Waste Management xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Physical and chemical characterization of waste wood derived biochars

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ARTICLE INFO

Article history:
Received 21 May 2014
Accepted 23 October 2014
Available online xxxx

Keywords:
Biochar
Biomass pyrolysis
Carbon sequestration
PAHs
Heavy metals
Waste wood

ABSTRACT

Biochar, a solid byproduct generated during waste biomass pyrolysis or gasification in the absence (or near-absence) of oxygen, has recently garnered interest for both agricultural and environmental management purposes owing to its unique physicochemical properties. Favorable properties of biochar include its high surface area and porosity, and ability to adsorb a variety of compounds, including nutrients, organic contaminants, and some gases. Physical and chemical properties of biochars are dictated by the feedstock and production processes (pyrolysis or gasification temperature, conversion technology and pre- and post-treatment processes, if any), which vary widely across commercially produced biochars. In this study, several commercially available biochars derived from waste wood are characterized for physical and chemical properties that can signify their relevant environmental applications. Parameters characterized include: physical properties (particle size distribution, specific gravity, density, porosity, surface area), hydraulic properties (hydraulic conductivity and water holding capacity), and chemical and electrochemical properties (organic matter and organic carbon contents, pH, oxidation–reduction potential and electrical conductivity, zeta potential, carbon, nitrogen and hydrogen (CHN) elemental composition, polycyclic aromatic hydrocarbons (PAHs), heavy metals, and leachable PAHs and heavy metals). A wide range of fixed carbon (0–47.8%), volatile matter (28–74.1%), and ash contents (1.5–65.7%) were observed among tested biochars. A high variability in surface area (0.1–155.1 g/m^2) and PAH and heavy metal contents of the solid phase among commercially available biochars was also observed (0.7–83 $mg\ kg^{-1}$), underscoring the importance of pre-screening biochars prior to application. Production conditions appear to dictate PAH content – with the highest PAHs observed in biochar produced via fast pyrolysis and lowest among the gasification-produced biochars.

1. Introduction

Recent innovations in environmental applications have focused on improving environmental accountability, either through the use of more sustainable materials or better management practices, into project design and implementation. Biochar has been a widely researched material for its ability to be used in environmental management and soil improvement, and has shown promise as a sorbent for some environmental contaminants, including heavy metals (Park et al., 2011; Mohan et al., 2011; Reddy et al., 2014a), polycyclic aromatic hydrocarbons (Chen and Yuan, 2011; Chen et al., 2012), and other organic contaminants (Cao et al., 2009; Sun et al., 2011; Reddy et al., 2014a). Ongoing research indicates biochar may be a favorable landfill cover amendment for enhanced microbial methane oxidation due to its high internal microporosity, sorption properties, and stability in soil (Yaghoubi, 2011; Reddy et al., 2014b). Because biochar is often produced from waste biomass such as agricultural residues (e.g. corn stover, rice husks), scrap wood or other feedstocks (e.g. sewage sludge, poultry litter, dairy manure), biochar production and application is considered a sustainable process (Laird, 2008). Biochar amendment to soil is often deemed "carbon negative" as it can be considered as a mechanism to sequester organic carbon in vegetative biomass that would otherwise be discarded and released into the atmosphere as carbon dioxide (Spokas, 2010; Enders et al., 2012); thus the organic carbon is moved to a more slowly cycling reservoir (biochar) potentially for centuries.

Biochar has recently gained considerable interest for its potential use as a carbon sequestration agent and as a soil amendment for improved agricultural productivity (Lehmann et al., 2006; Shackley et al., 2013). Though demand for biochar in agricultural and environmental applications has increased in recent years, the

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http://dx.doi.org/10.1016/j.wasman.2014.10.029
0956-053X/

use of carbonized biomass (or 'black carbon') in agriculture is not new, with archaeological and geological evidence pointing to the use of charcoal for soil improvement by indigenous people several centuries earlier in the Amazon basin of Brazil (Glaser et al., 2001) and ancient Egyptian culture (Lucas et al., 1962). The Amazonian soils, known as Terra Preta, are rich in charred biomass and as a consequence have much higher fertility than surrounding soils lacking charred material, suggesting that the char may improve plant growth by furnishing the soil with additional organic matter and nutrients (Glaser et al., 2001). However, attempts to recreate these soils have largely been unsuccessful (Kookana et al., 2011), and results from field and laboratory studies on effects of biochars on agricultural productivity have been highly variable, with some studies reporting minimal and even negative effects from biochar addition (Spokas et al., 2012). To date, there is no known correlation between biochar properties and crop yield improvements (Crane-Droesch et al., 2013).

