Journal of Analytical and Applied Pyrolysis 108 (2014) 301–309

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Production and characterization of biochars from agricultural by-products for use in soil quality enhancement

D. Rehrah[a], M.R. Reddy[e], J.M. Novak[d], R.R. Bansode[b], K.A. Schimmel[f], J. Yu[c], D.W. Watts[d], M. Ahmedna[a,*]

[a] Department of Health Sciences, College of Arts and Sciences, Qatar University, Doha, Qatar
[b] Center for Excellence in Post-Harvest Technologies, North Carolina Agricultural and Technical State University, North Carolina Research Campus, 500 Laureate Way, Suite 4222, Kannapolis, NC 28081, USA
[c] Department of Family and Consumer Sciences, North Carolina Agricultural and Technical State University, 1601 East Market Street, Greensboro, NC 27411, USA
[d] USDA-ARS, Coastal Plains Research Center, 2611 West Lucas Street, Florence, SC 29501, USA
[e] Department of Natural Resources and Environmental Design, North Carolina Agricultural and Technical State University, 1601 East Market Street, Greensboro, NC 27411, USA
[f] Department of Energy & Environmental Systems, North Carolina Agricultural and Technical State University, 1601 East Market Street, Greensboro, NC 27411, USA

ARTICLE INFO

Article history:
Received 10 July 2013
Accepted 7 March 2014
Available online 24 April 2014

Keywords:
Agricultural by-products
Pyrolysis
Biochar
Physicochemical characteristics

ABSTRACT

Byproducts are produced in significant amounts from crop residues such as pecan shells (PC), peanut shells (PS), and cotton gin (CG) trash. These residues can be used to produce biochar suitable for use in agricultural soil to sequester carbon and enhance plant growth by supplying and retaining nutrients while improving soil physical and biological properties. The objectives of this study were to produce biochars from different byproducts [PC, PS, CG, and switchgrass (*Panicum virgatum* L.)] at different pyrolysis temperatures and residence times, and to evaluate the resulting biochar's physico-chemical properties [yield, ash, pH, total surface area (TSA), surface charge (SC), and electrical conductivity (EC)] and elemental composition. Feedstocks were pyrolyzed under N_2 at 3 temperatures (300, 500, and 750 °C) and residence times each (8, 16, and 24 h), (4, 8, and 12 h), and (1, 2, and 3 h), respectively, depending on the nature of the feedstock. Higher pyrolysis temperatures resulted in lower biochar recovery, greater TSA, higher pH, minimal SC, and higher ash contents. Among the eight biochars, switchgrass-derived biochar produced at 750 °C had the highest TSA (276 $m^2 g^{-1}$) followed by PC biochar (185 $m^2 g^{-1}$). Substantial increase in biochar pH (up to 9.8) occurred at the higher temperatures. Biochars produced at lower temperatures (350 °C) had measurable SC with PS biochar having the highest value (3.16 mmol H^+ eq g^{-1} C). The highest ash content was observed in CG (up to 34%) compared to other biochars which contained <10% ash. These soil-related properties suggest that different biochars types can be produced to selectively improve physicochemical properties of soil through selection of specific feedstocks and pyrolysis conditions.

1. Introduction

The production and processing of various agricultural commodities yield significant amounts of by-products in the form of crop residues such as nutshells, cotton gin, corn cobs, sugarcane bagasse, rice hulls, and straws, etc. Many of the agricultural residues can be used to produce biochar for its use in agricultural soil applications with the double advantage of sequestering carbon (improve soil structure, nutrient retention, and pH) and increasing the crop productivity [1,2]. In many cases, these agricultural by-products are left as waste materials with little or no economic value while their disposal is sometimes costly and may cause environmental issues. For instance, large amounts (more than 50% of total available agricultural residues in the United States) can be acquired between $40 and $60 per Mg of biomass [3].

Conversion of low value and underutilized agricultural by-products and high volume/low cost industrial biomass (e.g., switchgrass) is ecologically and economically attractive given the fact that energy can be produced at the same time as biochar. Some crop residues such as nut shells (e.g., groundnut, hazelnut, walnut,

Abbreviations: PC, pecan shells; PS, peanut shells; CG, cotton gin; TSA, total surface area; EC, electrical conductivity.

* Corresponding author. Tel.: +974 4403 4848.
E-mail address: ahmedna@qu.edu.qa (M. Ahmedna).

http://dx.doi.org/10.1016/j.jaap.2014.03.008
0165-2370/

chestnut, and coconut), bagasse from sugarcane processing, olive or tobacco waste are particularly suitable as precursors for biochar and are often available in large quantities in some locations [4].

Land application of biochar is not a new concept since certain dark earths in the Amazon Basin (so-called Amazonian Dark Earths or "terra preta") are well known as early applications of biochar for soil enhancement. The dark earths result from large amounts of charred materials from biomass burning [5]. These early biochars applications were most likely the result of both habitation activities and deliberate soil application by Amerindian populations before the arrival of Europeans [6].

