Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Charcoal from anaerobically digested dairy fiber for removal of hydrogen sulfide within biogas

Manuel Raul Pelaez-Samaniego [a,b,*], Matt W. Smith [b], Quanbao Zhao [c], Tsai Garcia-Perez [a,d], Craig Frear [e], Manuel Garcia-Perez [b]

[a] Faculty of Chemical Sciences, University of Cuenca, Cuenca, Ecuador
[b] Department of Biological Systems Engineering, Washington State University, Pullman, WA, USA
[c] DVO Inc., Chilton, WI, USA
[d] Faculty of Agricultural Sciences, University of Cuenca, Cuenca, Ecuador
[e] Regenis, Ferndale, WA, USA

ARTICLE INFO

Article history:
Received 27 November 2017
Revised 5 March 2018
Accepted 6 March 2018
Available online xxxx

Keywords:
Dairy manure fiber
Anaerobic fiber
Carbonization
Charcoal
Biogas cleaning

ABSTRACT

Anaerobically digested fibrous solid (AD fiber) is an abundant material that offers potential to produce value-added products such as biochar. The objective of this paper is to better understand how thermochemical processing conditions affect the capacity of biochars derived from AD fiber to adsorb H_2S from biogas. AD fiber was pyrolyzed in an electric tube reactor at temperatures up to 600 °C and 60 min. The chars were employed for H_2S scrubbing tests from a synthetic biogas. Results showed that the chars' capacity for H_2S removal is comparable to that of activated carbon. An additional step consisting of impregnation of the chars with Na_2CO_3 resulted in an improved capacity for H_2S removal. To study the effect of ash, the AD fiber was also subjected to an alternative thermal treatment, hot water extraction (HWE), at 200 °C for 60 min. The resulting HWE material showed no removal of H_2S from biogas, indicating that the ash and the environment employed for the thermal treatment of AD fiber play an important role in the char's performance for H_2S removal. Results also suggest that a portion of the S in the charcoal after the H_2S sorption process exists as free or adsorbed S (i.e., not chemically bonded to the charcoal).

1. Introduction

Managing large amounts of dairy manure on concentrated animal feeding operations (CAFOs) is a pressing problem worldwide in the farming industry. In the United States (US), large CAFOs exist with up to 20,000 cows, and manure production rates of up to 69 kg of wet manure per cow per day (Pelaez-Samaniego et al., 2017), from which approximately 50% (dry basis) corresponds to recalcitrant fibrous matter surviving the animal digestive process (Chen et al., 2003; Liao et al., 2008). One of the options for managing such large amounts of dairy manure is via anaerobic digestion (AD) to produce biogas. However, despite the high potential for producing biogas in the US dairy industry, as of November 2017, the amount of CAFOs producing biogas through AD was limited to 203 (US EPA, 2018), mostly due to the lack of economic viability. Further adoption of AD in CAFOs could result if value added products can be reclaimed from the by-products of the process and, at the same time, improvements are made to the quality of biogas obtained. Ideally, this should result from an integrated production of biogas and value-added products from the fiber resulting from the AD process (Ferraz et al., 2016; Pelaez-Samaniego et al., 2017).

The fiber surviving both the cow and commercial digestion processes (AD fiber) has shown potential to produce several products such as composites, biochar, a component within growth substrates used in container plant production, and for thermochemical processing (e.g., gasification) (Pelaez-Samaniego et al., 2017). Although the moisture content (MC) of fresh AD fiber after typical solid/liquid separation from the digestate is as high as 72% (See Section 2.1), the use of additional mechanical dewatering (Spencer, 2016), drying utilizing recovered heat (Pelaez-Samaniego et al., 2017), or air drying when suitable within local climates could allow for more suitable MC for downstream pyrolysis for charcoal production. Charcoal production offers several opportunities, especially if it is conducted in the same AD facility to increase the value (i.e., by improving the quality) of biogas. One of the critical contaminates that must be removed from biogas is hydrogen sulfide (H_2S) (Greene, 2018), which is corrosive to internal combustion engines (Fulton, 1991) and can be an

