Bioresource Technology 245 (2017) 90–97

Contents lists available at ScienceDirect

Bioresource Technology

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

Instability mechanisms and early warning indicators for mesophilic anaerobic digestion of vegetable waste

Dong Li[a], Lin Chen[a], Xiaofeng Liu[a], Zili Mei[b,*], Haiwei Ren[c], Qin Cao[a], Zhiying Yan[a]

[a] Key Laboratory of Environmental and Applied Microbiology, Environmental Microbiology Key Laboratory of Sichuan Province, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China
[b] Key Laboratory of Development and Application of Rural Renewable Energy, Ministry of Agriculture, Biogas Institute of Ministry of Agriculture, Chengdu 610041, China
[c] School of Life Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, China

ARTICLE INFO

Keywords:
Vegetable waste
Anaerobic digestion
Early warning
Instability mechanisms
Indicators

ABSTRACT

In order to elucidate the instability mechanism, screen early warning indicators, and propose control measures, the mesophilic digestion of vegetable waste (VW) was carried out at organic loading rates (OLR) of 0.5, 1.0, and 1.5 g volatile solid (VS)/(L d). The process parameters, including biogas components, volatile fatty acids (VFA), ammonia, pH, total alkalinity (TA), bicarbonate alkalinity (BA), and intermediate alkalinity (IA), were monitored every day. Digestion was inhibited at OLR of 1.5 g VS/(L d). The primary causes of instability are a high sugar and negligible ammonia content, in addition to the feed without effluent recirculation, which led to BA loss. The ratios of CH_4/CO_2, VFA/BA, propionate, *n*-butyrate and *iso*-valerate were selected as early warning indicators. In order to maintain the digestion of VW at a high OLR, control measures including effluent recirculation and trace element addition are recommended.

1. Introduction

The China Statistical Abstract 2015 reported that 760 million tons of vegetables were produced in 2014 in China. More than 30% of vegetables were lost as vegetable waste (VW) during harvest, transportation, storage, marketing, and processing (Liu, 2000). It was estimated that more than 80% of VW were either dumped or transported to landfill sites and incineration plants with other municipal solid wastes (MSW) (Liu et al., 2012). Consequently, the high water content (> 80%), high organic content (> 95% dry basis), and easy biodegradability of VW have led to serious negative effects on the landfill and incineration systems, such as an abundant production of leachate from landfill and unstable combustion during incineration (Cheng and Hu, 2010). However, VW with these characteristics are suitable for anaerobic digestion (AD) for recovering energy. Many studies have confirmed that the specific methane yield of VW is higher than any other MSW (Gunaseelan, 1997).

However, carbohydrate-rich substrates such as VW are easily perishable. They have a tendency to accumulate volatile fatty acids (VFA), which can lead to acidification, low pH, and process inhibition. Several studies indicate that the anaerobic digestion of VW can be stably operated only at low organic loading rates (OLR). A preliminary study by Knol et al. (1978) showed that the OLR was < 1.6 g volatile solid (VS)/(L day) for the stable digestion of VW, producing average biogas yields of 0.30–0.58 L/g VS. Mataalvarez et al. (1992) found that the maximum OLR that could be achieved was < 3 g VS/(L d) for mesophilic single-stage digestion of fruit and vegetable wastes (FVW). These studies suggested that there might be some instability in the anaerobic digestion of VW or FVW at a high OLR. In order to operate at high OLR, two stage digestion and co-digestion were used to treat VW (Shen et al., 2013; Zuo et al., 2014).

Effective monitoring and diagnosis of processes is a great challenge for anaerobic digestion reactors, which limits their stable operation. The effective process parameters are the basis for ensuring the process monitoring and control. A number of parameters have been frequently adopted in the process monitoring, including pH, redox potential, ammonia, alkalinity, VFAs, biogas production rate, biogas composition, microbial community and activity (Boe, 2006). However, most of these parameters can only reveal the current reactor status, but it is often too late for an effective process control once the threshold values are reached. In order to develop an effective method for AD reactor diagnosis and risk prediction, intensive studies have focused on screening early warning indicators. Such indicators should be ideally accurate and sensitive to environmental fluctuations, reveal the change dynamics of reactor status, and be adaptive to online monitoring, auto alert, and control systems. Li et al. (2014) carried out AD of food waste

* Corresponding author at: No. 13, Section 4, Renmin Nan Road, Chengdu, Sichuan, China.
E-mail address: meizili_biogas@163.com (Z. Mei).

http://dx.doi.org/10.1016/j.biortech.2017.07.098
Received 15 June 2017; Received in revised form 18 July 2017; Accepted 20 July 2017
Available online 21 July 2017

using a continuous stirred tank reactor (CSTR), and concluded that a combination of total VFA, the ratio of VFA to total alkalinity (VFA/TA) and the ratio of bicarbonate alkalinity to total alkalinity (BA/TA) can reflect the metabolism of the digesting system and realize rapid and effective early warning. Dong et al. (2011) proposed two indexes, i.e., stability index S (Eq. (1)) and auxiliary index a (Eq. (2)), which incorporate both gas- and liquid-phase parameters for upflow anaerobic sludge blanket (UASB).

$$S = \frac{1}{Q_{CH_4}} \times \frac{dVFA}{dt} \times 100 \quad (1)$$

$$a = \frac{dQ_{CH_4}}{dt} \quad (2)$$

where (dVFA)/(dt) (mmol/L/h) is the change rate of total VFA concentration at time t and Q_{CH_4} (mmolCH_4/L/h) is methane production rate.