Today, the emerging interest in the application of biochar to soil is driven by many considerations including environmental sustainability benefits. It is considered as a novel approach to establish a significant and long-term sink for atmospheric CO_2 in terrestrial ecosystems while reducing the need for synthetic fertilizers, and economic benefits through value-added to agricultural production system and higher crop yield resulting from improved soil fertility. In fact, recent studies in the field suggest that the production of biochar and its application to soil can deliver immediate benefits through improved soil fertility and increased crop production [7–9].

Conversion of biomass carbon to biochar carbon leads to sequestration of about 50% of the initial carbon compared to the low amounts retained after burning (3%) and biological decomposition (<10–20% after 5–10 years). Hence, production of biochar yields more stable soil carbon than burning or direct land application of biomass [4].

In a well managed system, biochar could become a key component for a doubly green revolution (sustainable food production and land degradation prevention) while offering one of the best practical ways to counter global warming (GHGs reduction) and counter pollution of streams and groundwater [10].

Many studies have been conducted on the pyrolysis of biomass residues for biochar production [11–13]. However, comparison of the properties of biochars obtained from different biomass residues produced under similar pyrolysis conditions has received limited attention in the literature.

Therefore, this research effort was undertaken to produce agricultural byproducts-based biochars from different biomass residues and compare their potential in soil applications to enhance soil quality, improve plant growth, and help decrease GHGs emissions. The specific objectives of this study were to (1) produce biochars from different byproducts (pecan shell, peanut shell, cotton gin) and switchgrass (a high yield and low cost forage crop) at different pyrolysis temperatures and residence times, and (2) determine specific physicochemical and surface properties of the resulting biochars that serve as predictors of their suitability in soil quality enhancement applications.

2. Materials and methods

2.1. Preparation of biochars

Four agricultural byproducts (pecan shells, peanut shells, cotton gins) and a high yield forage crop (switchgrass) were used as feedstocks to produce biochars. These residues were chosen due to their common and wide availability in the southeast region of the U.S.A. Pecan shells were obtained from Carolina Grains, Lumberton, North Carolina, and peanut shells from Golden Peanuts Company (Alpharetta, GA, USA). Cotton gin and switchgrass were obtained from the USDA-ARS Coastal Plain Research Center, Florence, South Carolina, where cotton, soybeans, and switchgrass were grown for research purposes.

The four precursors were dried overnight at 60 °C using a laboratory oven (Fisher Scientific, USA). The peanut and pecan shells were used as received without any further treatment while the cotton gin and switchgrass were cut into pieces of 0.1 cm long before pyrolysis. A Lindberg box high temperature furnace equipped with a retort (model 51668HR; Lindberg, Watertown, WI) was used for pyrolysis. The sealed furnace retort was purged using N_2 prior to initiation of pyrolysis to prevent carbon losses due to oxidation.

A 4 × 3 factorial design with nested residence time within pyrolysis temperature was used in this study with the first factor consisting of four different agricultural precursors (three feedstocks: cotton gin, peanut and pecan shells, and one forage crop: switchgrass), and the second factor consisting of 3 sets of pyrolysis temperatures (300, 500, and 750 °C) and 3 sets of pyrolysis residence time [(8, 16, and 24 h for 300 °C), (4, 8, and 12 h for 500 °C), and (1, 2, and 3 h for 750 °C)]. The choice of this nested design was based on previous results obtained from preliminary range finding experiments conducted in our laboratory in which we observed that no biochar remained when high temperatures were used along with long residence time, especially for soft materials. To account for these observations, we opted to use longer residence time at lower temperatures for soft materials like switchgrass and cotton gin. Hard materials like pecan shells allowed the use of high temperature and short time. Feedstocks were pyrolyzed following the above design under N_2 gas at a flow rate of 0.1 mL min^{-1} using a Lindberg box programmable furnace equipped with retort. Mass yield for biochar recovery was calculated using the following equation [14]:

$$\text{Mass yield}\,(\%) = \left[\frac{W_f}{W_0}\right] \times 100 \quad (1)$$

where W_f is the dry mass (g) of the produced biochars and W_0 is the dry mass (g) of the precursors.

2.2. Measurement of biochars properties with relevance to soil applications

Physical (surface area) and chemical (ash content, pH, surface charge, electrical conductivity, and total elemental analysis) properties of biochars were determined according to the procedures described in previous studies [15–17]. The total elemental analysis was determined using standard EPA method (EPA SW 846 Method 3050B; EPA, 1989) with minor modifications [18].

2.2.1. Ash content

Pre-weighed ceramic crucibles containing approximately 2 g of oven dried biochar were used to measure the ash content of the biochars. The samples were heated in a laboratory muffle furnace (Fisher Scientific, USA) at 760 °C for at least 6 h. After cooling, the remaining solids (ash) were weighed [17]. The percent ash content was calculated as follows:

$$\text{Ash}\,(\%) = \left[\frac{\text{remaining solids wt(g)}}{\text{original carbon wt(g)}}\right] \times 100 \quad (2)$$

2.2.2. pH measurement

The pH measurements of biochar were determined using the method described by Ahmedna [15]. A 1% (w/w) water suspension of each type of biochar was heated to approximately 90 °C and stirred for 20 min then allowed to cool to room temperature before pH measurement with a Corning pH 10 portable pH meter (Acton, MA). The pH meter was calibrated with standard pH 4 and pH 7 buffers [17].