Bioresource Technology 100 (2009) 5097–5102

Contents lists available at ScienceDirect

Bioresource Technology

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

Buffer requirements for enhanced hydrogen production in acidogenic digestion of food wastes

Heguang Zhu [a,b,*], Wayne Parker [b], Robert Basnar [c], Alex Proracki [c], Pat Falletta [a], Michel Béland [a], Peter Seto [a]

[a] Aquatic Ecosystems Management Research Division, Water Science and Technology, Environment Canada, 867 Lakeshore Road, P.O. Box 5050, Burlington, Ontario, Canada L7R 4A6
[b] Civil Engineering, University of Waterloo, 200 University Ave. W. Waterloo, Ontario, Canada N2L 3G1
[c] Chemical Engineering, University of Waterloo, 200 University Ave. W. Waterloo, Ontario, Canada N2L 3G1

ARTICLE INFO

Article history:
Received 24 January 2008
Received in revised form 9 February 2009
Accepted 9 February 2009
Available online 2 July 2009

Keywords:
Hydrogen fermentation
Buffering effect
pH
Food waste
Volatile fatty acid

ABSTRACT

The requirements for pH buffer addition for hydrogen production and acidogenesis in batch acidogenic digestion of a food waste (FW) feedstock with limited alkalinity was studied at various initial pH conditions (6.0–8.0). The results showed that, without buffer addition, hydrogen production from this feedstock was insignificant regardless of the initial pH. With buffer addition, hydrogen production improved significantly if the initial pH was greater than 6.0. Substantial hydrogen production occurred when the pH at the end of the batch digestion was higher than 5.5. The maximum hydrogen production was found to be 120 mL/g VS added when the initial pH was 6.5 and buffer addition was in the range of 15–20 mmol/g VS. The effect of pH buffering on the formation of volatile fatty acids (acetic acid, propionic acid and butyric acid) was similar to its effect on hydrogen production. The results of this study clearly indicated shifts in the metabolic pathways with the pH of fermentation. The changes in metabolic pathways impacted upon the dosage of buffer that was required to achieve maximum hydrogen generation.

1. Introduction

Two stage anaerobic digestion (i.e. acidogenic–methanogenic) is a promising technology for generating biogases (i.e. hydrogen and methane) from concentrated organic substrates such as food wastes. If correctly operated, the first stage of these systems can achieve several objectives including hydrolysis, acidification, and hydrogen gas production. Enhancing production of hydrogen gas is of interest because of its value in the alternative energy economy. In addition, the performance of the acidogenic reactor in a two stage system can impact on the design and operation of the downstream methanogenic reactor. Enhanced hydrolysis and acidogenesis in the first stage will reduce residence time requirements in the downstream reactor.

The performance of acidogenic digesters is known to be a function of pH (Fang and Liu, 2002). The pH conditions impact on the rate of hydrolysis, the types and quantities of acidogenic products and rate and extent of H_2 generation (Li and Fang, 2007). The establishment of appropriate pH conditions in acidogenic reactors that are operated for H_2 gas production is made complex by the fact that these digesters are often operated in a batch or semi-batch mode to minimize the establishment of hydrogenotrophic methanogens in the digester and hence increase hydrogen yields (Chen et al., 2002). The transient nature of batch operations presents a challenge with respect to establishing the appropriate pH range during the digestion. Acid formation during fermentation will act to depress the pH; however, the pH affects the types and quantities of acids that are generated. Hence, there is a natural feedback between digester pH and acid generation. On-line pH monitoring with addition of acid and base into operating biological reactors is challenging to implement in practice. An alternate approach is to supplement the feedstock with sufficient buffer to counteract pH decreases that result from the generation of organic acids during batch digestion. The latter operating procedure was explored in this study.

This study focused on identifying the impact of the initial pH and feedstock buffer supplementation on enhanced hydrogen production from batch acidogenic digestion of food waste. The impact of these variables on the properties of the digester effluent was also characterized to facilitate an assessment of the impact of the acidogenic stage operation on the design and operation of a subsequent methanogenic stage.

2. Methods

The FW was collected from a cafeteria for 10 consecutive days and sorted manually, removing any non-food particles. The FW consisting of a variety of grains, vegetables and meats, was

* Corresponding author. Address: 7496 Wellington Road 34, RR #3, Guelph, Ontario, Canada N1H 6H9. Tel.: +1 519 767 9100x239; fax: +1 519 767 1824.
E-mail address: hzhu@biorem.biz (H. Zhu).

0960-8524/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2009.02.066

homogenized using a Waring blender to obtain uniform slurry. The slurry was allotted to 2.5 L containers and stored at −70 °C for future use.

The FW feedstock was prepared from the frozen FW slurry. The frozen slurry was thawed, diluted with water and strained through a No. 40 mesh sieve. Ten milliliters of water were added per gram of slurry to obtain a VS concentration of approximately 10 g/L. The resulting feedstock was used for all of the following experiments.

A hydrogen producing inoculum was cultivated from a digested municipal wastewater treatment sludge using a sucrose medium as described previously (Zhu and Béland, 2006). In the current study, some modifications were made during the cultivation. The cultivation was conducted in a respirometer (AER-200, Challenge Technology, USA) instead of in an incubator with a reciprocal shaker as employed in the previous study. Sucrose medium (100 ml) and 25 ml of digested sludge were added to a 250 mL serum bottle. The serum bottle was placed in a water bath at 35 °C, and connected to a bubble counter through a silicon tube and a 24-gauge syringe needle to record the gas production. The solution in the bottle was agitated by a magnetic stirrer at 250 rpm and the cultivation period continued for approximately 16 h. The quality of the inoculum was evaluated by measurement of the hydrogen production during the digestion period. All of the inoculum used in this research produced over 300 ml of biogas (containing 40–50% v/v hydrogen) from each serum bottle during digestion.

