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Operating conditions-induced changes in product yield and characteristics during thermal-conversion of peanut shell to biochar in relation to economic analysis



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Ruijia Liu^{a, b}, Guijian Liu^{a, b, *}, Balal Yousaf^{a, b}, Qumber Abbas^a

^a CAS-Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China,

Hefei 230026, PR China ^b State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, The Chinese Academy of Sciences, Xi'an, Shaanxi 710075, China

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ABSTRACT

The influences of pyrolysis conditions on the products yield distribution and physico-chemical characteristics of biochar derived from peanut shell in a fixed-bed reactor were investigated in this study. The pyrolysis conditions included the pyrolysis temperature $(300-700 \,^{\circ}\text{C})$, retention time $(15-90 \,\text{min})$, heating rate $(1-10 \,^{\circ}\text{C} \,\text{min}^{-1})$, gas flow rate $(20-200 \,\text{mL} \,\text{min}^{-1})$ and feedstock particle size (<0.075, 0.075 -0.150, 0.150-0.300 and 0.300-2.00 mm). Various analytical techniques were used to characterize the biochar for ultimate and proximate analyses, higher heating value $(23.99-30.44 \,\text{MJ} \,\text{kg}^{-1})$, pH (8.11 -12.89), electrical conductivity (22.78-34.44 mS cm⁻¹), surface functional groups (acidic, carboxylic and basic groups), Fourier transform infrared spectroscopy analysis, pore volume (0.055-1.241 cm³ g⁻¹) and specific surface area (7.12-20.96 m² g⁻¹). The results demonstrated that the temperature predominantly regulated the product yields distribution and characteristics of produced biochar. Furthermore, the heating rate considerably influenced the biochar proximate composition, micropore surface area and pore size. Particle size had significant influences on biochar surface porosity and bio-oil yield. The economic analysis of the pyrolysis system indicated its feasibility and superiority with a positive net present value of $12.07 \times 10^6 \,$ USD after twenty-five years of operation.

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1. Introduction

Biochar is the carbonaceous solid product of the carbonization of lignocellulose. In recent years, the application of biochar and the industrial-scale carbonization of lignocellulose have received increasing attention due to its renewability, easy availability and efficient use of wastes (Chu et al., 2017). Researchers have demonstrated that biochar possesses a high specific surface area with varieties of functional groups; therefore it can be used for the adsorption of various organic and inorganic contaminants (Luo et al., 2015). The application of biochar in soil has been proved to improve the overall productivity of soil, microbial and plant growth (Ronsse et al., 2013; Yousaf et al., 2016). Moreover, biochar, when used as a soil amendment, has a promising potential to mitigate

E-mail address: lgj@ustc.edu.cn (G. Liu).

global climate change (Mohammadi et al., 2017). The recalcitrant carbon found in biochar has a long half-life in soil, and it can be used for carbon sequestration (Maroušek et al., 2017; Yousaf et al., 2017b). Biochars are also important renewable clean energy sources to substitute for fossil fuels (Lee et al., 2017; Yousaf et al., 2017a). Bio-oil and syngas (including CO₂, CO, H₂ and light hydrocarbons), other bio-products of lignocellulose carbonization, can be used as raw materials for the industrial production of chemicals (Kan et al., 2016; Moral1 and Şensöz, 2015). Furthermore, bio-oil and syngas have successfully been used as fuels to heat the pyrolysis system, and gas from the fermentation of silage or mixture of lignocellulose and manure could provide energy for generating high-quality biochar, which is economically viable (Mardoyan and Braun, 2015; Maroušek, 2014; Maroušek et al., 2014).

Lignocelluloses are complex mixtures of biological organic and inorganic compounds (Tripathi et al., 2016) that are usually derived from agricultural wastes, forestry wastes, municipal sludge and manures (Lee et al., 2017; Zhang et al., 2013). A variety of agricultural wastes has been widely used for biochar production. Peanut is



^{*} Corresponding author. CAS-Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, PR China.

an important crop in China and has an annual production of 1.6×10^7 t, thus making peanut shells an abundant resource of bioenergy. The technologies used to convert lignocelluloses into bioenergy and other chemicals are classified as physical, biochemical and thermochemical techniques. The thermochemical methods are further classified as combustion, gasification, hydrolysis and pyrolysis, during which heat and chemical catalysts are used to convert lignocelluloses into three major products: biochar, bio-oil and syngas (Sharma et al., 2015; Tripathi et al., 2016). Pyrolysis is the thermal decomposition of lignocelluloses under a limited supply or absence of oxygen (Qian et al., 2015; Zama et al., 2017). It is the most promising and widely used thermochemical conversion method at the industrial scale due to the flexibility of pyrolysis conditions to obtain the desired products (Chen et al., 2016a; Tripathi et al., 2016).

