Biomass and Bioenergy xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Biomass and Bioenergy

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

Research paper

Effect of bio-char on methane generation from glucose and aqueous phase of algae liquefaction using mixed anaerobic cultures

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ARTICLE INFO

Keywords:
Biochar
Activated carbon
Methane production
Microbial analysis
Interspecies electron transfer

ABSTRACT

Activated carbon is known to enhance methane formation in anaerobic reactors via interspecies electron transfer between fermentative bacteria and methanogenic archaea. Biochar, a by-product of biomass pyrolysis process, could also perform similar functions due to its conductive properties and the presence of redox active moieties. Hence, this study was conducted to evaluate the effectiveness of different types of activated carbons and biochars on anaerobic digestion. Biochars obtained from canola meal, switchgrass and Ashe juniper were tested for methane production from both glucose and aqueous phase of bio-oil generated via hydrothermal liquefaction of algae. The results suggested that absorbents enhanced methane production. Furthermore, biochars synthesized at intermediate temperatures significantly increased methane yield and reduced the lag time required for methane formation. In addition, the results suggested that the redox active moieties such as *quinones* and *phenazines* in biochars are responsible for electron transport, which ultimately enhanced methane production.

1. Introduction

Anaerobic digestion (AD) is an effective method to treat organic wastes and recover energy in the form of biogas (methane). Fossil fuels utilized for power generation can be substituted with biogas produced via AD process [1,2]. Methane generation via AD is carried out by several groups of microorganisms involved in hydrolysis, acidogenesis, acetogenesis and methanogenesis [3]. Typically, about 25–65% of waste organics are converted to methane in a mesophilic AD process [4]. Performance of the AD process is determined by the effectiveness of interspecies electron transfer (IET) between secondary fermenting bacteria producing diffusive electron carriers (such as formate and hydrogen) and methanogenic archaea [5].

Disruption of syntrophic association between these bacteria often results in instabilities in reactor performances due to a decrease in pH followed by the accumulation of volatile fatty acids (VFAs). Adsorbents such as granular activated carbon (GAC), powdered activated carbon (PAC), silica gel, gelatin, pectin, aluminium powder, and bentonite are added to methanogenic reactors to overcome the disruption problem and stabilize the AD process [5,6]. In addition, these adsorbents were found to increase the methane yields in the AD process. For example, Lee et al. [5] observed a 1.8-fold higher methane production rate in GAC added reactors in comparison to control reactors with no GAC addition. Desai and Madamwar [6] claimed that addition of silica gel (4 g/L) resulted in a two-fold enhancement in total gas production and 17% increase in methane composition of biogas. Addition of adsorbents helps in sorption of toxic organic compounds, which are inhibitory to methanogenesis, and provides a high surface area for microbial growth, which in turn favors higher methane production rates.

In addition, activated carbon (AC) adsorbent acts as a good conductive material (such as an electrode) to facilitate direct interspecies electron transfer (DIET) between secondary fermenting bacteria (acting as anode-reducing microorganisms) and methanogenic archaea (acting as cathode oxidizing microorganisms) [5,7,8]. For example, a study conducted by Liu et al. [7] showed that DIET occurred between *Geobacter* sp. (anode reducing bacteria) and *Methanosarcina barkeri* (cathode oxidizing bacteria). Thus, the addition of conductive materials leads to an increase in the energy efficiency and biogas production via DIET by removing several steps associated with hydrogen production and consumption [5,7]. Further, a study conducted by Kato et al. [8] concluded that electron transport via conductive materials is much faster than molecular transport of electron carriers.

Similar to activated carbon adsorbents, biochar (BC) could also be used to enhance methane production via DIET during AD process due to its conductive properties similar to that of AC. BC is a carbon rich residue produced during the thermochemical decomposition of biomass via gasification or pyrolysis. BC is an inexpensive and eco-friendly solid material used for a number of purposes, such as soil remediation, waste management, greenhouse gas reduction and energy production [9]. The major element of BC is carbon (C), along with minor amounts of

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http://dx.doi.org/10.1016/j.biombioe.2017.10.034
Received 2 March 2017; Received in revised form 16 October 2017; Accepted 24 October 2017

hydrogen (H), oxygen (O) and trace amounts of sulfur (S) and nitrogen (N). The elemental composition of BC depends upon the nature of raw biomass material and on the carbonization process [10]. Owing to its porous structure, specific surface area, surface functional groups, and high nutrient content (both micro- and macro-nutrients), BC, could be used to support bacterial growth and enhance biogas production. Addition of BC to enhance biogas production during AD process has been gaining some research attention [11–14]. BC, however, has low surface area in comparison to AC, but it contains certain redox active moieties (RAMs) such as quinones and phenazines, which act as electron transfer catalysts during redox reactions in many soil and biogeochemical environments. In addition, BCs produced at different temperature were found to have different characteristics [15].

Although there is a growing interest of utilizing BCs in AD, studies focused on the treatment of complex organic wastes with addition of BC are very limited in the open literature. To the best of our knowledge, no studies have been conducted to compare the effectiveness of BC (derived from both herbaceous and woody biomass) versus AC (both powder and granular) on methane production. Hence, this study was conducted to investigate the effect of biochars produced from different biomass and process conditions on methane production with microbial community analysis. AD experiments were carried out using simple substrate such as glucose and complex organic waste such as aqueous phase of bio-oil (BOAP) generated during hydrothermal liquefaction (HTL) of algae.