Subsequent acidogenic digestion tests with food waste were conducted in the respirometer utilizing a method that was similar to that employed to cultivate the hydrogen producing inoculum. 100 mL of FW feedstock and 25 mL of hydrogen producing inoculum, were added to each batch digester (250 mL). The initial pH of the mixtures was adjusted with 1 M NaOH and 1 M HCl solutions as required. After pH adjustment, different amount of two phosphate buffer solutions (1 M K_2HPO_4 and 1 M KH_2PO_4) were added to the digester according to the initial pH and the buffer dosage set for this digester. The ratio of concentrations of the two pH buffer salts required in order to maintain a particular pH was calculated as per Henderson–Hasselbalch equation (Sawyer et al., 2003). The ranges of initial pH and buffer addition tested were 6–8 and 0–20 mmol/g VS, respectively. All tests were repeated two or three times and some of the individual samples were also duplicated within the runs.

The pH buffering capacity of the FW, as determined based on its total acidity and alkalinity, were examined using an acid–base titration method (APHA, 2004). Fifty milliliters of the feedstock solution was added to a 100 mL beaker, stirred with a magnetic stirrer, and titrated with either 1 M HCl or 1 M NaOH. The pH change of the sample was monitored using a pH meter (30 Barnant, USA). The total acidity and alkalinity were computed from the titration curves. The pH end points used for acidity and alkalinity calculations were 9.0 and 4.5, respectively.

The hydrogen content of the biogas was measured using a gas chromatograph (Agilent 3000, Wilmington, DE, USA), according to the instruction of manufacturer. The gas chromatograph was equipped with MolSieve 5A and PLOT U columns operating in parallel; and the temperature, carrier gas type and flow rate in the two columns were controlled separately. The MolSieve 5A column was used for the measurement of hydrogen and methane and operated at an injector temperature of 95 °C, a column temperature of 100 °C, using argon as the carrier gas, at 30 ψ. The PLOT U column was used for measurement of carbon dioxide and hydrogen sulfide and operated at an injector temperature of 70 °C, a column temperature of 70 °C, using helium as carrier gas, at 15 ψ. Each column was connected to a separated TCD for detection.

The concentration of carbohydrates in the culture liquid was determined using the anthrone method (Gaudy, 1962). Total solids (TS), volatile solids (VS), total COD (tCOD), soluble COD (sCOD), total Kjeldahl nitrogen (TKN) and dissolved PO_4–P were measured according to standard methods (APHA, 2004). The COD analysis adopted the closed reflex colorimetric method using potassium dichromate as oxidant. The TKN analysis used a semi-micro-Kjeldahl method and the automated phenate method was used for final ammonia analysis. The vanadomolybo-phosphoric acid method was used for colorimetric determination of dissolved PO_4–P. Alcohols in the liquid sample were analyzed using a gas chromatograph (5890 Series II Plus GC, Hewlett Packard, Wilmington, DE, USA) equipped with a flame ionization detector and a Restek Stabilwax-DA (30 m × 0.25 mm) capillary column according the manufacturer's instruction. Hydrogen carrier gas at a flow rate of 1.2 mL/min was used at a column pressure of 0.77 kg/cm^2. VFAs were analyzed using an Ion Chromatograph (ICS-2000, Dionex, CA, USA) equipped with a AS15 column at a temperature of 30 °C with a gradient carrier solution (8–60 mM KOH), according to the instruction of manufacturer.

3. Results and discussions

3.1. Characteristics of FW

The characteristics of the FW feedstock are presented in Table 1. TS and VS concentrations averaged 11.4 and 10.5 g/L, respectively, indicating that a majority of the solid content was organic matter. Soluble COD represented approximately 50% of the total COD, indicating that the organic matter was approximately equally distributed between the particulate phase and soluble phase. The concentration of carbohydrates in the liquid phase was approximately 4.5 g/L which counted for 42% of the VS, showing that a majority of the organic matter (more than 80%) in this food waste was composed of carbohydrates. Total TKN and dissolved PO_4–P were determined at 505 and 45 mg/L, respectively, indicating a COD:N:P ratio of 430:11:1 which was deemed to be sufficient for anaerobic digestion (Tay et al., 2003). The FW feedstock had a relatively low pH buffering capacity as indicated by acidity and alkalinity values of 340 and 40 mg $CaCO_3$/L respectively. Given the relatively high organic matter content of the food waste and hence the potential for elevated VFA concentrations during acidogenic digestion it was apparent that the pH buffering capacity of the waste would likely be insufficient to maintain the initial pH during digestion.

3.2. Effect of buffer and initial pH on hydrogen production from FW

A preliminary experiment that measured hydrogen production and the corresponding changes in pH over the course of a batch digestion was conducted using FW feedstocks with and without buffer addition starting at an initial pH of 7.0. The results are shown in Fig. 1. Without buffer addition, a negligible quantity of hydrogen was produced and the pH decreased from 7 to 4.0 in

Table 1
Characteristics of FW feedstock.

Items	Concentration (mg/L)
TS	11400 ± 750
VS	10500 ± 780
Soluble COD	9230 ± 300
Total COD	19250 ± 1360
Soluble carbohydrates	4480 ± 106
Total TKN	505 ± 45
Soluble PO_4–P	45 ± 30
Total acidity as $CaCO_3$	340
Total alkalinity as $CaCO_3$	40
pH	4.7