Waste Management 78 (2018) 198–207

Contents lists available at ScienceDirect

Waste Management

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

Thermogravimetric, thermochemical, and infrared spectral characterization of feedstocks and biochar derived at different pyrolysis temperatures

Simeng Li *, Gang Chen

Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering, 2525 Pottsdamer Street, Tallahassee, FL 32310, USA

ARTICLE INFO

Article history:
Received 16 January 2018
Revised 22 May 2018
Accepted 25 May 2018

Keywords:
Biochar characterization
Thermogravimetric analysis
Thermochemical analysis
Fourier-transform infrared spectroscopy (FTIR)
Carbon sequestration
Cost analysis

ABSTRACT

Biochar is a promising biomass product for soil amendment, remediation, and carbon sequestration. In this study, the effect of pyrolysis temperature and feedstock type on biochar physiochemical properties including stability, recalcitrance, and surface functionality were investigated through thermogravimetric, thermochemical, and infrared spectral analyses. It is concluded in this research that pyrolysis temperature was the dominating factor determining the inherent characteristics of the derived biochar. High-temperature pyrolysis (≥600 °C) derived the biochar with a high pH, stability, recalcitrance, and higher heating value (HHV). On the other hand, the biochar produced from low-temperature pyrolysis (≤400 °C) had a larger mass yield, energy recovery, more volatile content, and diverse surface functional groups. The different biochar characteristics will lead to different agricultural and environmental applications. Also in this research, a carbon-based recalcitrance index ($R_{50,C}$) based on a novel multi-element scanning thermal analysis (MESTA) was proposed to improve the current recalcitrance index (R_{50}) based on the conventional thermogravimetric analysis (TGA) for the evaluation of biochar's carbon sequestration potential. The direct comparison of the two indexes, as well as the results from the infrared spectral analysis and ultimate analysis, indicated that $R_{50,C}$ was better at characterizing biochar's recalcitrance, especially when the mineral content of the feedstock was high. In addition, the cost breakdown indicated that the pretreatment of feedstock was the costliest process during biochar production.

1. Introduction

Biochar is the solid product of biomass from oxygen-limiting or oxygen-absent pyrolysis and its field applications can contribute significantly to carbon sequestration (Hangs et al., 2016) and soil fertility improvement (Lusiba et al., 2017). As a soil amendment, biochar has an enduring ability to improve soil physical and chemical properties by optimizing soil pH (Agegnehu et al., 2015), soil water retention (Uzoma et al., 2011), nutrient retention, ion exchange capacity (Novak et al., 2009), water infiltration and nitrogen use efficiency (Rogovska et al., 2014). The use of biochar and compost in combination has also been reported to significantly benefit soil fertility, improve crop yields and help mitigate greenhouse gas emissions in certain systems (Agegnehu et al., 2016). The greatly enhanced compost quality with the addition of biochar is believed to be a promising solution to the dilemma of the current compost business aching for low-quality products (Marousek et al., 2016). In addition, a number of studies have investigated the alternation of soil biogeochemistry by biochar field applications (Ahmad et al., 2014; Lehmann et al., 2011), including the decontamination of pollutants such as heavy metals (Melo et al., 2013; Woldetsadik et al., 2016), pesticides (Khorram et al., 2016), and hydrocarbons (Anyika et al., 2015). The effectiveness of the diverse biochar field applications depends on its physiochemical properties, which are determined by the pyrolysis conditions (e.g., heating temperature, heating rate, and duration) (Ashworth et al., 2014) as well as the composition of the original feedstock (Jindo et al., 2014; Mohanty et al., 2013).

During the production of biochar, pyrolysis temperature plays a key role in the thermochemical conversion of biomass (Angin, 2013). The biochar derived from relatively high-temperature pyrolysis is more depleted of H and O but possesses a larger proportion of aromatic C in comparison with that from a lower temperature (Heitkotter and Marschner, 2015). Consequently, biochar derived from by high-temperature pyrolysis has greater chemical recalcitrance and resistance to microbial and chemical decomposition in soil. This makes it more suitable for carbon

---

* Corresponding author.
E-mail address: sl16b@my.fsu.edu (S. Li).

https://doi.org/10.1016/j.wasman.2018.05.048
0956-053X/© 2018 Elsevier Ltd. All rights reserved.

sequestration (Woolf et al., 2010). Intensified thermochemical decomposition at higher pyrolysis temperatures also results in greater electrical conductivity and higher pH (Novak et al., 2009). In general, high-temperature biochar is usually characterized by porous structures with a high surface area, which increase the adsorption capacity for the retention of moisture and nutrients in soil as well as microorganisms (Uzoma et al., 2011). In contrast, the biochar derived from low-temperature pyrolysis has been reported to have a high content of volatile matter, which is easily decomposable and favors plant growth (Mukherjee and Zimmerman, 2013). The currently high biochar pricing (typically 250 USD/t in 2015) is considered the major barrier for its application being profitable in conventional farming (Marousek et al., 2017). When a relatively low pyrolysis temperature is used for the production, the yield of biochar can be significantly higher with most feedstocks (Angin, 2013), which is desirable for the cost reduction and commercialization of biochar products.