Boe et al. (2010) considered that a combination of acetate, propionate and biogas production is an effective early warning indicator for CSTR using cattle manure as substrate. According to the running of a hybrid USBF (UASB + anaerobic filter) pilot plant (Molina et al., 2009a), the best indicators both for the carbohydrate-based and protein-based wastewaters, considering both process steady states and organic load perturbations are: methane flow rate and hydrogen concentration in the gas phase, volatile fatty acids and partial alkalinity in the liquid phase.

Even though lots of researches on early warning indicators have been conducted, the proposed early warning indicators are only effective when applied to these specific substrates and operating conditions, while less effective in systems with different substrates and operation conditions. Unfortunately, there are no reports regarding the screening of early warning indicators for anaerobic digestion of VW using CSTR. In this study, early warning indicators were screened, instability mechanisms were analyzed, and control measures were recommended for stable mesophilic single-stage digestion of VW.

2. Material and methods

2.1. Substrates and inoculum

VW was obtained from the Chengdu HIGREEN wholesale vegetable market. Impurities such as plastic bags were manually removed. The main constituents of the VW were cabbage leaves, potatoes, lettuce leaves, Benincasa hispida, and pumpkins. The collected and sorted VW was chopped into particles 4–5 mm in size, uniformly mixed, and stored at 4 °C. The characteristics of VW are listed in Table 1.

The inoculum was the digested residue, filtered by a 1-mm sieve. The digested residue was taken from an anaerobic digester fed with pig manure. The inoculum was acclimated for 20 days using VW as a substrate, until the methane content was above 60%. The pH of the acclimated inoculum was 7.6.

2.2. Experimental setup and design

The continuous experimental system consisted of three parts, including the digester, online gas monitoring, and online liquid monitoring (Fig. 1). The total volume of the reactor was 70 L. To avoid pipe blockage due to the expansion of the digested material, the loading volume was restricted to 55 L. AD was carried out at 35 ± 2 °C. The contents of the reactor were mixed 8 times per day at 40 rpm for 30 min.

The mesophilic AD of VW was carried out at OLRs of 0.5, 1.0 and 1.5 g VS/(L d). The hydraulic retention time (HRT) was fixed at 20 d by restricting the total feed to 2750 g, with different substrate concentrations. The daily feed and discharge for different OLRs are listed in Table 2.

2.3. Analytical methods

The TS and VS were determined using standard techniques (APHA, 1998). Analyses for C and N were conducted using a Vario EL element analyzer (Elementar Analysensysteme GmbH, Germany). The compositions of carbohydrate, soluble sugar, crude fiber, crude lipid, and crude protein were determined based on the Chinese Standard (GB/T 5009–2003). Biogas production was monitored online by a gas flowmeter (Beijing Sevenstar Electronics Co., Ltd, China). Biogas components (0–100% CH_4, 0–100% CO_2, 0–5% H_2, 0–3% CO) were detected online by an automatic biogas analyzer (Wuhan Cubic Optoelectronics Co., Ltd, China).

Liquid samples were centrifuged at 12,000 rpm for 10 min and subsequently filtered with a 0.45 μm membrane filter to analyze the ammonia nitrogen level, alkalinity, and VFA. Ammonia nitrogen was analyzed using a DR-1900 spectrophotometer (HACH, USA). Total alkalinity (TA), partial alkalinity (PA), bicarbonate alkalinity (BA), and intermediate alkalinity (IA), were analyzed using a ZDJ-4B Automatic Potentiometric Titrator (Shanghai Precision & Scientific Instrument Co., Ltd, China), in accordance with Anderson and Yang (1992). The pH end-points for PA, IA, and TA titration were 5.75, 4.3, and 3.8. BA is PA

Table 1
Composition of vegetable wastes and other materials used for co-digestion.

Characteristics	VW	VW	VW	VW	FVW	CS	CM	PM	CS	CM
TS (g/kg)	105.7	54.0	91.2	77.4	167.0	118.5	375.0	334.3	125.4	249.5
VS (% of TS)	92.1	90.7	86.7	93.5	93.4	88.5	185.0	70.4	73.8	73.8
Carbon (% of TS)	44.5	41.5	35.5	47.8	–	–	–	55.8	49.9	47.6
Nitrogen (% of TS)	2.64	3.8	2.9	4.3	–	–	–	4.8	3.7	8.7
C/N	17.1	10.9	12.2	11.0	–	–	–	11.7	13.6	5.5
Ammonia nitrogen (mg/kg)	0.2	–	–	–	< 10	1483	9900	1844	747	4891
pH	5.60	–	–	5.8	4.2	7.8	7.3	–	–	–
Carbohydrate (% of TS)	73.6	–	67.5	–	–	–	–	–	–	–
Soluble sugar (% of TS)	63.0	–	60.0	–	–	–	–	–	–	–
Crude fiber (% of TS)	11.9	30.2	7.5	23.88	–	–	–	–	–	–
Crude fat (% of TS)	3.4	–	–	–	–	–	–	–	–	–
Crude protein (kJ/kg TS)	13.2	–	–	–	–	–	–	–	–	–
Ref.	This study	Zuo et al. (2014)	Verrier et al. (1987)	Jiang et al. (2012)	Callaghan et al. (2002)	Callaghan et al. (2002)	Callaghan et al. (2002)	Li et al. (2016)	Li et al. (2016)	Li et al. (2016)

Note: VW: vegetable waste; FVW: fruit and vegetable waste; KW: kitchen waste; CS: cattle slurry; CM: chicken manure; PM: pig manure.