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Intermittent-vacuum assisted thermophilic co-digestion of corn stover and liquid swine manure: Salinity inhibition

Renchuan Zhang[a], Erik Anderson[a], Paul Chen[a], Min Addy[a], Yanling Cheng[a], Lu Wang[a], Yuhuan Liu[b], Roger Ruan[a,*]

[a] Center for Biorefining and Department of Bioproducts and Biosystems Engineering, University of Minnesota, 1390 Eckles Avenue, St. Paul, MN 55112, USA
[b] The Engineering Research Center for Biomass Conversion, Ministry of Education, Nanchang University, 235 Nanjing Road, Nanchang City, Jiangxi 330047, China

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ABSTRACT

In this study, the effects of Intermittent-Vacuum Stripping (IVS) on activities of methanogenesis in co-digestion of corn stover with liquid swine manure (LSM + CS) under thermophilic anaerobic digestion (TAD) conditions were evaluated. A 65% methanogenesis activity inhibition was observed in pretreated LSM plus corn stover (pLSM + CS), while 60 and 165 mL/L/day CH_4 productions were achieved in pLSM + CS and LSM + CS, respectively. The high salinity condition (5.28%) after IVS pretreatment was considered the primary inhibitor in pLSM + CS, while the ammonia (≤600 mg/L), C:N ratio (15.52) and volatile solid loading rate (3 g/kg^{-1}·day^{-1}) didn't show a negative effect on CH_4 production. When salinities were increased from 2% to 4% and 8%, 50% and 100% inhibition were observed respectively. The butyrate accumulation was a potential indicator of the non-salinity-inhibition status for methanogenesis in TAD.

1. Introduction

Millions of tons of untreated liquid swine manure (LSM) are applied directly to crop fields as liquid fertilizers, causing serious groundwater contamination (Khatri and Tyagi, 2015). Thermophilic anaerobic digestion (TAD) has been considered as a primary method for the nutrients utilization and the particle degradation of LSM, which shows impressive energy recovery efficiency, higher solid degradation rate and less hydraulic retention time (HRT) (Streitwieser, 2017). However, compared with food waste, the low C:N ratio, low biodegradable carbon source and high concentration total ammonia nitrogen (TAN) of LSM limit the nutrients utilization efficiency and biogas yield through TAD process (Kafle and Kim, 2013; Liu et al., 2017; Yenigün and Demirel, 2013). The quality of LSM need to be upgraded to improve the TAD efficiency for complete nutrient utilization purpose.

Co-digestion of animal wastewater with lignocellulose rich substrates in TAD has been widely investigated. Adding lignocellulosic biomass to the process is mainly to increase the C:N ratio and supply the biodegradable organic components. It is also considered as an efficient way to utilize lignocellulosic wastes from agricultural production (Chen et al., 2014; Li et al., 2014; Streitwieser, 2017; Tsapekos et al., 2017). Corn Stover (CS) is an abundant lignocellulosic waste with a high C:N ratio (> 28) in U.S and agriculturally-developed countries. Adding CS to the digestion of animal manure shows a significant 63% biogas production improvement (Fujita et al., 1980) and a stable CH_4 productivity around 223 ± 7 mL/g VS_{added} in both batch and continuous AD processes (Li et al., 2014). Study shows that C:N ratio adjustment with carbon rich feedstocks has been widely used to mitigate TAN inhibition of CH_4 production, while the TAN concentration was not higher than the critical level(Rajagopal et al., 2013). Additional measures must be applied to further minimize TAN inhibition of LSM, because LSM contains serious amount of nitrogen with a considerable TAN accumulation risk in TAD and especially in prolonged operation.

To improve removal of TAN with liquid swine manure plus corn stover (LSM + CS), intermittent vacuum stripping (IVS) was employed as a pretreatment step of TAD in this study. Previous study showed IVS was an efficient way to decrease TAN concentration in LSM to less than 100 mg/L and recycle TAN as liquid nitrogen fertilizer ($(NH_4)SO_4$) in a short period (Zhang et al., 2017a). Enhanced removal of TAN by IVS also effectively raises the C:N ratio in LSM. In addition, the alkaline condition is necessary to maintain most TAN in molecular form NH_3 instead of ionic form NH_4^+ to facilitate fast mass transfer from liquid phase to gas phase and achieve high TAN removal (Bousek et al., 2016; Huang et al., 2016; Ukwuani and Tao, 2016). However, the effective pH level of substrates after IVS is much higher than the reported optimal pH range (7–7.5) of TAD, and therefore it is inevitable that a large

* Corresponding author.
E-mail address: ruanx001@umn.edu (R. Ruan).

