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Physicochemical properties of biochar derived from anaerobically digested dairy manure

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ABSTRACT

Biochar was produced from anaerobically digested dairy manure under different processing temperatures (300, 600 and 1000 °C). The process could transform the biomass waste to high-value-added biochar products in high efficiency as well as reduce the manure biological pollution to the environment. By the results of thermogravimetric analysis (TGA) two kinetic models (FWO and Starink) were used to evaluate the activation energy. The biochar was studied for its surface area and pore size, chemical functionality, and crystalline structure by BET analysis, Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD). More porous and channel structures were observed under higher temperature and inert gas atmosphere, as characterized by scanning electron microscopy (SEM). The biochar with tunable physicochemical properties that was produced under different temperatures may be used for soil amendment or other fields.

1. Introduction

Biochar (BC) is a solid carbon-rich black material obtained from the carbonization of biomass (Mohan et al., 2014). It has been reported that the application of biochar as soil amendment can significantly ameliorate agricultural productivities by preventing loss of nutrients, chemicals and water (Chan et al., 2007). In addition, the biochar also has great potential in climate change mitigation. Due to its highly recalcitrant nature, the biochar can act as a modifier or a carbon absorbent to quench carbon, therefore, it is able to reduce the atmospheric carbon dioxide concentration, (Woolf et al., 2010). Furthermore, the biochar is considered asan alternative sorbent for activated carbon or other water purifiers to treat heavy metals in wastewater (Inyang et al., 2012). Meanwhile, the commonly applied processes for biochar production also generated coproducts, including oil and gas that can be used for valuable fuels and chemicals generation (see Table 1).

Over 500 million tons wet dairy manure was created in the United States of America annually (Coats et al., 2011). These waste deposits exhibit serve environmental concerns such as odors, greenhouse gas emission, water pollution, and soil contamination etc. Anaerobic digestion (AD) of dairy manure is one of the most efficient waste management methods that are adapted to produce significant amount of methane and to reduce solid volume. Despite of the efficiency of AD method, the effluents from AD facilities still contain recalcitrant grassy materials that consist of 25–50% cellulose, 20–25% hemicellulose, 10–15% lignin, and 10–20% ash (Spelter et al., 2008). These indigestible wastes hold additional potential for further thermochemcial conversion into valuable products. The biochar production from a variety of biomass materials, including pine, willow, miscanthus, chestnut shell, grape seed, potato peel, and anaerobically digested swine and sugarcane bagasse, have been extensively studied and reviewed (Maroušek, 2014b). For application, there're some new ideas in reducing the nitrate level of plant or in the cultivating method (Maroušek et al., 2017, 2018). This is the first research to study the biochar production from anaerobically digested dairy manure under different temperatures. This study/communication aims to characterize the physicochemical properties of the biochar products from anaerobically digested dairy manure, and the results can provide insights for scientists and engineers on the closed loop management of diary manure waste. It also support to have good potential in adsorption and holding substance, which can be used in many fields.

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Table 1
The Biochar yield and ash content under different process situations.

	BC yield	Ash
Biomass	–	11.0%
BC-300	72.6%	14.9%
BC-600	50.1%	32.2%
BC-1000	43.3%	33.9%

2. Materials and methods

2.1. Biochar production

The anaerobically digested dairy manure samples were collected from a local AD facility in Wisconsin. Firstly, the samples were dried in an oven and were passed through a Wiley mill with 80-mesh sieve prior to use. Subsequently, the biochar production was conducted in a tubular pyrolyzer under the program that raises the temperate at rate of 10 °C min^{-1} from ambient temperature to the preset temperature of 300, 600 and 1000 °C, respectively. A continuous supply of nitrogen purge was applied to keep the biochar production under oxygen-free condition. The reaction was equilibrated at desired reaction temperature for 1 h, followed by quenching reaction on ice bath and cooling down the system to the ambient temperature. Finally, the biochar yield was calculated and its properties were further analyzed according to the procedures described below.

2.2. Biochar characterization

2.2.1. Ash content

The approximate analysis of ash content, fixed carbon, and unstable matters from biomass and biochar samples was performed according to the standard methods of ASTM E870-82. The ultimate analysis was measured using a CE-440 elemental analyzer, and the O was determined by weight difference of C, H, N, and ash content from 100%.