* Corresponding author at: Faculty of Chemical Sciences, University of Cuenca, Av. 12 de Abril and Av. Loja, Cuenca, Ecuador.
E-mail address: manuel.pelaez@ucuenca.edu.ec (M.R. Pelaez-Samaniego).

https://doi.org/10.1016/j.wasman.2018.03.011
0956-053X/

environmental and human health hazard due to its odor and toxicity (Speece, 1996). In addition, H_2S produces emission concerns for combined heat and power (CHP) systems, as it is transformed to sulfur oxides (SOx) (Ecology, 2012). When raw biogas is converted to compressed natural gas (CNG) for vehicle use, near complete removal of H_2S is required. Accordingly, manure digester projects often actively scrub H_2S out of the raw biogas stream.

There are several methods currently used for H_2S removal. Among those, the more common approaches are: (a) addition of various types of iron salts prior to the digestion process (Wellinger and Lindberg, 2005), (b) oxygen injection to the digester (Díaz et al. (2011)), (c) biological treatment post digestion (Syed et al., 2006), and (d) physical-chemical adsorption post digestion, using materials such as iron sponges and/or activated carbon (AC) (Ryckebosch et al., 2011). Reviews on these techniques can be found in Jensen (2011), Ryckebosch et al. (2011), Muñoz et al. (2015), and Awe et al. (2017).

In addition to the above industrialized approaches, there is a growing interest on replacing traditional media such as sponges and AC with charcoal (biochar) filters (Ryckebosch et al., 2011). Several publications have reported that biochar produced from sewage sludge (Yuan and Bandosz, 2007; Xu et al., 2014), pig manure (Xu et al., 2014), camphor tree (Shang et al., 2012; Shang et al., 2013), bamboo and rice hull (Shang et al., 2013), black liquor (Sun et al., 2016), or potato peel waste (Sun et al., 2017) can be an alternative to commercial AC for H_2S removal from biogas. However, only a few works (e.g., Kirk et al., 2013) have explored the use of biochar from AD fiber. The use of on-site produced AD fiber could benefit dairy farmers that are looking to both (a) reduce or avoid the purchase costs of necessary media and inputs, and (b) find value-added uses for the AD fiber. Further work could help to better understand the importance of the conditions of the thermal treatment for designing AD fiber chars for H_2S scrubbing and the behavior of the chars during the scrubbing process. The objective of this paper is to better understand how the thermochemical processing conditions impact the capacity of charcoal derived from AD fiber to remove H_2S from biogas.

2. Materials and methods

2.1. Materials

25 kg of anaerobically digested dairy fiber (AD fiber) (approximately 72% moisture content) were obtained from DeRuyter and Sons Dairy Farm in Outlook, WA. Upon receipt, the AD fiber was dried at 90 °C for 48 h in an oven and stored in dry conditions until use. Particle size of the AD fiber (after drying) was determined as per ASTM D5644-01, using a Ro-Tap testing sieve shaker and 14, 16, 20, 30, 40, and 45 US mesh sieves. Activated charcoal (Sigma-Aldrich, untreated activated charcoal C2889, granular, 8–20 mesh) was used for comparison of results (i.e., as control) on H_2S sorption from biogas. Sodium carbonate (Na_2CO_3) (Sigma-Aldrich, anhydrous) was used for impregnation of char. Synthetic gas containing H_2S (65.2 vol% CH_4, 2045 ppm H_2S, balance CO_2) was supplied by Air Liquid Compressed Gases (https://industry.airliquide.us/).

