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Research article

Understanding water retention behavior and mechanism in bio-char

Svetlana Bikbulatova[a], Arash Tahmasebi[a], Zhiqiang Zhang[a], Salman Khoshk Rish[a], Jianglong Yu[a,b,*]

[a] Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, People's Republic of China

[b] Chemical Engineering, University of Newcastle, Callaghan, NSW 2308, Australia

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ABSTRACT

Bio-char has been applied to soil as an amendment to improve soil water holding capacity due to its porous nature. In this study the behavior of water in bio-char was investigated for better understanding mechanisms of water retention by bio-char. Bio-chars with different structures were prepared by partial gasification of peanut shell (PT) and palm kernel shell (PKS). It was observed that the BET surface area and total pore volume of bio-char increased with gasification conversion. Water holding capacity and water adsorption rate showed a direct correlation with micropore volume of bio-char, suggesting that physical structure of bio-char played a key role during interaction with water. These results indicated that partial gasification is a promising method for production of bio-char suitable for soil remediation. Two types of freezable water i.e. freezable free water (FFW) and freezable bound water (FBW) were directly detected in bio-char samples during Differential Scanning Calorimetry (DSC) analysis. The phase transition temperature of freezable bound water correlated well with pore size distribution of bio-chars. The presence of non-freezable (NFW) water in bio-char was also confirmed from the difference between total water content of samples and the sum of FFW and FBW. The amount of FFW showed an indirect correlation with micropore volume of bio-chars, suggesting that FFW is present in macropores. However, an opposite trend was observed for FBW and NFW in bio-chars, indicating that these two types of water were present in micropores. The low-temperature XRD results were used to define the boundary between the freezable and non-freezable water in bio-char samples.

1. Introduction

The large share of fossil fuels in energy consumption and the increasing global energy demand has resulted in depletion of these fuels and has raised environmental concerns [1]. A shift to utilization of alternative and renewable energy resources such as biomass is therefore inevitable due to limitations of fossil fuels. Biomass is a promising source of energy and fuels due to its abundance and carbon neutral nature [2–4]. Bio-char as a by-product of biomass utilization can be utilized as catalyst support, waste management, energy production, and soil remediation [5–8].

Bio-char has been used for soil amendment to improve soil properties and for soil carbon sequestration [9]. It has been reported that bio-char can improve the physical and chemical characteristics of soil and promote crop yield [10,11]. Addition of low density bio-char to soil can decrease the bulk density of soil and improve soil softness and terrene [12,13]. Different quality factors of soil such as mineral nutrition and reproduction of microbes increase with fertilization by bio-char [14,15]. Change in moisture retention capacity of soil is one of the key factors that can explain the crop growth with addition of bio-char [16]. It is well documented that water holding capacity of soil can be increased by addition of bio-char [17–19]. Such factors as total pore volume, specific surface area, pore structure, and surface functional groups can affect water holding capacity and water absorption rate of bio-char [20,21]. Sun et al. [22] reported that bio-char increased the water retention and water holding capacity of soil, and increased plant available water due to increased pore volume and total porosity of soil. Ulyett et al. [23] investigated the effect of bio-char on water retention of two sandy loam soils and observed that addition of bio-char reduced bulk density and increased moisture retention, which was attributed to the porous nature of bio-char. Although it is generally agreed that bio-char has a high water holding capacity, the exact interaction between

Abbreviations: PT, peanut shell; PKS, palm kernel shell; DSC, Differential Scanning Calorimetry; XRD, X-ray diffractometry; FFW, freezable free water; FBW, freezable bound water; NFW, non-freezable water

* Corresponding author at: Key Laboratory of Advanced Coal and Coking Technology of Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, People's Republic of China; and Chemical Engineering, University of Newcastle, Callaghan, NSW 2308, Australia.

E-mail address: jianglong.yu@newcastle.edu.au (J. Yu).

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water and bio-char and the influence of bio-char structure on water behavior and retention, and the types of water absorbed by bio-char is not fully understood.

Relatively extensive research has been carried out in order to investigate the behavior of water in porous media such as silica [24,25], low-rank coals [26,27], and lignite char [28]. The presence of different types of water has been reported in porous media such as low-rank coals [26]. Three types of "freezable free water" (FFW), "freezable-bound water" (FBW), and "non-freezable bound water" (NFW) have been reported in lignite [27,29]. Freezable free water is mainly present on particle surface and in larger pores [28], while freezable-bound water is condensed in micropores [30]. Although much research has been carried out on the removal of water from biomass (drying), its effects on thermochemical conversion, and the effect of bio-char on soil moisture retention, there is a significant knowledge gap in the types of water in bio-char and the effects of physical and chemical structure of bio-char on behavior of water. It has been reported that meso and macropores in bio-char act as the passageways of water to micropores, where most of the adsorption takes place [31–33].

The changes in different types of water as a function of moisture content and the effect of physical and chemical structure on wettability of bio-char has not been reported in the literature. The aim of this study was to expound the nature of water in bio-char and establish the effect of bio-char structure on its interaction with water and ultimately on water holding capacity and water adsorption rates of bio-char. For this purpose, char samples with different porous structures were prepared by partial gasification of two types of biomass in steam and the changes in different types of water in bio-char, water holding capacity, and water adsorption rate as a function of porous structure of bio-char were investigated systematically. The amount of FFW, FBW, and NFW in bio-char were quantified by using DSC and low-temperature XRD and correlated with physical properties of bio-chars. The findings of this study advanced the knowledge of water retention in bio-char and how bio-char structure affects water adsorption and water holding capacity.