Feedstock types, pretreatments, pyrolysis conditions and pyrolysis reactors (fluid-bed/fixed-bed) have different influences on lignocellulose pyrolysis (Kan et al., 2016). Lignocelluloses consist of cellulose, hemicellulose, and lignin (Chen et al., 2016a). Researchers have demonstrated that lignocelluloses with higher oxygen and lignin contents led to biochar with higher reactivity and a greater quantity, respectively (Li et al., 2014; Tripathi et al., 2016). Additionally, a higher moisture content of lignocelluloses results in more energy being required during pyrolysis and a lower char yield (Tripathi et al., 2016). Usually, feedstock pretreatments are performed to modify its structure and the proportions of different compounds by physical (such as grinding), thermal (such as drying), chemical (such as activating with chemicals) and biological methods (Kan et al., 2016; Maroušek, 2013). The pyrolysis conditions that can influence product characteristics include the atmosphere, temperature, heating rate, retention time, particle size, gas flow rate and pressure. Previous researchers have concluded that a higher temperature led to a higher specific surface area, lower O/C and H/C molar ratios of biochar and higher char and syngas yields. The maximum bio-oil yield was usually obtained at approximately 500 °C (Aysu and Küçük, 2014; Demiral et al., 2012; Kloss et al., 2012). In the study of Li et al. (2017), magnetic biochar produced at 600 °C adsorbed the maximum amount of aromatic contaminants compared to biochar produced at 400 °C and 800 °C. Yuan et al. (2014) demonstrated that the application of biochar produced under a longer retention time and at a higher temperature contributed to the negative effect on soil and reduced CO₂ emission. Other studies reported that a higher heating rate (>10 °C min⁻¹) resulted in less char and more bio-oil and that a higher gas flow rate led to less bio-oil (Saikia et al., 2015). Haykiri-Acma (2006) studied the influence of the feedstock particle size (ranging from 1.400 mm to 0.150 mm) and concluded that smaller particles increased biochar specific surface area.

The economic analysis of the pyrolysis system estimates the feasibility of the system for real plants and its benefits for the environment by applying different models (Ji et al., 2017). The typical model includes 1) feedstock collection and hauling; 2) feedstock storage and pre-processing; 3) pyrolysis unit construction and operation; 4) energy sales (biochar, bio-oil and syngas); 5) biochar hauling and application; and 6) biochar-induced agronomic benefits and carbon offset credits (Kung et al., 2015; McCarl et al., 2009). Wrobel-Tobiszewska et al. (2015) found that the total benefit was more sensitive to the distribution of the final product and biochar price. Consequently, it is necessary to study the influences of operating conditions on pyrolysis.

However, the influences of an extremely low heating rate and a small particle size of feedstock on products yield distribution and characteristics have not yet been studied. These two factors taking extreme values would have significant influences on the product yield and characteristics. To further understand the lignocellulose conversion mechanisms and provide suggestions for pyrolysis at the industrial scale, this paper investigated the combined influences of pyrolysis temperature, retention time, heating rate, gas flow rate and particle size of peanut shell (PS) on product yield and characteristics. The heating rate and particle size chosen were much lower than others. Furthermore, the economic analysis of slow pyrolysis was conducted to estimate the feasibility of the system.

2. Materials and methods

2.1. Materials

PS was used as the feedstock in this study, collected from Anhui Province, China. The sample was first washed with deionized water and oven-dried at 105 °C for 24 h to remove moisture. The grinding of PS was performed with Thomas Model 4 Wiley mill (Thomas Scientific, USA) and then sieved to obtain the particle size < 2 mm for pyrolysis (one portion of the feedstock was sieved into four different sizes: < 0.075, 0.075–0.150, 0.150–0.300 and 0.300–2.00 mm, to study the influence of particle size).

2.2. Procedure of biochar production

The schematic diagram of the fixed bed pyrolysis system (model BTF-1200C, Anhui BEQ Equipment, Technology Co., Ltd, China) is shown in Fig. 1. The dried PS particles were weighed (approximately 30g) with the quartz boat and placed together by the sample feeder in the middle of the tube furnace. The digital proportional-integral-derivative controller integrated with the tube furnace was used to set different operating conditions of the tube furnace, with a maximum operating temperature of 1200 °C. The pyrolysis temperature, temperature rising rate and retention time were set to 500 °C, 10 °C min⁻¹, and 60 min, respectively. When the target pyrolysis temperature was reached, the sample was kept under constant conditions for 60 min. N₂ was used as the carrier gas to sweep the air from one side of the tube and provide an inert atmosphere, and the constant gas flow rate was regulated to 20 mL min⁻¹ with a mass flow controller. Five influencing factors of biochar properties were investigated in this study. Each corresponding operating condition was adjusted as follows and the other conditions were kept constant: 1) pyrolysis temperature (300, 400, 500, 600, and 700 °C); 2) retention time (15, 30, 60, and 90 min); 3) heating rate (1, 2, 5, and 10 °C min⁻¹); 4) gas flow rate (20, 50, 100, and 200 mL min⁻¹); 5) particle size (<0.075, 0.075–0.150, 0.150-0.300 and 0.300-2.00 mm). The liquid product from lignocellulose pyrolysis was collected by applying a filter unit and condenser system that was connected to the outlet of the furnace and composed of the organic phase (bio-oil and other organic compounds) and an aqueous phase. After pyrolysis, the produced



Fig. 1. The schematic diagram of the fixed bed pyrolysis system.

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