



# Comparative study on the evolution of physicochemical characteristics of biochar produced from bio-oil distillation residue under different induction atmosphere

Xiefei Zhu, Kai Li\*, Liqiang Zhang, Xing Wu, Xifeng Zhu\*

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

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## ABSTRACT

In the study, biochar was easily produced from bio-oil distillation residue through a tube furnace at a broad induction temperature range of 200–700 °C under nitrogen and carbon dioxide. The comparative evolution of biochar was characterized by evaluating its physicochemical properties including elements, calorific values, functional groups, graphitization degree and thermal stability. The results showed that compared with nitrogen atmosphere, carbon dioxide first contributed to biochar yield. After 600 °C, biochar yield in carbon dioxide dropped rapidly, while nitrogen had little effect on biochar yield. Through bomb calorimeter, the maximum calorific value of biochar was 34.13 MJ·kg<sup>-1</sup> at 200 °C under carbon dioxide. Based on elements analysis, O/C, H/C and N/C of biochar induced by nitrogen were higher than those of carbon dioxide. Fourier transform infrared spectrometry (FTIR) indicated that induction temperature and atmosphere selectively affected the evolution of biochar functional groups. C=O stretching vibration in carbon dioxide was more durable than that in nitrogen, whereas the stretching vibration of –CH<sub>2</sub> and C–C had opposite phenomenon. In addition to 200 °C, the biochar under nitrogen possessed less graphitization with temperature increasing by Raman spectra analysis. Furthermore, the biochar induced by nitrogen was more stable than that induced by carbon dioxide according to the thermogravimetric analysis.

## 1. Introduction

With the growth of petroleum consumption and the depletion of fossil resources, bio-oil derived from biomass pyrolysis is considered one of the best alternatives to petroleum because it can be used as raw materials for the production of fuels and chemicals. Moreover, bio-oil is a renewable and carbon dioxide neutral substance that is environmentally friendly [1,2]. Unfortunately, bio-oil has many shortcomings that seriously hinder its applications, such as low calorific value, high acidity, high corrosiveness and poor stability, etc [3,4]. At present, a lot of techniques have been used to improve the physicochemical properties of bio-oil to produce high-quality chemicals and fuels [5–7]. Among them, distillation is a simple and effective method according to the boiling point of different compounds in bio-oil [8,9]. Although some high quality chemicals and high quality fuels can be obtained from the light and middle fractions, about 20–50% of solid residue will be left at the bottom [10,11].

In order to improve the comprehensive utilization of bio-oil, distillation residue can be used as chemical and fuel raw materials to be further utilized. Some scholars have extracted chemical components

from bio-oil distillation residue through chemical methods. The pyrolytic lignin was obtained from bio-oil distillation residue by methanol-water and water extraction methods [12]. The monophenols and sugars were co-extracted from bio-oil distillation residue through the combination of extraction, heat treatment and column chromatography [13]. In addition, co-pyrolysis and co-combustion are also one of the ways in which bio-oil distillation residue is used, which are mainly to investigate the interaction and synergistic effects between raw materials [14,15]. In fact, bio-oil distillation residue as a by-product from bio-oil distillation is also a special biomass material which has less ash and smaller molecules than general biomass, so it can be used as a feedstock for secondary pyrolysis to produce high-value chemicals and fuels.

Biomass pyrolysis is a type of thermochemical conversion technology which is considered as one of the most promising technologies for biomass conversion [16,17]. The literature on the factors affecting pyrolysis is mainly related to induction temperature, reaction time, catalyst, etc. Ji et al. [18] studied the effect of operating conditions on bio-oil production from microalgae. And the results revealed that the optimal operating conditions for bio-oil yield and conversion rate were reaction temperature of 300 °C and reaction time of 45 min. Khanday

\* Corresponding authors 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 addresses: [likai11@ustc.edu.cn](mailto:likai11@ustc.edu.cn) (K. Li), [xfzhu@ustc.edu.cn](mailto:xfzhu@ustc.edu.cn) (X. Zhu).

et al. [19] focused on catalytic pyrolysis of oil palm mesocarp fiber by adding zeolite derived from low-cost oil palm ash. Nitrogen and helium and other inert gases are often used as induction atmosphere, but carbon dioxide is rarely used as reaction atmosphere. Essentially, carbon dioxide can be used as reaction medium for the production of syngas and magnetic biochar [20]. At low and medium temperature range, the study about the effect of pyrolysis atmosphere on biochar is relatively lacking. For biomass pyrolysis, the investigation of pyrolysis mechanism has focused on the mass change and the kinetics in pyrolysis process [21–23]. And it is also important to investigate the mechanism of biomass pyrolysis by analyzing the evolution of product properties. The content and composition of liquid and gas products derived from different biomass pyrolysis have been widely analyzed [24–26], but it is not detailed through the evolution of solid products after pyrolysis to study the pyrolysis mechanism. Biochar, as a pyrolytic solid product, has been widely applied in industry and agriculture, such as fuels, activated carbon, absorbents [27], soil amendment [28], catalyst carriers [29], reducing agent in smelting, supercapacitor materials and battery electrodes, etc [30–32]. The application of biochar depends mainly on its physicochemical properties, while induction conditions and biomass types are the main factors affecting the characteristics of biochar. Bio-oil distillation residue can be used to produce biochar, which is also one of the applications of bio-oil. However, there are few reports on the pyrolysis of bio-oil distillation residue under low and medium temperature combining different atmosphere for the simultaneous production of high-value chemicals, biochar and fuel. In order to better understand the pyrolysis mechanism of bio-oil distillation residue, which provides a theoretical basis for further gasification of bio-oil distillation residue, it is necessary to study the evolution of physicochemical properties of biochar derived from bio-oil distillation residue under different induction atmosphere. The comparative study on the evolution of biochar is also conducive to the better selection of operating process to produce products.

