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Upgrading biochar from bio-oil distillation residue by adding bituminous coal: Effects of induction conditions on physicochemical properties

Xiefei Zhu, Chu Wang, Shanshan Li, Xifeng Zhu*

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

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ABSTRACT

In this study, biochar was produced by co-pyrolysis of bio-oil distillation residue and bituminous coal under different induction temperature and gas flow rate in a tube furnace. Central composite design was introduced to explore the combined effects of experimental conditions on biochar. The physicochemical properties of biochar from different induction conditions were comprehensively evaluated by elemental analysis, Fourier transform infrared spectrometry (FTIR) and Raman spectroscopy based on response surface methodology. The results showed that bituminous coal was beneficial to the increase in biochar yield, whereas temperature had the opposite effect and the effect of gas flow rate was not obvious. Moreover, C/O ratio increased with the increase of pyrolysis temperature and bio-oil distillation residue in feedstocks, while C/H ratio increased only with increasing temperature. Gas flow rate had a more pronounced descent effect on C/H compared with C/O. In addition, induction conditions caused a relative weakening of C=C stretching vibration and the relative enrichment of C–H in biochar. Bituminous coal, temperature and gas flow rate all contributed to the conversion of small aromatic rings of biochar to large aromatic rings during the co-pyrolysis process.

1. Introduction

Biochar derived from biomass has been considered a multi-functional material, which could be widely used as a low-cost adsorbent [1], metal immobilization [2,3], carbon sequestration [4], catalytic carrier [5], soil fertilizer [6], and so on. At present, a variety of biomass including municipal sludge and waste paper pulp sludge have been used as raw materials to produce biochar [7–9]. Bio-oil distillation residue as a special biomass is recognized as an excellent biocarbon raw material due to its rich carbon content and functional groups [10–12]. Simultaneously, bio-oil distillation residue is a particular waste remained at the bottom of instrument during the process of upgrading bio-oil, which has an unpleasant odor. If it is not effectively treated, it can become an environmental pollutant. Therefore, the conversion of bio-oil distillation residue into biochar is a multiple benefit treatment that not only prevents the contamination of the distillation residue, but also further utilizes the bio-oil distillation residue to improve the overall efficiency of biomass pyrolysis [13,14].

In general, biochar is produced through pyrolysis of individual biomass, whereas this biochar produced by a single preparation method does not have multiple properties due to some defects. Currently, there are many methods to modify biochar for multiple functions. Feng et al. [15] took advantage of heterogeneous reforms with tar to optimize biochar through water and carbon dioxide. As a result, water and carbon dioxide could convert small aromatic rings of biochar into large aromatic rings and tars increased the hydrocarbons of biochar. In addition, a novel method of modifying biochar was explored through acrylonitrile [16]. The results showed that the introduction of cyanogen group into the biochar could significantly improve the adsorption capacity of heavy metal cadmium (Cd). Zhang et al. [17] produced nitrogen enriched biochar by co-processing of carbon dioxide and ammonia at high temperatures. This modification not only significantly increased the surface area of biochar but also introduced abundant nitrogen-containing functional groups into biochar. However, these modification methods of biochar require additional steps that require more process and energy. Therefore, co-pyrolysis is proposed as a very promising technology to produce biochar with multiple properties by adding some other substances during the preparation process. Young et al. [18] prepared biochar for sorbent and electron transfer mediator through co-pyrolysis of polymer and biomass. It was found that co-pyrolysis contributed to the increase in aromaticity and hydrophobicity, cation exchange capacity, pH and surface area of biochar. These physicochemical properties could effectively enhance the absorption of 2,4-dinitrotoluene (DNT) and Pb. Wang et al [19] upgraded biochar to

* 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).

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remove arsenic by co-pyrolysis of pinewood and natural hematite. Compared with unmodified biochar, the induced biochar had stronger magnetic properties and better ability to remove arsenic. Moreover, Sewua et al. [20] investigated cationic dye adsorption of biochar obtained from pyrolysis of spent mushroom substrate with Saccharina japonica. The results indicated that biochar derived from mixed raw materials exhibited superior physicochemical properties, such as abundant functional groups and high adsorptive capacity. In order to upgrade the biochar from bio-oil distillation residue, bituminous coal is considered to be a suitable co-substrate based on the fact that bituminous coal not only has a large number of different functional groups but also rich alkali/alkali earth metal minerals [21–23].

