Bioresource Technology 219 (2016) 29–36

Contents lists available at ScienceDirect

Bioresource Technology

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

Effect of biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates food waste

Nimas M.S. Sunyoto, Mingming Zhu *, Zhezi Zhang, Dongke Zhang

Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

HIGHLIGHTS

- Two-phase anaerobic digestion of food waste for H_2 and CH_4 production was studied.
- Biochar significantly increased maximum production rates of H_2 and CH_4.
- Biochar shortened the lag phases of H_2 and CH_4 production.
- Biochar enhanced VFA formation in H_2 phase and VFA degradation in CH_4 phase.

ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form 19 July 2016
Accepted 20 July 2016
Available online 21 July 2016

Keywords:
Anaerobic digestion
Biochar
Carbohydrates
Food waste
Hydrogen
Methane

ABSTRACT

Effect of biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates was studied using bench-scale bioreactors. The cultures with biochar additions were placed in 100 ml reactors and incubated at 35 °C and pH 5 for hydrogen production. The residual cultures were then used for methane production, incubated at 35 °C and pH 7. Daily yields of hydrogen and methane and weekly yield of volatile fatty acids (VFA) were measured. The hydrogen and methane production potentials, rate and lag phases of the two phases were analysed using the Gompertz model. The results showed that biochar addition increased the maximum production rates of hydrogen by 32.5% and methane 41.6%, improved hydrogen yield by 31.0% and methane 10.0%, and shortened the lag phases in the two phases by 36.0% and 41.0%, respectively. Biochar addition also enhanced VFA generation during hydrogen production and VFA degradation in methane production.

1. Introduction

Anaerobic digestion (AD) provides an effective means of organic waste treatment and utilisation (Sung and Santha, 2003; Parawira, 2004). Conventional, single phase AD, where a whole series of biochemical processes occur in a one reactor, is common practice (Demirel and Yenigün, 2002; Mumme et al., 2014). However, the biogas produced from single phase AD is less than desirable due to high CO_2 content, low specific energy value and, therefore, poor ignition quality (Porpatham et al., 2007; Zhang et al., 2015).

Two-phase anaerobic digestion (TPAD) is a sequential process, in which the AD is separated into two phases, namely acidogenesis and methanogenesis, respectively. Hydrogen and CO_2 are produced in the first phase and methane and CO_2 are produced in the second phase. In an innovative process concept for renewable electric power generation (Zhang et al., 2015), the two exit streams are then combined to form a hydrogen-enriched biogas, which is expected to have a much improved ignition quality for gas engine applications (Porpatham et al., 2007). This system has been successfully demonstrated in laboratory research (Zhang et al., 2015) for several waste streams including agriculture waste (Klocke et al., 2008; Zhu et al., 2008), dairy wastewater (Lateef et al., 2014; Antonopoulou et al., 2008; Venetsaneas et al., 2009), sewage sludge (Song et al., 2004; Roberts et al., 1999), food waste (Browne and Murphy, 2014; Kim et al., 2014; Ventura et al., 2014; Lee and Chung, 2010) and industrial wastewater (Ke et al., 2005).

Biochar, a carbon rich residue from thermal decomposition or pyrolysis of biomass, has been found to enhance biogas production in the single AD due to its ability to promote biofilm formation and mitigate ammonia and acid inhibition (Mumme et al., 2014; Luo et al., 2015; Torri and Fabbri, 2014). Mumme et al. (2014) reported that 6.7% (on inoculum weight basis) addition of hydro-char, a type of biochar produced from hydrothermal carbonisation, prevented mild ammonia inhibition and increased methane yield by up to 32.0%. Luo et al. (2015) found that 10 g.l^{-1} pyrolytic fruitwoods

* Corresponding author.
E-mail address: mingming.zhu@uwa.edu.au (M. Zhu).

http://dx.doi.org/10.1016/j.biortech.2016.07.089
0960-8524/

biochar addition shortened methanogenic lag phase by 30.3% and increased maximum methane production rate by 86.6% than the control without biochar. Inthapanya et al. (2012) observed that 1% (dry substrate weight basis) pyrolytic rice husk biochar addition increased gas production by 31.0% and higher concentrations of biochar addition did not bring further benefits in enhancing the biogas production.

To the best of our knowledge, the performance of biochar addition in TPAD has never been reported. The contribution reports new findings of the effect of biochar addition on the production of hydrogen and methane from carbohydrates wastes in a simulated TPAD process. To this end, bench-scale batch TPAD experimentation was conducted. The yields and production rates of hydrogen, methane, and volatile fatty acid (VFA) as a function of biochar addition ratio and incubation time were measured. The anaerobic digestion processes and biodegradability in both phases were also analysed using the Gompertz model to obtain maximum hydrogen and methane production potentials, rates and lag phases in the two phases.

2. Experimental

2.1. Materials

To ensure the consistency in the feedstock quality and characteristics, white bread obtained from a local supermarket was used to simulate carbohydrate-rich food waste in an aqueous environment for TPAD. Proximate and elemental analyses of the bread are listed in Table 1. The bread was shredded to ca. 1 mm in size before being used in the TPAD experimentation.

