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Characteristics of slow pyrolysis biochars produced from rhodes grass and fronds of edible date palm

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ABSTRACT

Biochars from two different biomass (rhodes grass and fronds of date palm) were produced using the same pyrolysis condition (1 atm, 400 °C, heating rate of 5 °C min^{-1}, duration of 11 h) and compared in terms of chemical composition, thermal stability, and respective microstructures. Proximate analysis of the biochars showed rhodes grass has higher fixed carbon (56.6 wt%), lower volatile (11.8 wt%) and higher ash (28.8 wt%) compared to date palm biochar (fixed carbon 45 wt%; volatile 43.2 wt%; ash 7.1 wt%). The pH of the two biochars were similar (~9.6). Elemental analysis showed that carbon becomes enriched, whereas hydrogen, oxygen and sulfur become depleted after pyrolysis. The elemental O/C and (O + N)/C ratios are lower in rhodes grass biochar (0.11 and 0.12 respectively) compared to date palm biochar (0.32 and 0.33 respectively), but both biochars have a similar H/C ratio (0.46 for rhodes grass and 0.49 for date palm). Thermogravimetric Analysis (TGA) performed in inert gas (N_2) showed considerable differences in the thermal degradation profile of the two biochars. Only one degradation event occurring over a wide temperature range (120–1000 °C; no obvious degradation maximum) was observed in rhodes grass, whereas two degradation events were observed in date palm – the first occurring rapidly (280–380 °C; maximum at 340 °C) and the second event occurring slowly over a wider temperature range (380–1000 °C; no temperature maximum detected). The Fourier transform infrared (FTIR) spectra of both biochars are featureless in comparison to raw biomass, but bands assigned to O–H stretching (3200–3000 cm^{-1}) and C–H stretching (3100–3000 cm^{-1}) while markedly decreased suggest cellulose might not have been completely decomposed during pyrolysis. The BET surface area of rhodes grass biochar is higher (16.78 m^2 g^{-1}) compared to date palm biochar (1.99 m^2 g^{-1}). This is in agreement with scanning electron microscopy investigations (SEM) which show that the average pore size diameter is smaller in rhodes grass biochar (3.1 μm + 0.3 μm) compared to the one of date palm biochar (7.2 μm ± 2.9 μm). Changes in the distribution of pore size diameter in the two biomass before and after pyrolysis suggests date palm is relatively heat sensitive in comparison to rhodes grass. Overall, our results demonstrate that both biochars are substantially different despite being produced under the same pyrolysis condition.

1. Introduction

Biochar is charcoal produced from organic materials – usually plant biomass – by means of pyrolysis. It is a porous inert form of carbon with low bulk density and high cation exchange capacity [1]. Because of these characteristics, the application of biochar to soil has been demonstrated to improve certain properties such as nutrient adsorption, structure and water retention [1,2]. Indeed, the historic use of biochar can be traced back to 2000 years ago when ancient civilizations indigenous to the Amazon basin used it as a practice to enrich soil fertility [3]. Furthermore, some of the most fertile soils in the world contain natural deposits of biochar resulting from forest or grassland fires [4,5]. Biochar is also being considered as an inexpensive sustainable option for long term carbon storage in soils [6] as some studies demonstrated that the mean residence time of biochar can be greater than 1000 years [7,8].

Pyrolysis of biomass also yields gas and bio-oil as co-products alongside biochar. The fraction of each that is produced depends

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on the pyrolysis process, but slow heating rates (<30 °C min^{-1}) are recommended when biochar is the main product desired [9–11]. Furthermore, pyrolysis temperatures above 250 °C are recommended for conversion of lignocellulosic biomass because decomposition of hemi-cellulose and cellulose begins at 250 °C and is maximal at 400 °C [12,13], whereas changes in lignin structure only start to occur after heating for long durations (>8 h) [12]. Clearly then, the conditions used to produce biochars are related to the type of biomass and pyrolysis conditions. Variability in these parameters ultimately results in different physiochemical properties of the biochars and affects their performance and utility for soil and other applications [14]. For this reason, many studies have been directed toward determining suitable sources of biomass [11,15] as well as optimizing pyrolysis conditions [9,17,18]. The challenge is to be able to predict quality and performance of biochars produced from a given biomass and a given pyrolysis process via analysis of its physicochemical properties.

In this study, two types of lignocellulosic biomass – fronds of date palm (*Phoenix dactylifera*) and rhodes grass (*Chloris gayana*) – were converted to biochar using the same condition of slow pyrolysis (1 atm; heating 5 °C min^{-1} up to 400 °C; duration of 11 h) and subsequently compared in terms of chemical composition, thermal stability, and microstructures. The motivation to explore these two biomass is related to environmental issues surrounding their cultivation in the United Arab Emirates (UAE). Palm tree cultivation in the UAE results in a large amount of lignocellulosic waste, (approximately 20 kg per tree annually) [19] that is transported to landfills. Achieving the conversion of palm tree waste to biochar may have a useful application in soil while providing a solution for waste management. Rhodes grass is valued among farmers because of the relative ease in setting the seed, and its tolerance to drought and soil salinity [20,21]. However, its cultivation in the sandy soils of the UAE is water-intensive (15,700 m^3 ha^{-1} $year^{-1}$) and not sustainable [22]. A plausible solution is to improve the water holding capacity of the soils through the use of biochar soil amendment [23] by converting some of the rhodes grass harvest to biochar on-site and re-application to soil. The current study focuses on comparing the properties of the two biomass before and after their pyrolysis to biochar as basis for future studies involving their application to soil.

