetric analyzer combined with a fixed bed reactor [25]. Moreover, Song et al. [26] analyzed the co-pyrolysis behavior and product composition of heavy oil and low-rank coal. The synergistic effect and hydrogen donation redistributed co-pyrolysis products to increase the yield of pyrolysis tar and drastically reduce carbon monoxide. Wu et al. [27] also observed the synergistic effect between the model components of lignocellulosic biomass and bituminous coal during co-pyrolysis. The synergistic effect in co-pyrolysis process is generally due to the fact that different materials has different hydrogen-carbon ratios, and the materials with higher hydrogen-carbon ratios could be used as effective hydrogen donors [23]. Meanwhile, the different inorganic metal contained in material ash is a catalyst in the co-pyrolysis process, which could affect the formation of pyrolysis products [28]. In addition, the structure of different materials also affects the co-pyrolysis effect between the materials [27,29].

Although bio-oil distillation residue cannot be used directly, it could be considered as a special biomass material. It is a novel idea to use bio-oil distillation residue for mixing some other raw materials for co-pyrolysis to produce new fuels and chemicals. Additionally, the bio-oil distillation residue selected in this study is derived from the bio-oil produced by pyrolysis of walnut shell. In order to improve the overall pyrolysis efficiency of walnut shell, and to rationally use distillation residue to reduce environmental pollution, the co-pyrolysis of walnut shell and bio-oil distillation residue was proposed. Moreover, the co-pyrolysis of bio-oil distillation residue and walnut shell may be an effective way to improve the individual pyrolysis of walnut shell and bio-oil distillation residue. The co-pyrolysis products of walnut shell and bio-oil distillation residue may be more concentrated relative to co-pyrolysis with other materials because bio-oil distillation residue is derived from walnut shell bio-oil. Additionally, the co-pyrolysis of walnut shell and distillation residue derived its bio-oil may provide certain theoretical support for the design and construction of a complete set of system equipment for biomass pyrolysis, bio-oil upgrading, and residue re-use. Therefore, it is very important to comprehensively study the co-pyrolysis of bio-oil distillation residue and walnut shell to reveal the relevant pyrolysis mechanism and interaction effects.

In this study, the co-pyrolysis characteristics of bio-oil distillation residue and walnut shell at various mixing ratio were investigated through thermogravimetric analysis under nitrogen atmosphere. Meanwhile, using Gaussian deconvolution, the optimal reaction models of separation peak of bio-oil distillation residue and walnut shell were explored to predict the approximate composition of raw materials. At the same time, the pseudo-components of the blend samples at different ratios were compared through the optimal reaction model in the co-pyrolysis process. And volatile gases in the co-pyrolysis process were detected by the infrared. Moreover, activation energy was calculated through two different kinetic analysis methods (FWO and KAS methods). Based on the above, the corresponding pyrolysis mechanism and interaction effect were revealed. The results of this study demonstrated a comprehensive study of the co-pyrolysis of bio-oil distillation residue and walnut shell, which may contribute to the design and construction of biomass pyrolysis systems coupled with bio-oil upgrading and bio-oil residue re-use.

## 2. Methods

### 2.1. Materials

Walnut shell (D0W100) used in this study was collected from a local plant of walnut production in Anhui. In addition, bio-oil distillation residue (D100W0) was a by-product obtained during the atmospheric distillation of bio-oil to extract light fraction and the distillation temperature was 120 °C, while bio-oil was produced through the pyrolysis of walnut shell using a self-made pyrolysis instrument from University of Science and Technology of China. Prior to use, walnut shell and bio-oil distillation residue were milled and sieved through 50 and 80 mesh sieves. Then, these desired particles were dried at 90 °C for 24 h. After that, several binary blend samples of bio-oil distillation residue and walnut shell were prepared by mechanical mixing. The mass percentages of walnut shell in the blend samples were 25%, 50% and 75%, and the corresponding blend samples were labeled as D75W25, D50W50, D25W75, respectively.

### 2.2. Analytical method

In the study, the proximate analysis and ultimate analysis of bio-oil distillation residue and walnut shell were performed according to GB/T 28731-2012 and the Vario EL III cube elemental analyzer, respectively. The corresponding results were given in Table 1. Compared with the walnut shell, bio-oil distillation residue had more C and less O elements. This may be due to the fact that more oxygen-containing functional groups were separated during the process of pyrolysis and atmospheric distillation. Simultaneously, N and S elements were enriched in the bio-oil distillation residue. Moreover, bio-oil distillation residue had less ash and less volatile than walnut shell. The component analysis of walnut shell was conducted according to GB/T 2677.9-94. And the cellulose, hemicellulose, lignin, and extractives (alcohol/benzene) were 26.03%, 21.16%, 49.57%, and 2.52%, respectively.

A series of pyrolysis experiments were performed through thermogravimetric analyzer (TGA Q500) coupled with FT-IR spectrophotometer (Nicolet 6700) from room temperature to 750 °C. The range of infrared spectrum was 4000–500 $cm^{-1}$ wavenumber with a resolution of 4 $cm^{-1}$. And all experiments were conducted under nitrogen atmosphere with a flow rate of 100 ml/min. For each test, the sample weight was about 10 mg. Meanwhile, the heating rates of pyrolysis experiments were 10, 20, 30 °C/min. Each experiment was carried out in triplicates to ensure the accuracy and repeatability of results. And the standard deviation of the experiments was within 1%.

### 2.3. Kinetic method

In order to further investigate the pyrolysis characteristics of bio-oil distillation residue, walnut shell and their mixtures, Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods were employed for the analysis of pyrolysis kinetics [30–32]. The formulas for the FWO

**Table 1**
Proximate and ultimate analyses of bio-oil distillation residue and walnut shell.

| Samples | Proximate analysis $w_{ad}$/% | | | | Ultimate analysis $w_{ad}$/% | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | M | A | V | FC[a] | C | H | O[a] | N | S |
| D100W0 | 1.19 | 0.52 | 71.94 | 26.35 | 72.72 | 6.21 | 18.92 | 1.32 | 0.31 |
| D0W100 | 1.06 | 2.36 | 74.53 | 22.05 | 61.09 | 6.42 | 29.81 | 0.16 | 0.16 |

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