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amount of salts will be accumulated in pretreated liquid swine manure (pLSM) by two pH adjustments, one to raise the pH to up to 10 and the other to neutralize the pH to around 7.5 in the IVS pretreatment. The high salinity in the pretreated manure is a stressful condition for bacteria in TAD because the high osmotic pressure would affect enzymes activity and the mass transfer between the cytoplasm and the environment of bacteria (Vyrides and Stuckey, 2017).

The goal of this study was to evaluate the effects of IVS pretreatment on TAD performance with LSM + CS and pretreated liquid swine manure plus CS (pLSM + CS) in terms of CH_4 production, short-chain volatile fatty acids (SVFAs) degradation and solid degradation. Then, the variations of TAN, C:N ratio, volatile solid (VS), salinity and SVFAs were assessed to discuss the primary inhibition remained in TAD after IVS pretreatment. Finally, the effects of salinity on LSM + CS were investigated through serum bottle test with inhibited pLSM + CS inoculum, while the profiles of SVFAs, biogas and VS were analyzed for a better understanding of IVS pretreatment application in future.

2. Materials and methods

2.1. Experimental TAD and IVS pretreatment apparatuses

The anaerobic digestion reactors, designed to facilitate continuous process, were stirring-tank reactor (CSTR) type. Each reactor was a 50 L plastic carboy tank with 40 L working volume (Nalgene, Thermo Fisher Scientific, USA) insulated by fiberglass sheets (McMaster-Carr Supply, USA). An immersion heater, and PID temperature controllers (ThermoMart Ltd, USA) were installed to control the temperature at 55 °C. The mixing speed was set as 150 rpm achieved by mechanical seal agitators (White Mountain Process, USA) with drum bung folding impellers (Fusion Express LLC.). A 4 L cylindrical reaction vessel was used as the IVS reactor for daily LSM pretreatment. The TAN absorption units were made up of 3-N H_2SO_4 solution, 3-N NaOH solution, drierite and a graham condenser (Zhang et al., 2017a).

The fresh substrates (LSM and CS) were collected from Holden Farms, Inc. Northfield, Minnesota, U.S. and Agriculture Utilization Research Institute, Waseca, U.S., respectively. The fresh LSM was filtered through 2 mm opening size sieve, then stored at 4 °C for later use in the experiments. The CS was ground and passed through 1 mm opening size sieve before mixed with LSM and pLSM.

2.2. TAD of LSM + CS and pLSM + CS

To prepare the pLSM + CS feeding, the pH of LSM was raised to 10 using 8 N NaOH before IVS pretreatment, and then lowered to 7.5 using 4 N HCl. Daily feeding of pLSM + CS (Table 1) was a mixture of by 95% CS and 1.56% pLSM based on volatile solids (VS) value. The daily loading VS was set as 4.5% while the HRT of experiment was set to 15 days. The LSM + CS feeding, a mixture of raw LSM (VS = 13.1 g/kg^{-1}) and CS (VS = 950 g/kg^{-1}) (Table 1) was used as the control with same loading VS rate (45 g/kg^{-1}), HRT (15 days) and feeding pH (7.5).

To start the experiment, the whole mixture in a continuous 50 L TAD reactor was equally transfer to two 50 L TAD reactors with 1:1 inoculum-to-water ratio, and 30 mins N_2 flushing were applied to two reactors. The daily nutrients profiles of TAD were measured with effluent before feeding. The VFAs profile and degradation rates of COD, organic nitrogen, and total solids of the TAD elution were analyzed every 5 days. The biogas compositions were measured every 8 h. The biogas sample was collected by 2 L gasbag for 30 mins in each measurement period for determination of CH_4 yield and biogas composition using a micro-GC.