2. Materials and methods

2.1. Feedstock and biochars

Feedstock (rhodes grass and fronds of date palm) were obtained from a farm located in Sweihan, United Arab Emirates, air-dried for 72 h, oven dried at 100 °C for 24 h then milled into pieces of approximately 2 mm prior to charring at atmospheric pressure in an electrically heated CrNiMoTi vessel reactor (Versoclave type 3E/2L, Buchiglauster Switzerland) using a heating rate of 5 °C min^{-1} up to 400 °C and maintained at this temperature for 11 h (Fig. 1). Pyrolysis conditions were chosen based on several studies where the maximal temperature of decomposition of hemi-cellulose and cellulose by slow pyrolysis was reported to occur at 400 °C [12,13], and changes in lignin structure only start to occur after heating for long durations [12], whereas a heating rate of 5 °C min^{-1} was selected as it has been commonly used for biochar production elsewhere [24–26].

2.2. Chemical composition, FTIR, and pH

Unless specified, all analyses were conducted in duplicate. TGA performed on an SDT Q600 (TA Instruments, New Castle, DE, USA) was used for proximate analysis [27]. A heating rate of 10 °C min^{-1} was used, first in an inert (nitrogen) atmosphere up to 700 °C (for moisture and volatile determination) followed by a switch to a reactive (oxygen) atmosphere up to 1300 °C (fixed carbon determination) (Supplementary Fig. S1). Ultimate composition analysis (CHNS) was determined on a dry weight basis using a Flash 2000 series elemental analyzer (Perkin Elmers, Watham, MA, USA). The oxygen content was determined on a dry weight basis by taking the difference (O% = 100 − ash% − C% − N% − H%) [28]. Elemental analysis was used to calculate atomic molar ratios: H/C, O/C and (O + N)/C and (O + N + S)/C. FTIR spectroscopy was performed using a Vertex 80 v spectrophotometer (Bruker Corporation, Billerica, MA, USA) equipped with a diamond–platinum attenuated total reflectance (ATR), scanning in the range of 4000–400 cm^{-1} regions and having a spectral resolution of 4 cm^{-1}. Functional group identification from FTIR spectra was completed using data compiled from literature [12,29,30]. The pH of raw material and biochars were measured in milliQ water from a 1% (w/v) suspension after shaking at 150 rpm over 24 h at 25 °C [28].

2.3. Thermal stability

Thermal stability experiments were performed using TGA on an SDT Q600 (TA Instruments, New Castle, DE, USA) using a heating rate of 10 °C min^{-1} to a final temperature of 1000 °C in inert gas (nitrogen) atmosphere (Supplementary Fig. S2). The temperature at which maximum weight loss occurred was determined from the 1st derivative of weight loss from TGA curves. The data was then used to generate Table 2 and is representative of the thermal degradation of lignocellulosic biomass [12,18,31] – mainly the de-polymerization/volatilization of hemicellulose (220–315 °C), cellulose (250–400 °C) and lignin (160–900 °C) which occurs over several stages depending on the complexity of the biomass.

2.4. Microstructure analysis and water sorption

Surface area measurements were determined as multipoint Brunauer–Emmet–Teller (BET) obtained from N_2 adsorption isotherms at 77 K using Nova 2000e (Quantachrome Instruments, Boynton Beach, FL, USA). Water sorption experiments were performed on a VTI-SA Analyzer (TA Instruments, New Castle, DE, USA) – controlled relative humidity (RH%) was applied to dry samples and weight changes were measured gravimetrically. SEM observations were conducted at the Electron Microscopy Facility of Masdar Institute (Abu Dhabi, UAE) using a Quanta 250 SEM (FEI Company, Hilsboro, OR, USA). All samples were first quenched in liquid nitrogen for 5 min, cleaved and coated with fine film (5 nm) of gold palladium using PECS coating machine (Gatan Inc., Pleasanton, CA, USA) prior to imaging to reduce charging effects. SEM micrographs were processed and enhanced using Image J freeware (http://imagej.nih.gov/ij/) for quantitative measurement of pore size distribution (Supplementary Fig. S3).

3. Results

3.1. Composition analysis and pH

Proximate composition analysis of the raw materials and resulting biochars are presented in Table 1. Conversion of raw biomass to biochars resulted in higher contents of fixed carbon and ash, and lower contents of moisture and volatiles (Table 1). Comparison of the two biochars revealed that rhodes grass biochar has a higher content of fixed carbon, but lower contents of volatiles and moisture (56.6%, 11.8% and 1.8% wet wt. respectively) compared to date palm (45% and 43.2% and 4.8% wet wt., respectively). However, the