Bioresource Technology 130 (2013) 345–350

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1

Yongwoon Lee [a], Pu-Reun-Byul Eum [a], Changkook Ryu [a,*], Young-Kwon Park [b], Jin-Ho Jung [c], Seunghun Hyun [c]

[a] School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea
[b] Faculty of Environmental Engineering, University of Seoul, Seoul 130-743, Republic of Korea
[c] Division of Environmental Science and Ecological Engineering, Korea University, Seoul 136-713, Republic of Korea

HIGHLIGHTS

- Geodae-Uksae 1 (Giant *Miscanthus*) is a variety of *Miscanthus sacchariflorus* for energy crop.
- Ideal temperature to produce biochar by slow pyrolysis was 500 °C.
- The biochar had a mass yield of 27 wt.% at 500 °C with a carbon content of 79 wt.%.
- The surface area and large pores of biochar was well-developed at 500 °C for application to soil.

ARTICLE INFO

Article history:
Received 30 March 2012
Received in revised form 2 December 2012
Accepted 5 December 2012
Available online 13 December 2012

Keywords:
Biochar
Biomass
Geodae-Uksae 1
Miscanthus
Slow pyrolysis

ABSTRACTS

This study investigated producing biochar from Geodae-Uksae 1 for soil applications to sequestrate carbon from the atmosphere and improve the productivity of crops. Using a lab-scale packed bed reactor, pyrolysis products of Geodae-Uksae 1 were produced over a temperature range of 300–700 °C with a heating rate of 10 °C/min. Pyrolysis at 500 °C was found appropriate for biochar production considering the properties of char and the amount of heat required. It yielded biochar of 27.2 wt.% that contained approximately 48% carbon in the raw biomass. The surface area of the biochar rapidly increased to 181 m^2/g. Large cylindrical pores with diameters of 5–40 μm developed within the biochar due to the vascular cell structure of the parent biomass. The byproducts (bio-oil and gases) were also analyzed for use as fuel.

1. Introduction

Geodae-Uksae is the Korean term for giant *Miscanthus*. Geodae-Uksae 1 is a variety of *Miscanthus sacchariflorus* (Amur silvergrass) recently discovered in Korea (Moon and Koo, 2011) that grows approximately 4 m tall with an average stalk diameter of 1 cm, which is approximately twice as tall and thick as common *M. sacchariflorus*. The mass yield of the dry stalk is as much as 30 ton/ha, which is twice that of common *Miscanthus*. Due to the superior yield, Geodae-Uksae 1 is being mass-cultivated in Korea as an energy crop for bioenergy. Various methods are being considered for the energy conversion of Geodae-Uksae 1, including hydrolysis and fermentation for bioethanol production, combustion through pelletization and fast pyrolysis for the production of bio-oil.

This study investigates a method for producing biochar from Geodae-Uksae 1 for the sequestration of carbon in soil and to increase the productivity of various food crops (Lehmann, 2007). Biochar is the highly carbonaceous solid product of the pyrolysis of biomass, which can be used to improve the yield of various agricultural crops as a soil amendment. Due to its strong resistance to biological decomposition, the carbon in biochar can be removed from the atmosphere to mitigate climate change. Since carbon originates from atmospheric carbon dioxide, the application of biochar to soil may contribute to reductions of CO_2 concentration. Biochar has been used in horticulture and agriculture with its appearance in literature as early as 1697 (Lehmann and Joseph, 2009). Biochar has drawn interest from a wider scientific community due to a study by Lehmann et al. (2003) examining the sustained fertility of Amazonian dark soil, also known as Terra Preta. When applied to soil, biochar can effectively retain nutrients and water, and therefore reduce the need for fertilizers. In addition to carbon removal, biochar in soil reduces the emissions of other major greenhouse gases, such as N_2O and CH_4 (Van Zweiten et al., 2009), which have a global warming potential of 298 and 25, respectively, compared to the greenhouse effect of CO_2 over a 100 year period (IPCC, 2007). These

* Corresponding author. Tel.: +82 31 299 4841; fax: +82 31 290 5889.
E-mail address: cryu@me.skku.ac.kr (C. Ryu).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.12.012

benefits suggest that the application of biochar from biomass to soil could be as effective as producing energy from the valuable resource. Depending on the type of biomass, the amount of biomass available for energy production widely varies by location and time of year. Due to its typically low bulk density, it is sometimes not economical to collect and transport biomass to a large-scale bioenergy plant. In contrast, biochar that is locally produced by a small-scale pyrolysis unit can be consumed locally, minimizing transport needs.

Slow pyrolysis is an ideal technology to produce biochar, which involves thermal decomposition in an inert atmosphere at a slow heating rate (~10 °C/min) (Mohan et al., 2006). Pyrolysis converts solid fuels, such as coal and biomass, into char (solid), vapors of condensable hydrocarbons (called 'oil' for use after condensation) and non-condensable gases (e.g., CO, CO_2, H_2 and CH_4). Biochar, or char originating from biomass, is typically 20–40 wt.% of dry lignocellulosic biomass. However, the yield and characteristics of the pyrolysis products are strongly influenced by the operating conditions (e.g., temperature, heating rate, pressure, purge gas and particle size) and the properties of the feedstock (Antal and Grønli, 2003; Enders et al., 2012). Therefore, the operating conditions of the pyrolysis process can be adjusted to meet the product requirements, however the actual process needs to be carefully designed and performed.