Given the many sources of feedstock that can be used to produce biochar and the availability of multiple production technologies, the physical and chemical properties of biochars used in these studies can vary tremendously, likely leading to the high variability observed in terms of their effects on soil fertility. Accordingly, attempts have been made to characterize the physical and chemical properties of biochars that are relevant for the targeted application in order to relate the type of source material and production method to the properties of the resultant char (Brewer et al., 2009, 2011; Singh et al., 2010; Peng et al., 2011; Fabbri et al., 2012; Kloss et al., 2012). Previous work has found that the physical and chemical properties of the source material, as well as the production conditions and post-production treatments applied, play a notable role in governing key functional properties of the resultant biochar, such as sorption characteristics, surface area, porosity and structural arrangement, surface charge and alkalinity, and organic carbon content (Brewer et al., 2009; Spokas et al., 2011; Uchimiya et al., 2011; Kloss et al., 2012). The amount of toxic constituents contained in biochars has also recently been investigated by several authors (Hale et al., 2012; Lucchini et al., 2013; Oleszczuk et al., 2013). In particular, PAHs are produced during incomplete combustion of biomass, and thus are inherently generated during biochar production. Due to their known toxicity and carcinogenic traits, the risk of leaching these toxins to the surrounding environment requires careful scrutiny prior to actual field application of biochars (Oleszczuk et al., 2014).

In addition to the original feedstock composition, key production parameters governing the resulting elemental composition are the temperature and duration of heat treatment. With increasing heat treatment temperatures, the degree of carbonization of biochar increases, resulting in decreasing H:C and O:C ratios and amorphous organic matter contents (Uchimiya et al., 2011; Spokas, 2010; Beesley et al., 2011). Increases in treatment temperature from 300 to 500 °C are also associated with a rapid loss of volatile matter (Keiluweit et al., 2010; Spokas, 2010). Volatile organic compounds tend to form cyclic, aromatic molecules as pyrolysis temperature increases, with condensation of smaller aromatics also occurring to generate larger aromatic structures (Keiluweit et al., 2010; Spokas, 2010). Once biomass is heated to approximately 400 °C, most oxygenated aliphatic functional groups are thermally degraded; at 500 °C, condensation reactions begin to take place (Keiluweit et al., 2010). High heat treatment temperatures as well as chemical activation of charred materials both increase the degree of aromatic condensation on the char surface (McBeath and Smernik, 2009). An increase in surface area with increasing pyrolysis temperature is also typically observed (Downie et al., 2009). Higher surface area in biochar has been associated with improved sorption of organic chemicals, such as pesticides and herbicides (Cabrera-Mesa and Spokas, 2011; Kasozi et al., 2010; Yu et al., 2009). By these mechanisms, bioavailability of these toxins can be reduced (Yu et al., 2009), which is one application of biochar for environmental remediation. However, strong sorption properties may be less desirable if biochar is applied for agricultural use, as herbicide efficiency may be impacted (Spokas et al., 2009; Nag et al., 2011; Graber et al., 2012). For example, Sun et al. (2011) found that biochars with the greatest amount of amorphous carbon (production temperature of 400 °C) also had the highest sorption affinities for fluorinated herbicides fluridone and norflurazon. They attribute the considerable increase in herbicide sorption from low to high temperature biochars to a concomitant increase in amorphous carbon content (Sun et al., 2011). Nag et al. (2011) also observed reduced herbicide effectiveness (by up to 3.5 times for atrazine) in soils amended with wheat straw biochar produced at 450 °C, indicating that increased herbicide application rates may be needed for biochar-amended soils. As a result of the varying properties and end uses of biochar, it is essential to characterize biochar properties prior to selecting a particular char for a specific application.

Research regarding the physical and chemical properties of biochars has responded to increased interest in biochar amendments for environmental applications. Design of biochars for targeted applications calls for employing suitable feedstock and conversion technologies that are capable of producing biochars with desired physical–chemical properties. Several researchers have characterized the physicochemical properties of laboratory-produced biochars with respect to source materials and pyrolysis technology employed (Brewer et al., 2009; Lee et al., 2010; Koide et al., 2011; Kloss et al., 2012). However, limited studies have emphasized characterizing commercially-available biochars, which often have distinct properties from those that have been produced under controlled laboratory conditions (Spokas and Reicosky, 2009). In this study, six biochars produced commercially using waste wood are characterized relative to a manufactured granular activated carbon (GAC) to provide further insight on the effects of production and post-production processes on relevant physicochemical properties of commercial, wood-derived biochars in order to assess their suitability for use in environmental applications.

2. Materials and methods

Six different wood-derived biochars and granular activated carbon (GAC) were obtained from commercial vendors and selected for detailed characterization tests as outlined in Fig. 1. Biochars were selected based on local availability and potential for use in large-scale applications; a photo of each tested biochar is shown in Fig. 2. Table 1 summarizes the feedstock sources, production processes and conditions, and type of post-treatment applied (if any) for each of the studied biochars. In addition to physical and chemical characterization, both the total and leachable PAHs and heavy metals of biochars and GAC were determined in order to assess the total and leachable amounts of toxic constituents in the selected wood-derived biochars. All characterization tests were performed using each biochar obtained as received from the vendor unless otherwise stated.

2.1. Particle size distribution, specific gravity and dry density

Particle size distribution and specific gravity of dry biochar samples were characterized according to ASTM D 422 and ASTM D 854, respectively. Dry density was determined using the Harvard miniature compaction test setup (Humboldt Mfg. Co.) according to the suggested test method described by Wilson (1970). After weighing the empty Harvard miniature mold, it was filled with the dry biochar sample in three uniformly spaced layers with five compaction strokes per layer. Once filled, the biochar samples

Please cite this article in press as: Yargicoglu, E.N., et al. Physical and chemical characterization of waste wood derived biochars. Waste Management (2014), http://dx.doi.org/10.1016/j.wasman.2014.10.029