2. Materials and methods

2.1. Materials

Seven types of adsorbents (two types of AC and five types of BC) were investigated to understand the effect of adsorbents during AD of simple organics (glucose) and complex organics (BOAP) in this study. Both PAC (Product code: C3014) and GAC (product code: 31616) were purchased from Sigma Aldrich (St. Louis, MO, USA) and used without further modifications. Biochars such as CBC, SBC and ABC were produced using pyrolysis of canola meal, switchgrass and Ashe juniper, respectively. Briefly, CBC was collected during bench-scale slow pyrolysis of canola meal operating at a temperatures of 700 °C (CBC-700) and 900 °C (CBC-900), respectively with a residence time of 2 h. SBC was collected during pyrolysis of switchgrass in an auger reactor operating at a temperature of 500 °C (SBC-500) with a residence time of 72 s, and the details are explained in the published document [16]. Similarly, ABC was collected during bench-scale slow pyrolysis of Ashe juniper biomass operated at temperatures of 400 °C (ABC-400) and 600 °C (ABC-600) with a residence time of 30 min. The detailed operation of bench-scale pyrolysis system is described elsewhere [17]. All these seven types of adsorbents were characterized for proximate analysis [17], BET (Brunauer-Emmett-Teller) surface area [18], average pore diameter [18], and pore volume [18], electrical conductivity (EC), particle density [18], particle size distribution [18] and pH (at point of zero charge, pH_{PZC}) [19]. The EC of BC and AC was measured according to the standard procedure used to measure electrical conductivity of soil. In addition, all these adsorbents were analyzed for the presence of metal elements using the inductively coupled plasma-optical emission spectroscopy (ICP-OES; PerkinElmer Life Sciences 9300-DV system). Adsorbents were also characterized using FT-IR using the methods previously described elsewhere [20] to detect the presence of functional groups such as quinones and phenazines known to involve in IET.

2.2. Anaerobic digestion experimentation

Mixed anaerobic culture obtained from Jackson Pike wastewater treatment facility (Columbus, Georgia, USA) was used for AD experiments of glucose and BOAP. Inoculum source, inoculum characterization, and basal media preparation for conducting AD experiments were similar to what was described in the published document [20]. The initial study using glucose was conducted to compare the effectiveness of BCs (ABC-400 and SBC-500) with ACs (GAC and PAC). Addtional anaerobic digestion experiments were also performed using biochars (BCs) synthesized at different temperatures (400 °C, 600 °C, 700 °C, and 900 °C) to understand the effect of these BCs in treatment of complex organic wastes. BCs synthesized from two different materials such as Ashe Juniper biomass (ABC-400 and ABC-600) and canola meal (CBC-700 and CBC-900) were evaluated. BOAP collected during HTL of algae was used as a complex organic substrate in this study. Information regarding algal composition, HTL operation, and BOAP characteristics can be found elsewhere [20,21].

AD experiments were conducted using a 160 mL serum bottle batch reactor with a 55 mL working volume comprising basal medium, inoculum and substrate. In order to study the effect of adsorbents on the performance of methane production process from glucose and BOAP, batch reactors (serum bottles) were supplemented with 1% of each adsorbent (0.55 g in 55 mL). Control reactors for each type of adsorbent were also ran in parallel with no adsorbent addition. AD experiments were conducted at mesophilic temperature (37 ± 1 °C) in an orbital shaker (with no shaking). The initial volatile suspended solids (VSS) used for AD experiments were 3000 ± 105 mg/L (4260 ± 149 mg COD/L) using a conversion factor of (1.42 g COD/g VSS). The initial pH and substrate concentration of all experimental sets were 7.8 ± 0.05, and 1 g COD/L, respectively. The substrate to inoculum ratio was maintained at 0.24 in all experimental sets (on COD basis). Separate culture control (no substrate addition) and adsorbent control (adsorbent with no substrate addition) experiments were also conducted to analyze any background CH_4 production. Background CH_4 yields of the corresponding experimental controls were subtracted from the experimental sets in the data presented. The batch reactors (both with different types of adsorbents and no adsorbents) were prepared and left for incubation in an orbital shaker (at 250 rpm) for a period of 7 days prior to the initial experiment to allow acclimation. At the end of 7 days, each batch reactor was fed with 1 g COD/L of glucose and BOAP and the reactors were not shaken. This procedure was followed to understand the role of IET in adsorbent added and non-adsorbent added cultures. However, the batch reactors were shaken only once at 250 rpm briefly (for 1 min) before performing the gas sampling. The CH_4 yields from all experimental sets were reported in mL/g COD.

2.3. Analytical methods

Liquid samples (1.5 mL) collected at the beginning and the end of AD experiments using pure glucose and complex organic waste (BOAP) were analyzed for TOC and COD according to the methods described previously [20]. In addition, volatile fatty acids (VFAs) composition was examined using a Shimadzu high performance liquid chromatograph (HPLC) equipped with UV and RI detectors. Both glucose and VFAs (lactic acid, acetic acid, propionic acid, formic acid and butyric acid) were analyzed using Aminex HPX-87H column with 5 mM sulfuric acid as eluent. The column temperature was set at 50 °C with an eluent flow rate of 0.6 mL/min. Headspace biogas composition was analyzed according to the method described previously [20]. Statistical difference between multiple means of the gas metabolite data were evaluated using a Tukey's paired comparison procedure at 95% confidence level [22].

2.4. Microbial community analysis

At the end of the batch experiment (using glucose), microbial samples were collected for community analysis using sterile 1.5 mL Eppendorf tubes from all experimental sets of glucose study. The liquid supernatant was discarded and 1.5 mL of settled microbial cultures were collected in these tubes. In batch reactors with adsorbents, both the adsorbents along with microbial cultures were taken in order to