2.2. Char production and preparation

The dry AD fiber, with particle size as received, was subjected to pyrolysis at 300 °C, 400 °C, 500 °C, and 600 °C, for 30 and 60 min, using a single zone Lindberg Blue M® tube furnace (spoon reactor, capacity of approximately 3 g of biomass per batch, metallic process tube, internal diameter of 25.4 mm), in duplicates, following the procedure described in Pelaez-Samaniego et al. (2014). Nitrogen (150 ml/min) was used as a carrier gas. Although higher temperatures can be used for AD fiber pyrolysis, we focused on carbonization temperatures up to 600 °C for 60 min, since it was our intention to understand the process of removing H_2S from biogas when charcoal is employed. The temperature of the biomass during the pyrolysis was measured with thermocouples immersed at the center of the AD fiber charge (at two different points) and coupled with a data logger. After pyrolysis, the chars and commercial activated charcoal were ground to guarantee approximately similar particle size, using a laboratory Thomas® Mini Wiley mill (http://www.thomassci.com/wileymill) equipped with a 40-mesh screen. Preliminary tests showed that materials processed at or below 400 °C for 30 and 60 min had very poor H_2S scrubbing ability (i.e., the H_2S scrubbing was negligible). Therefore, attention was paid only to materials pyrolyzed at 500 and 600 °C.

Charcoals processed at 500 and 600 °C for 60 min were additionally subjected to an impregnation process, using a 3 mass% Na_2CO_3 solution prepared using E-pure water (Type I, ASTM D1193-06); then, 5 ml of the solution was mixed with 1 g of the corresponding char and dried at 105 °C for 24 h. The Na_2CO_3 salt has previously been employed for impregnating activated carbon for environmental remediation (Xiao et al., 2008; Sitthikhankaew et al., 2011). The selection of this level of Na_2CO_3 concentration is close to values of impregnation percentages that are used in commercial impregnated ACs (see, for instance, DESOREX ® (Donau Carbon, n.d.)) or that have been employed in previous works (Ikeda et al., 1988; Boppart, 1996; Mescia et al., 2011).

An alternative thermal treatment of the AD fiber, hot water extraction (HWE), was employed to evaluate the effect of the conditions of the thermal treatment and the presence and characteristics of ash in the char. Contrary to pyrolysis, which tends to result in ash accumulation, HWE removes part of the soluble ash from the material (Pelaez-Samaniego et al., 2015; Ferraz et al., 2016). The HWE process was conducted at 180 °C and 200 °C for 60 min, following the procedure reported in previous works (Pelaez-Samaniego et al., 2015; Ferraz et al., 2016). Approximately 40 g of AD fiber were used for the treatments. E-pure water was added to the container (a 1 L glass liner, Parr) to maintain a water to wood mass ratio of 5:1. The HWE materials were then ground and tested for H_2S scrubbing following the same approach used in the case of the chars produced via pyrolysis (Section 2.3).

2.3. Hydrogen sulfide breakthrough experiment

The synthetic gas containing H_2S was used for testing the performance of char produced from AD fiber for H_2S removal. Scrubbing capacity of each material (i.e., chars and activated carbon) was tested in a column breakthrough experiment. One gram of the scrubbing material was placed into each of two parallel columns (to guarantee duplicates) in a laboratory experimental setup, as shown in Fig. 1. The H_2S scrubbing column was manufactured from a polycarbonate tube (6.35 mm internal diameter, 250 mm long). The scrubbing material was fixed inside the tubes using small amounts of cotton near the ends of the tubes. A 0.01 N HCl solution (500 ml, using distilled water) was employed to moisturize the biogas prior to the column. The pH of the solution was measured before (value was 2.3) and after each test (close to pH of 2.0, depending on the conditions of the experiment), using a pH meter (Mettler Toledo SevenEasy).

The (synthetic) biogas flow was adjusted to 5 ml/min by means of needle valves (See Fig. 1). The gas flow was verified daily using a VARIAN intelligent digital flowmeter and the system was checked for leaks employing a Restek electronic gas leak detector. Two blanks were run prior to each test. The H_2S content in the biogas, after passing through the char columns, was monitored online using a gas chromatograph (GC; Varian GC3800, equipped with a CP-Silica PLOT 50 m × 0.53 mm × 4 μm column). Measurements

Please cite this article in press as: Pelaez-Samaniego, M.R., et al. Charcoal from anaerobically digested dairy fiber for removal of hydrogen sulfide within biogas. Waste Management (2018), https://doi.org/10.1016/j.wasman.2018.03.011