2.2.2. Thermogravimetric analysis (TGA)

The TGA of biomass was conducted by using a method as follows: TGA-9 (PerkinElmer) instrument using a temperature program of 30 to 900 °C at a heating rate of 10, 20, 30, and 40 K min^{-1} under N_2 (30 mL min^{-1}). TGA and differential thermogravimetry (DTG) data were analyzed using Pyris v8 software.

2.2.3. Kinetic modelling

The decomposition rate kinetic equation of solid-state may be expressed as a product of Arrhenius expression and a function of the extent of conversion.

Follow the derivation process by Balogun et al. (2014), the FWO expression could be given as Eq. (1):

$$\log \beta = \log \frac{AE}{g(\alpha)R} - 2.315 - 0.457\frac{E}{RT} \quad (1)$$

Flynn gave iso-conversional lines whose slopes can be calculated from Eq. (2) by a series of TGA experiments.

$$\text{Slope} \cong 0.457\frac{E}{R} \quad (2)$$

Thus, the E at each conversion step can be evaluated from the plot of log β against the reciprocal of absolute temperature. To reduce the error introduced by Doyle's approximation, an iterative procedure was used to obtain the final value of Arrhenius E. (Balogun et al., 2014; Flynn, 1983; Standard, 2007).

Kissinger-Akhira-Sunose (KAS) method and FWO method were examined by Starink and both could be expressed as Eq. (3)

$$\ln\left(\frac{\beta}{T^s}\right) = C_s - \frac{BE}{RT} \quad (3)$$

Starink's method was reported more accurate than the other two iso-conversional methods (Starink, 1996). It can be expressed as Eq. (4)

$$\ln\left(\frac{\beta}{T^{1.8}}\right) = C_s - 1.0037\frac{E}{RT} \quad (4)$$

A plot of $\ln\left(\frac{\beta}{T^{1.8}}\right)$ against reciprocal of absolute temperature gives a straight line of which the slope corresponds to $-1.0037\frac{E}{RT}$. And the E can be calculated from the slope of the graph (Balogun et al., 2014).

2.2.4. Fourier transform infrared (FTIR)

The FTIR analyses was carried out to characterize the surface functional groups using a Thermo Nicolet iZ10 FTIR spectrometer with an attenuated total reflection (ATR) probe and a smart iTR Basic accessory (Thermo Scientific, Verona, WI). The absorbance spectra were obtained with 128 scans in the range of 4000–600 cm^{-1} with the resolution of 4 cm^{-1}. Samples were measured in triplicate, spectra averaged, and ATR and baseline corrected using Omnic V9.0 software.

2.2.5. X-ray diffraction (XRD)

The XRD analysis was performed on a wide angle XRD spectroscopy (D8 Discover diffracrometer, Bruker AXS Inc, WI) for crystallographic structure. The crystalline compounds in the samples were identified by comparing diffraction data against a standard database.

2.2.6. Scanning electron microscopy (SEM)

The morphology studies were conducted with a higher magnification by field emission scanning electron microscopy (LEO Gemini) at 3.5–5.0 KeV after a light gold and carbon coating.

2.2.7. Surface area and total pore volume (V_T)

The specific surface area of the biochar (0.10 g, in duplicate) was determined by N_2 and CO_2 (g) adsorption using a TriStar II plus automatic physisorption analyzer (Micromeritics Instrument Corporation). Before analysis the sample was vacuum degassed for 10 h at 200 °C. N_2 isotherms were collected at 77 K and a partial pressure range of 0.0001–0.99, within this range 50 absorption and 35 desorption points were specified to fully resolve the isotherm. CO_2 isotherms were collected at 273 K and a partial pressure range of 0.00001–0.03 with 75 points specified for the absorption isotherm. BET analysis was used to determine the apparent surface area (SA) from the N_2 isotherm using data from points collected at partial pressures between 0.001 and 0.1. SA, micropore volume (V_{mi}), and average pore width (W_{avg}) were determined by the Dubinin–Radushkevich (DR) equation fit to data points between $2 < \log_2 / (P_0/P) < 6$ for both N_2 and CO_2 isotherms. W_{avg} was calculated from the characteristic binding energy (E_0) given by the DR equation.

Total pore volume (V_T) was determined from the maximum adsorption quantity at a partial pressure of approximately 0.99 for the N_2 isotherms. Total mesopore volume (V_{me}) was determined by subtracting the micropore volume determined by N_2 from V_T.

3. Results and discussion

3.1. TG kinetic study of digested manure biomass

Thermal degradation behavior including pyrolysis temperature and decomposition kinetics of biochar was conducted using