The source of inoculum was a sludge obtained from Woodman Point Wastewater Treatment Plant, Western Australia. For hydrogen production, the sludge was heated and stirred at the 95 °C for 30 min to eliminate methanogens. A biochar obtained from pyrolysis of pine sawdust using an indirectly fired kiln reactor at 650 °C with a retention time of ca. 20 min. The biochar was ground and sieved to a size fraction of 3.5–25.9 μm. The biochar sample was dried in an oven at 105 °C prior to use. The elemental analysis, pH, BET surface area, pore size and pore volume of the biochar samples are also listed in Table 1.

2.2. Anaerobic digestion experimentation

The TPAD experimentation was conducted in batch mode. Schematic diagrams showing the experimental set-up and the typical experimental procedure are shown in Fig. 1. For hydrogen production, ~0.82 g of bread, 10 ml of heated sludge and water were added in a 100 ml serum bottle with a working volume of 60 ml. The initial pH was adjusted to 5 by adding an appropriate amount of hydrochloric acid (HCl) or sodium hydroxide (NaOH). Prior to an experimental run, the reactors were flushed with high purity nitrogen (>99.99%) at 10 $l.min^{-1}$ for one minute and then carefully sealed with rubber plugs and secured with aluminium caps (Koch et al., 2015; Davila Vazquez et al., 2008). The bottle was then placed in an incubator maintained at 35 °C until the gas production stopped, within approximately 8 days. The bottle was shaken once a day prior to sampling the gas for composition measurement. A 500 μl sample of accumulated biogas was taken daily from each reactor using a gas tight syringe and a 1 ml liquid sample was taken on day 2 and 8, respectively, for further analysis. In order to study the effect of the amount of biochar addition on the performance of the hydrogen production process, reactors with different biochar addition ratios of 8.3, 16.6, 25.1 and 33.3 $g.l^{-1}$ were set up. These experiments were run following the same procedure as detailed above. Each set of experiments was repeated under identical conditions three times, involving a total of fifteen serum bottle reactors.

After 8 days, the remaining culture in a reactor was used as the feed for methane production in the second phase. The bottle tip was opened and 10 ml of unheated sludge was added to the bottle to bring the pH to 7. The bottle was then sealed and incubated at 35 °C for 39 days. Gas sampling was conducted daily and liquid samples were taken periodically for further analysis.

Table 1
The results of elemental, proximate and physical analysis of food waste and biochar.

Parameter	Food waste	Biochar
Carbon (%)	42.7	77.9
Nitrogen (%)	2.3	0.3
Hydrogen (%)	9.1	3.7
Sulfur (%)	0.3	0.1
C/N ratio	18.7	255.0
pH	4.9	9.6
Total solid (%)	61.2	N.D*
Volatile solid (%)	59.5	N.D
Particle size distribution (μm)	N.D	3.5–25.9
BET surface area ($m^2.g^{-1}$)	N.D	130.0
Pore volume ($cm^3.g^{-1}$)	N.D	0.0138

* Not determined.

2.3. Data analysis

The daily volumetric biogas production was measured by a water displacement method (Walker et al., 2009) and then converted to volumetric biogas production under the STP condition (273 K and 1 atm pressure) according to the ideal gas law. The daily volumetric hydrogen or methane production was calculated by multiplying the volumetric biogas production by the hydrogen or methane concentration as determined from the GC analysis. The total cumulative hydrogen or methane yield was then obtained by adding daily volumetric hydrogen or methane production, calculated according to the ideal gas law (in STP ml) Zhong et al., 2011. The compositions of the biogases from the two phases were measured using Gas Chromatography (GC; Agilent 7980) facilitated with thermal conductivity detector (TCD) (heater 200 °C, reference flow: 10 ml/min, helium make up flow: 2 $ml.min^{-1}$) and Sigma Porapach QS (2 m × 3 mm × 2.1 mm) column. A GC (Agilent 7980) using DB-WAX column (30 m × 250 mm × 0.25 mm), flame ionisation detector (FID) (heater 250 °C, H_2 flow: 35 $ml.min^{-1}$, air flow: 350 $ml.min^{-1}$, make up flow 4 $ml.min^{-1}$, total run time 13 min) was used to determine the volatile fatty acid (VFA) of liquid samples taken from both phases. In order to obtain the lag phase, maximum production potential and rate of both hydrogen and methane production in each treatment, the following modified Gompertz (Nath and Das, 2011) model was employed:

$$t = Ph \times exp - exp\, RG(t) = P \times \exp\left\{-\exp\left[\frac{R_{max} \times e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

where $G(t)$ is the cumulative hydrogen or methane production [$ml.l^{-1}$], t the time [days], P the maximum hydrogen or methane production potential [$ml.l^{-1}$], R_{max} the maximum hydrogen or methane production rate [$ml.l^{-1}$.per day] and λ is the lag phase [days] defined as a delayed period of a culture in responding to a new environment and starting to produce hydrogen or methane (Swinnen et al., 2004). The cumulative hydrogen and methane production results were fitted using the model. To compare the mean of hydrogen and methane yields from each phase of all treatments, the data were also statistically analysed using Analysis of Varians (ANOVA). Post hoc tests were carried out using the least squares difference (LSD).