Various types of feedstocks, such as oak wood, rice husk (Jindo et al., 2014), broiler litter (Ahmad et al., 2014), and livestock manures (Cantrell et al., 2012), have been used to synthesize biochar for diverse applications. Because of the different characteristics of the feedstocks, contrasting properties of the derived biochar have been observed under the same pyrolysis conditions. For instance, the biochar obtained from wood materials showed a better adsorption character than the biochar derived from rice materials, while the rice material biochar showed a higher yield and unique chemical properties as a result of the carbon encapsulation by the presence of silicon (Jindo et al., 2014). In addition, the biochar derived from manure or crop residue feedstocks had better ability to promote soil microbial abundance than that of wood and other lignocellulosic-rich feedstocks (Gul et al., 2015). Research has also demonstrated that not all biochar has the capacity to improve soil fertility (Gaskin et al., 2010; Van Zwieten et al., 2010). In addition, there are significant differences in the stability of biochar (Joseph et al., 2010). In practice, different biochar properties are needed depending on the soil and crop conditions (Van Zwieten et al., 2010). To meet the specific soil and management requirements, the physiochemical properties of the biochar derived from different feedstocks and pyrolysis conditions need to be fully characterized.

Many characterization approaches, such as thermogravimetric analysis (Chen et al., 2012), infrared analysis (Chia et al., 2012), and microscopic analysis (Jaafar et al., 2015), have been previously utilized to explore the biochar properties. Thermal analysis is a useful method to evaluate the pyrolytic characteristics and thermochemical properties of biochar (Jindo et al., 2014). Using a thermogravimetric analyzer (TGA) with differential scanning calorimetry (DSC) detector and a pack bed, together with on-line gas measurement using Fourier-transform infrared (FTIR) spectroscopy, the composition of hemicellulose, cellulose, and lignin in biomass is able to be characterized along with the gas products from the biomass pyrolysis (Yang et al., 2007). However, thermogravimetric analysis is based on the weight loss and heat transfer of material, thus the derivative difference peaks of each specific element (e.g., C or N), which are important for biochar characterization, are not available. The novel multi-elemental scanning thermal analysis (MESTA) method can be an alternative because the derived scanning thermograms are element-specific as the signals are processed by separate detectors (Hsieh, 2007). Similarly, chemical functionality and mineralogy of biochar can be analyzed according to their FTIR spectra (Chia et al., 2012; Jindo et al., 2014). However, due to the existence of a variety of mineral phases, various chemical bonds in a sample can be reflected by the complex infrared spectrum (Chia et al., 2012). The opacity of biochar samples is another significant challenge for FTIR analysis if samples are not finely ground. Using ATR techniques or measuring transmission of infrared light through a KBr disc can help improve the signal-to-noise for better spectral quality, but at the cost of spatial information (Wolkers et al., 2004). None of the above characterization methods are flawless, and therefore, a comprehensive comparison of different methods is required to fully characterize biochar.

The objectives of this study were to assess the various characteristics of biochar as a function of feedstock type and pyrolysis temperature and conduct a self-fulfilling discussion on the agronomic value and stability properties of the biochar based on biochar characterization. For quality control, the biochar was produced in a bench-scale reactor under controlled conditions using different feedstocks. The feedstocks and resulting biochar were thereafter analyzed via TGA, MESTA and FTIR. In addition, using the MESTA method, a carbon-based recalcitrance index was proposed in awareness of the drawbacks of the current TGA-derived recalcitrance index (Harvey et al., 2012) for the evaluation of biochar's carbon sequestration potential. It was hypothesized that the proposed carbon-based recalcitrance index would avoid being affected by the high mineral content of biochar, thus being more unbiased than the current recalcitrance index. Furthermore, it was anticipated that consistent conclusions could be drawn from the results of ultimate analysis and FTIR to support the proposed index.

2. Materials and methods

2.1. Biochar feedstock and production

Three different types of feedstocks were used to produce the biochar in this study: switchgrass (SG), water oak wood (WO), and biosolid (BS). The switchgrass was a perennial lowland species (*Panicum virgatum*) prevalent in Florida. The feedstock samples were dried at 60 °C for 48 h before being chopped into 1–2 cm chunks. The preparation of water oak (*Quercus nigra*) samples followed the same procedure as that of switchgrass. The biosolid (sludge), which was obtained from Thomas P. Smith Water Reclamation Facility (Tallahassee, FL), was dried at 60 °C until no significant weight change was observed. It was then crumbled to pieces of 1–2 cm in size.

The biochar was produced through slow pyrolysis under pure N_2 gas (purity > 99.99%) at 200, 400, 600, and 800 °C in a bench-scale pyrolysis apparatus described in a previous study (Li et al., 2018). About 7 g of the preprocessed feedstock was centered into a quartz tube (inner diameter: 2 cm, length: 45 cm). The quartz tube was fitted with airtight connectors, maintained absent of O_2 with continuous N_2 gas purge (80 mL/min), and heated in a controllable S-line single-zone split tube furnace (Thermcraft Inc., Wiston-Salem, NC) at a heating rate of 10 °C/min until the desired temperature and was held at the final temperature for 60 min. To prevent rapid oxidation and auto-ignition, the quartz tube was N_2 purged throughout the heating and cooling processes. The biochar yield was estimated as the proportion of solid product to the original feedstock (wt/wt). The feedstock and the produced biochar were finely ground using a pestle and mortar, sieved through a 0.5-mm mesh, and stored in sealed scintillation vials in a desiccator to prevent moisture absorption, respectively.

2.2. pH and volatile content

The feedstock and biochar were first mixed with deionized water following a weight-to-volume ratio of 1:10 (Jindo et al., 2014) and agitated for 2 h prior to pH measurement. The pH of