2. Materials and methods

2.1. Sample preparation

Two biomass samples, i.e. peanut shell (PT) and palm kernel shell (PKS) from North China and Malaysia, respectively, were used in this study. The proximate and ultimate analyses of the peanut shell and palm kernel shell sample are given in Table 1. The raw biomass samples were crushed and sieved to a particle size of 125–300 μm. Biomass samples were pyrolyzed in a fixed-bed reactor heated in an electric oven at 800 °C under high purity (99.999%) nitrogen flow of 200 ml/min for 1 h. In order to obtain bio-char samples with different physical structures, pyrolysis chars were partially gasified using steam (15 vol% balanced with nitrogen) at 900 °C in a vertical fixed-bed quartz reactor with an internal diameter of 2.0 cm. Gasified peanut shell and palm kernel shell char samples with 28%, 54%, and 75% conversions were obtained by controlling the gasification residence time.

Table 1
Proximate and ultimate analyses of peanut shell and palm kernel shell biomass.

Sample	Peanut shell	Palm kernel shell
Moisture (wt%, ar)	8.03	14.90
Volatiles matter (wt%, db)	58.39	74.68
Ash (wt%, db)	11.3	1.64
Fixed carbon (wt%, db)	30.31	23.68
C (wt%, daf)	37.87	49.90
H (wt%, daf)	5.18	5.25
N (wt%, daf)	1.57	0.36
S (wt%, daf)	0.14	0.95
O (By difference) (wt%, daf)	55.24	43.54

ar: as received; db: dry basis; daf: dry ash free.

Table 2
The BET results of peanut shell and palm kernel shell chars with different gasification conversions.

Sample		BET surface area (m^2/g)	Micropore volume (< 5 nm) (cm^3/g)	Total pore volume (cm^3/g)	Water holding capacity (g water/g of sample)
Peanut shell	Raw	0.7338	0.0003	0.013	–
	28%	626.22	0.035	0.072	2.40 (± 0.14)
	54%	1043.37	0.088	0.151	3.25 (± 0.001)
	75%	1009.02	0.142	0.248	4.62 (± 0.78)
Palm kernel shell	Raw	2.283	0.0037	0.008	–
	28%	680.35	0.033	0.103	2.48 (± 0.02)
	54%	835.45	0.066	0.394	2.64 (± 0.25)
	75%	1362.290	0.095	0.527	4.44 (± 0.75)

2.2. Sample characterization

The BET surface area analysis of bio-chars was measured by using N_2 gas adsorption method and a V-sorb 4800 P surface area and porosimeter at 77 K. The experiments were repeated 3 times and the average values are reported here. The Barrett–Joyner–Halendar (BJH) model was used for determination of the pore size distributions and calculation of cumulative micropore volume (< 5 nm) in samples. The BET analysis results of bio-chars with different gasification conversions are summarized in Table 2. All bio-char samples showed typical type I adsorption isotherms, indicating that majority of pores in bio-char were in micropore region.

The chemical structures of biomass and bio-chars were investigated by using a Thermo Fisher Nicolet IS5 mid-FTIR spectrometer. Around 1 mg of sample was grinded with 100 mg KBr for preparation of pellets. The IR spectra of the samples were recorded in a wavenumber range of 4000–400 cm^{-1}. The band assignments in the infrared spectra were done according to the literatures [34,35].

For measurement of water holding capacity of bio-char with different physical structure, around 1 g of each sample was placed in a container with wire mesh at the bottom and doused in glass beaker with water for 24 h. The container was then fixed in a bigger container in order to let excessive water drain for 20 h. Wet sample was then weighted and dried in an oven at 105 °C until no more weight loss was observed. A similar method has been reported in the literature [18]. Water holding capacity was calculated by using Eq. (1):

$$Water\ Holding\ Capacity\ (WHC)\ (\%) = \frac{M_2 - M_3}{M_3 - M_1} \times 100 \quad (1)$$

where M_1 is the weight of glass container, M_2 is the total weight of wet bio-char and glass container, and M_3 is the weight of oven-dried bio-char sample. All the measurements were repeated at least twice to ensure reproducibility of results.

For water absorption rate measurement, a 0.2 ml glass capillary was used. The mass (M_c) of 2 ml (bulk volume V_c) of each sample was pre-weighed. In the beginning of experiment, bio-chars were mixed with certain amount of de-ionized water (V_{H_2O}) in the capillary and timing was started. The volume of mixture (V_{mix}) was measured and recorded at different time intervals. Eq. (2) was used for calculation of specific water content in the samples as a function of time:

$$v_{ab} = (V_c + V_{H_2O} - V_{mix})/M_c \quad (2)$$

2.3. Low-temperature DSC analysis

In order to prepare the samples with different water contents for DSC and low-temperature XRD analyses, around 25 g of each sample was stirred in de-ionized water in a glass beaker for 16 h at room