At the same time, the performance of biochar from pyrolysis depends not only on the difference in raw materials, but also on the pyrolysis conditions. Hung et al. [24] evaluated the effect of temperature on the physicochemical and pore properties of biochar from biogas digestate and found that temperature exhibited different effects on different properties. Futhermore, gas flow rate could affect the residence time of volatiles during the pyrolysis process and disturb their exchange with the functional groups on the surface of biochar and secondary reactions [25]. Therefore, central composite design (CCD) was introduced to explore the effects of induction conditions on the physicochemical properties of biochar for the production of multi-functional biochar, which is an advantageous method to handle the effects of multiple experimental parameters on the results [26,27]. This investigation is useful for understanding the evolution of physicochemical properties of biochar from co-pyrolysis of bio-oil distillation residue and bituminous coal under different induction conditions and providing a theoretical guide for optimizing the production of multi-functional biochar of bio-oil distillation residue. In addition, it is beneficial to reveal the thermal decomposition of organic matter in the co-pyrolysis process of bio-oil distillation residue and bituminous coal.

In this study, biochar was prepared through co-pyrolysis of bio-oil distillation residue and bituminous coal under different induction temperature and gas flow rate. The physicochemical properties of biochar from different induction conditions were comprehensively evaluated by elemental analysis, FTIR and Raman spectroscopy. Further, the effects of induction conditions on biochar production and physicochemical properties were explored by response surface methodology. The corresponding co-pyrolysis mechanism of bio-oil distillation residue and bituminous coal was revealed. The results of this study will provide effective information for upgrading biochar from bio-oil distillation residue.

2. Methods

2.1. Materials

Bio-oil distillation residue (DR) was collected from University of Science and Technology of China, which was obtained through ordinary atmospheric distillation and the distillation temperature was fixed at 120 °C. Bituminous coal (BC) in the study was obtained from Shenfu coal mine (Shannxi Province, China). Prior to use, bio-oil distillation residue and bituminous coal were dried at 80 °C for 48 h. Then these samples were ground and sieved through 40 and 80 mesh sieves. The mixed samples of bio-oil distillation residue and bituminous coal were prepared through mechanical mixing.

2.2. Experimental design and pyrolysis procedure

Design-Expert is an excellent experimental design software that could fully optimize the experimental scheme. In the study, three experimental factors were explored, including the percentage of bio-oil distillation residue (A), pyrolysis temperature (B) and gas flow rate (C). The percentage of bio-oil distillation residue varied between 0 and 100%, while the range of pyrolysis temperature was 300–700 °C and the range of gas flow rate was 200–800 ml/min. Central composite design (CCD) was used to evaluate the combined effect of experimental factors on the co-pyrolysis of bio-oil distillation residue and bituminous coal. The experimental design summary and experimental results were shown in Table 1. According to the experimental results, the corresponding statistical analysis was performed.

Table 1
Experimental design matrix for co-pyrolysis and biochar yield.

Run	A: DR percentage (%)	B: Temperature (°C)	C: Gas flow rate (ml/min)	Biochar yield (%)
1	20	380	680	74.81
2	50	500	500	55.38
3	80	620	320	35.29
4	50	700	500	48.17
5	20	380	320	75.57
6	50	500	500	55.27
7	50	500	500	55.23
8	80	380	680	41.03
9	80	620	680	34.53
10	80	380	320	43.89
11	50	500	200	54.39
12	50	500	500	55.07
13	50	500	500	55.43
14	20	620	680	61.75
15	20	620	320	61.49
16	50	300	500	73.94
17	50	500	500	54.92
18	50	500	800	54.70
19	100	500	500	28.05
20	0	500	500	74.04

The co-pyrolysis experiment of feedstcoks was performed in a tube furnace and the schematic diagram of experimental apparatus was shown in Fig. 1. For each experiment, the sample ark containing about 5 g of sample was first placed in the cooling zone of quartz tube and purged with nitrogen. When the temperature reached the set temperature, the sample ark was pushed to the heating zone through the quartz rod. After the sample was held for 10 min in the heating zone, the sample ark was pulled into the cooling zone of quartz tube. The biochar yield was calculated by dividing the weight of solid biochar remaining in the sample ark after pyrolysis by the initial mass of the sample. Each experiment was replicated at least three times to ensure the repeatability and accuracy. And the relative standard deviation of the experimental results was within 3%.

2.3. Analytical methods

The proximate analysis of bio-oil distillation residue and bituminous coal was carried out through GB/T 28731-2012 (Table 2). Vario EL III cube elemental analyzer was used for the ultimate analysis of bio-oil distillation residue, bituminous coal and the biochar obtained from different induction conditions, which were all based on the dry basis without ash. FTIR spectra of biochar in 400–4000 cm^{-1} wavenumbers were obtained by FTIR spectrophotometer (Nicolet 8700). The sample (biochar: potassium bromide = 1:180) was prepared through compression method. Confocal-micro Raman spectrometer (LABRAM-HR) in the range of 400–3300 cm^{-1} was used to obtain the Raman spectrum of biochar.

3. Results and discussion

3.1. Yield analysis of biochar

3.1.1. Statistical analysis of biochar yield

The biochar yields of co-pyrolysis varied with experimental conditions, and the response values of biochar were summarized in Table 1. Through the analysis of variance based on central composite design, the