2.3. Assessment of salinity inhibition effect by serum bottles test

The working volume of serum bottles test was 50 mL in 125-mL serum bottles for 10 days TAD. Three mins N_2 flushing was used to purge the head space gas in each bottle before sealing. The inoculum (Table 1) was pLSM + CS reactor effluent with a 30 days HRT. The inoculum was first diluted 5 times to lower the salinity. To eliminate the interference from free ammonia nitrogen (FAN) inhibition, NH_4Cl were added to maintain the TAN concentration to inoculum level around 610 mg/L. NaCl was used as salinity supplement to create 3 different salinity levels, 2%, 4% and 8% by the salinity refractometer (D-D The Aquarium Solution Ltd), in which the 4% salinity condition was set as the control group to simulate the salinity environment in LSM + CS. To maintain the bioactivity of TAD, one g/L glucose was added as carbon source for biogas productivity and solid degradation efficiency analysis in serum bottles test. All serum bottles were maintained at 55 °C and 100 rpm conditions on a temperature-controlled shaker (New Brunswick, Innova 44/44R, Eppendorf, USA) for 10 days. Biogas samples were collected at room temperature using a monoject syringe for Micro-GC analysis.

Table 1
Characteristics of materials used in TAD and serum bottle test (SBT).

Particular	Units	LSM + CS	pLSM + CS	SBT inoculum*
CODt	g/L	90.82 ± 4.7	82.93 ± 6.02	57.45 ± 1.35
CODs	g/L	30.07 ± 1.6	30.22 ± 1.90	36.25 + 0.15
TNt	g/L	7.27 ± 0.31	1.62 ± 0.35	1.55 ± 0.13
Salinity	%	4.00 ± 0.08	5.28 ± 0.30	–
TPt (PO_4^--P)	g/L	1.21 ± 0.17	1.08 ± 0.10	–
TAN (NH_4^+-N)	mg/L	4864 ± 353	37 ± 6	610 ± 15
Nitrate (NO_3^--N)	mg/L	40.10 ± 2.31	41.58 ± 4.10	40.21 ± 1.52
Alkalinity ($CaCO_3$)	g/L	25.57 ± 2.23	21.53 ± 1.82	14.58 ± 0.35
VS	g/kg	43.01 ± 5.31	37.53 ± 4.14	31.16 ± 0.01
TS	g/kg	58.38 ± 5.52	81.07 ± 2.71	70.84 ± 0.06
Volatile Free Acids				
Acetic acid	mg/L	2740 ± 284	2571 ± 209	9100 ± 104
Propionic acid	mg/L	2214 ± 79	2322 ± 581	2157 ± 57
Iso-butyric acid	mg/L	447 ± 17	430 ± 34	524 ± 19
Butyric acid	mg/L	55.07 ± 8.64	49.48 ± 3.58	163 ± 7.80
Iso-valeric acid	mg/L	536 ± 28	500 ± 42	592 ± 28
Valeric acid	mg/L	18.47 ± 3.93	11.77 ± 3.80	820 ± 36.36
Isocaproic	mg/L	47.22 ± 2.03	43.91 ± 2.62	38.07 ± 1.24
Caproic acid	mg/L	33.78 ± 2.21	34.36 ± 1.46	41.39 ± 0.45

" ± " means standard deviation and all values presented are the means of independent quadruplicate (n = 3).
"*" means the 30 days degassing pLSM + CS medium profiles.
" – " means not results for that experimental group.

2.4. Analytical method and calculation

Total chemical oxygen demand (CODt), total nitrogen (TNt), Total phosphorus (TP_t), and alkalinity ($CaCO_3$) of raw effluent sample were measured using a Hach DR5000 spectrophotometer. Supernatant samples were prepared after 13,000 rpm centrifugation of the raw effluent for soluble chemical oxygen demand (CODs), total ammonia nitrogen (TAN) and Nitrate analysis with a Hach DR5000 spectrophotometer. Salinity of effluent supernatants was measured using a salinity refractometer (H_2 OCEAN, D-D the Aquarium Solution Ltd, USA). C:N ratio was calculated using Eq. (1):

$$[\mathrm{C{:}\ N}] = \frac{[COD_t]}{3 \times [TN_t]} \quad (1)$$

where [C:N] was C:N ratio value, [COD_t] was the concentration of total chemical oxygen demand, [TNt] was the concentration of total nitrogen.

The organic nitrogen (ON_t) was of the difference between TN_t and TAN, nitrate and nitrite according to our previous study (Zhang et al., 2017a). Volatile solid (VS) and total solids (TS) were measured following the standard method (Federation and Association, 2005).

Biogas compositions were analyzed using CP-4900 micro-GC (Varian, USA) with the thermal conductivity detector (TCD). Standard