In this study, Geodae-Uksae 1 was pyrolyzed in a lab-scale reactor to investigate the yield and properties of biochar for applications to soil. Biochar was produced by slow pyrolysis at a temperature of 300–700 °C and characterized for elemental composition, morphology, surface area and distribution of pore sizes and volumes. The byproducts of pyrolysis, i.e., bio-oil and gases, were analyzed for further use as energy sources.

2. Experimental

2.1. Geodae-Uksae 1 samples

Geodae-Uksae 1 samples were provided by the Korean Rural Development Administration (RDA), which discovered and cultivated the strain. Geodae-Uksae 1 was harvested in the second year of planting, in early spring of 2011. Late winter or early spring is suitable for harvest since the moisture content of the crop naturally drops at that time (Lewandowski et al., 2000; Fernando et al., 2008). The nutrients in the plant are transported in winter and stored in underground rhizomes for the formation of new shoots (Beale et al., 1996). The harvested samples were maintained in dry indoor storage. The sample consisted mostly of stalks with a few leaves, since the leaves of *Miscanthus* naturally fall in winter (Beale et al., 1996). The stalks were cut into 4 cm long pieces for feeding into a pyrolysis reactor. Each piece was cylindrical and hollow, with a diameter of 4–12 mm.

2.2. Pyrolysis reactor

The products of slow pyrolysis were produced at final temperatures ranging from 300 to 700 °C using a lab scale reactor. Fig. 1 shows a schematic diagram of the system. The reactor was made of stainless steel with a diameter of 10 cm and a height of 30 cm. It was placed inside an electrically-heated furnace with a temperature control. In each test, 20 g of sample was heated within the reactor from room temperature to the target temperature at a heating rate of approximately 10 °C/min. Once the temperature inside the reactor reached the target temperature, it was maintained for at least one hour to allow sufficient time for complete pyrolysis. Nitrogen was continuously supplied at a flow rate of 1.2 $\min^{-1}$ to purge the pyrolysis vapors from the reactor. The gas flow forced the pyrolysis vapors to pass through a series of condensers submerged in coolants at 20 °C (water) and −20 °C (acetone), respectively, for the separation of condensable (bio-oil) and non-condensable gases. Past the particulate filter, the gas flow rate was recorded using a mass flow meter (Tylan, FM-360). The gas compositions of the main gas species (O_2, CO, CO_2, H_2 and CH_4) were measured using an on-line gas analyzer (A&D System, A&D 9000). The reactor temperatures, gas flow rates and compositions were logged using a data acquisition system. The gases were also sampled into Tedlar bags for detailed compositional analysis by a gas chromatograph (Perkin-Elmer, Clarus 680 GC). After each test, biochar and bio-oil were collected from the reactor and condensers, respectively, to measure the mass yield and for detailed property analyses. The mass yield of gases was calculated by difference. The pyrolysis tests were repeated at least three times for key target temperatures (400, 500 and 600 °C). Pyrolysis at 450 °C, 550 °C and 700 °C was tested once in order to check the variations around 500 °C. The average mass yields are presented in this study as the deviation of the values in each test was less than 1.5 wt.% from the average, except for 300 °C.

2.3. Characterization of biomass and pyrolysis products

The biomass and biochar compositions were analyzed by proximate analysis based on standard methods (moisture content: ASTM E871-82, ash: ASTM D1102-84, volatile matter: ASTM E872-82 and fixed carbon: by difference) and ultimate analysis using an elemental analyzer (CE Instruments, EA 1108/NA 2000). The higher heating value (HHV) of biomass was measured using a bomb calorimeter (Parr-1261, Parr Instrument). Thermogravimetric analysis (TGA) for the biomass was carried out by using a Labsys. EVO TGA analyzer (Setaram) for 7 mg of powdered sample at a heating rate of 10 °C/min under nitrogen atmosphere (30 ml/min). Detailed characteristics of biochar were analyzed using a scanning electron microscope (SEM, JEOL, JSM-7600F) for surface morphology, N_2–BET (Micrometrics, Tristar 3020) for surface area, and a porosimeter (Micromeritics, AutoPore 4 9250) for distribution of pore volumes.

The hydrocarbon compositions in the bio-oil were analyzed by a GC–MS (Hewlett–Packard, HP5890/HP5972). To determine the elemental composition of bio-oil, it was separated into light and heavy phases in a centrifugal separator (ROTINA, 35R). Then, each phase was analyzed by an elemental analyzer (CE Instruments, EA 1108/NA 2000) to determine the C, H, O and N compositions and Karl-Fisher titration (Metrohm, 870 KF Titrino plus) to assess the water content. Based on the elemental compositions, the HHV of biochar and bio-oil were calculated using an empirical correlation proposed by Channiwala and Parikh (2002).

The HHV of the gases was estimated from the net mass yield and HHV of each gas component. The net mass yield of a gas component was acquired by integrating the concentrations history measured by the gas analyzer over the test duration.

3. Results and discussion

3.1. Properties of Geodae-Uksae 1

The air-dried sample of Geodae-Uksae 1 contained 7.3% moisture, 73.2% volatile matter, 15.9% fixed carbon and 3.6% ash. The volatile matter to fixed carbon ratio was 4.6, which is in a typical range for lignocellulosic biomass. The elemental composition on a dry-ash-free basis was 47.6% C, 5.5% H, 46.1% O and 0.8% N, which was equivalent to $C_{1.00}H_{1.39}O_{0.73}N_{0.01}$. Analyses were also conducted to compare different sections of stalks, but no significant differences were found. The HHV experimentally determined was