In this work, the biochar from bio-oil distillation residue was prepared by changing the reaction temperature and the inducing atmosphere. The pyrolysis mechanism of bio-oil distillation residue was revealed by the evolution of elements, calorific values, functional groups, graphitization degree and thermal stability of biochar. And the comparison in the characteristics of biochar derived from bio-oil residue distillation under different atmospheres was described in detail. The results of this article will provide valuable information for the simultaneous application of bio-oil distillation residue.

## 2. Methods

### 2.1. Materials

The bio-oil distillation residue (DR) used in this study was collected from University of Science and Technology of China. It was obtained by ordinary atmospheric distillation and the distillation temperature was set at 120 °C [10,11]. Prior to use, DR was milled and sieved using 150 and 180 mesh sieves to obtain the desired particle. And then, the desired particle was dried at 80 °C for 48 h in a drying oven. After that, the pyrolysis experiment of DR was performed using a tube furnace (OTF-1200X, Hefei Kejing Materials Technology Co., LTD, China). In each experiment, a ceramic boat loading about 3 g DR was put in the center of quartz tube with the inner diameter of 44 mm and the length of 1000 mm. The air in the quartz tube was discharged by introducing induction gas (pure nitrogen or carbon dioxide) into the system in advance for 30 min before heating. And then, DR was heated to the set temperatures of 200, 300, 400, 500, 600 and 700 °C in nitrogen or carbon dioxide, respectively. The heating rate and the gas flow rate in this process were 20 °C/min and 100 ml/min, respectively. The terminal temperature was maintained for 30 min to ensure sufficient carbonation of DR. When the furnace was cooled to room temperature, the biochar was taken out from the tube furnace to calculate the yield and

further analysis. The corresponding samples were named as DRN2, DRN3, DRN4, DRN5, DRN6, DRN7 (200, 300, 400, 500, 600, 700 °C in nitrogen) and DRC2, DRC3, DRC4, DRC5, DRC6, DRC7 (200, 300, 400, 500, 600, 700 °C in carbon dioxide), respectively. All the experiments in this study were carried out at least three times to ensure the reproducibility of the results. And the standard deviation was generally less than 1% by analyzing the experimental data.

### 2.2. Analytical methods

#### 2.2.1. Proximate, ultimate and calorific value analysis

The proximate analysis of DR was tested according to GB/T 28731–2012. The results showed that DR contained less water (1.00 wt%) and ash (0.50 wt%), while the volatile (72.90 wt%) and fixed carbon content (25.60 wt%) were relatively larger. The Vario EL III cube elemental analyzer and the bomb calorimeter (XRY-1B) were used for the ultimate analysis and the calorific value of the samples, respectively. Since the sulfur content of the samples was very low, the sulfur element was neglected in the later element analysis of samples. The contents of oxygen element and fixed carbon were calculated by difference.

#### 2.2.2. FTIR analysis and Raman analysis

FTIR spectrophotometer (Nicolet 8700) in the range of 400–4000  $\text{cm}^{-1}$  wavenumbers with the resolution factor 4  $\text{cm}^{-1}$  was used to obtain the chemical functional groups of samples. The mass ratio of sample to potassium bromide was 1: 180, and the sample was prepared by compression method. Raman spectrum of sample was measured using confocal-micro Raman spectrometer (LABRAM-HR). The range of Raman shift was 400–3300  $\text{cm}^{-1}$ , and the resolution ratio of spectra was 0.6  $\text{cm}^{-1}$ .

#### 2.2.3. Thermogravimetric analysis

The thermal stability of biochar was analyzed by thermogravimetric analyzer (TGA Q500) from room temperature to 900 °C under nitrogen atmosphere with a flow rate of 100 ml/min at a heating rate of 20 °C/min. For each test, the initial weight of all samples was about 5 mg.

## 3. Results and discussion

### 3.1. Yields and calorific values of samples

The yields of biochar under different temperatures and atmospheres were listed in Table 1. By increasing induction temperature, the yields of biochar decreased from 90.73% to 31.76% in nitrogen and from 90.27% to 18.97% in carbon dioxide, respectively. The yields of DRN and DRC were similar before 300 °C in different atmospheres, indicating that atmosphere at low temperatures had little effect on biochar yield. Compared with nitrogen atmosphere, carbon dioxide had a positive effect on biochar yield in intermediate temperature range (300–600 °C). This may be due to carbon dioxide inhibiting the volatilization or cracking of oxygen-containing functional groups in bio-oil distillation residue to produce oxygen-containing gases such as CO<sub>2</sub> and CO [20]. And another reason may be that carbon dioxide [44] has a greater relative atomic mass than nitrogen [28]. The molecular mass of gas can affect the contact between the particles of bio-oil distillation residue and induction gas according to diffusion property [33]. When induction

**Table 1**  
The yield and calorific value of biochar under different temperatures and atmospheres.

Induction conditions (°C)		200	300	400	500	600	700
Yields (%)	N <sub>2</sub>	90.73	64.08	44.62	36.79	33.60	31.76
	CO <sub>2</sub>	90.27	64.56	49.21	40.81	33.55	18.97
HHV (MJ·kg <sup>-1</sup> )	N <sub>2</sub>	31.23	31.99	31.52	31.08	32.12	32.21
	CO <sub>2</sub>	34.13	33.83	33.29	32.01	32.55	31.88

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