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# Biogas production from co-digestion of corn stover and chicken manure under anaerobic wet, hemi-solid, and solid state conditions



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# HIGHLIGHTS

• Synergistic effects were found in CS:CM ratios of 3:1 and 1:1.

• In W-AD and HSS-AD, highest methane yields were obtained at CS:CM ratio of 3:1.

• Highest volumetric productivity of 14.2 L/L was found in SS-AD at CS:CM of 1:1.

• VFA/TA value of 0.4 was a more important criterion than NH<sub>3</sub>-N or FA concentration.

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# ABSTRACT

Corn stover (CS) and chicken manure (CM) are ubiquitous agricultural wastes at low cost and have the potential to achieve a nutrient-balance when mixed together to produce biomethane via anaerobic digestion (AD). The main objective of this work was to investigate methane production at different CS to CM ratios and to evaluate the process stability under wet (W-AD), hemi-solid state (HSS-AD) and solid state (SS-AD) conditions. Results showed that synergistic effects were found when mixing two substrates at CS:CM ratios of 3:1 and 1:1 (on volatile solid basis). The highest methane yield of 218.8 mL/g VS<sub>added</sub> was achieved in W-AD at CS:CM ratio of 3:1. In SS-AD, the highest volumetric methane productivity of 14.2 L<sub>methane</sub>/L<sub>reactor volume</sub> was found at CS:CM of 1:1. The results of this work provide useful information to improve the efficiency and stability of co-digestion of CS and CM under different AD conditions.

1. Introduction

Anaerobic digestion (AD) can be classified as wet, hemi-solid, or solid state when the total solids of substrate are <10%, 10–15%, or >15%, respectively (Bolzonella et al., 2003; Li et al., 2011b). Generally, wet anaerobic digestion (W-AD) is commonly applied in experimental and full scale operations, because of low level of

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sludge generation, easy operation and maintenance, and increased methane production yield per unit mass of organic material fed to a digester (Fdez-Guelfo et al., 2010). However, for high solid content wastes, such as agricultural crop straws and municipal solid wastes, W-AD is not suitable due to the high consumption of water and large volume of digesters required to treat certain amount of feedstock. Recently, solid state anaerobic digestion (SS-AD) of high solid content feedstock has shown a continuous growth (Brown et al., 2012; Brown and Li, 2013; Xu and Li, 2012). SS-AD has been claimed to be advantageous over W-AD for a number of reasons including high volumetric methane productivity, small reactor volume, low energy requirements for heating, minimal material handling, and positive energy balances. One disadvantage of SS-AD is that it needs a lot of inoculum to achieve a fast start-up and efficient biogas production (Li et al., 2011b; Guendouz et al., 2008).

Balanced nutrients and carbon to nitrogen (C/N) ratio, pH, volatile fatty acids (VFA), alkalinity, and ammonia concentration are important factors affecting the performance of AD. A proper C/N



Abbreviations: AD, anaerobic digestion;  $B_{d}$ , biodegradability; BMP, biochemical methane potential; CM, chicken manure; CS, corn stover; EMY, experimental methane yield; FA, free ammonia; HSS-AD, hemi-solid state anaerobic digestion; NH<sub>3</sub>-N, ammonia-nitrogen; SD, standard deviation; S/I ratio, substrate/inoculum ratio; SS-AD, solid state anaerobic digestion; TA, total alkalinity; TMY, theoretical methane yield; TS, total solid; VFA, volatile fatty acid; VS, volatile solid; W-AD, wet anaerobic digestion; Weighted EMY, weighted experimental methane yield.

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ratio was found to be in the range of 15-30 (Mshandete et al., 2004). An excess of either nitrogen or carbon content could lead to process inhibition (Forster-Carneiro et al., 2007). A preferred pH value for AD ranged from 7.2 to 7.8 (Romano and Zhang, 2008). The drop in pH could inhibit methanogenesis and disrupt the performance of the anaerobic reactor (Brown and Li, 2013). VFA could cause the inhibition of the cellulolytic activity at a concentration of 2 g/L, and its inhibitory effect on the production of biogas was evident above 6 g/L (Siegert and Banks, 2005). Alkalinity was crucial to maintain stable pH in digesters. Properly operating anaerobic digesters typically had alkalinities in the range of 2000-4000 mg CaCO<sub>3</sub>/L (APHA, 1998). According to Hansen et al. (1998), total ammonia concentration of 6 g/L could inhibit methane production. Furthermore, based on Gallert and Winter (1997), 50% inhibition of methanogenesis was found at free ammonia concentration of 0.69 g/L.

Many studies have been conducted for anaerobic co-digestion of crop straws and animal manures (Ward et al., 2008; Wu et al., 2010). However, the selection of feedstocks for AD is influenced by accessibility and availability due to costs associated with collection and transportation (Frigon and Guiot, 2010; Li et al., 2011b). Corn stover (CS) and chicken manure (CM) are two typical organic solid wastes which widely exist in China, with huge production of 300 and 400 million tons per year, respectively (Zhang et al., 2009). CS and CM both contain high content of total solids, therefore, SS-AD may be an attractive way to produce biogas from them. Most of the previous studies were focused on methane production from CS and CM using W-AD systems (Li et al., 2013b; Wang et al., 2012; Wu et al., 2010). There is no literature so far on the evaluation of methane production and digestion stability of CS and CM with various mix ratios in hemi-solid state anaerobic digestion (HSS-AD) or SS-AD systems.

The objectives of the present study were to: (1) determine the proper ratios of corn stover and chicken manure to achieve high methane production yield using biochemical methane potential (BMP) assay; and (2) investigate the methane yield, volumetric methane productivity, and process stability during the digestion of corn stover, chicken manure, and their mixtures under W-AD, HSS-AD, and SS-AD conditions.

## 2. Methods

#### 2.1. Substrates and inoculum

Chicken manure (CM) was obtained in October 2012 from a hennery in Deqingyuan Company, Beijing, China, and kept at -20 °C to prevent biological decomposition. Corn stover (CS) was collected from a corn field nearby the chicken farm in Yanqing County, Beijing, China. A mill (KINGSLH, China) was used to grind CS to particle size of 1-mm. Inoculum used in this study was anaerobic sludge from Xiaohongmen municipal wastewater treatment plant in Beijing, China. The characteristics of substrates and inoculum are shown in Table 1. Prior to use, the inoculum was acclimated and degassed at 37 °C for 3 weeks to minimize the background methane production (Li et al., 2013a) and was partially pre-concentrated by a Legend RT+ centrifuge (Thermo Scientific, USA).

#### 2.2. Biochemical methane potential assay

Biochemical methane potential (BMP) assays of substrates were carried out in triplicate using 1 L glass bottles with a working volume of 0.5 L at 37 °C. The initial volatile solids (VS) concentration of organic substrates was adjusted to 3 g VS/L. Corn stover to

#### Table 1

Characterization of substrates and inoculum.

Parameter	CS	СМ	Inoculum
TS (%) <sup>a</sup>	$88.8 \pm 0.8$	$24.9 \pm 2.3$	$4.6 \pm 0.3$
VS (%) <sup>a</sup>	83.6 ± 1.1	$19.4 \pm 1.0$	$2.7 \pm 0.2$
VS/TS (%)	94.1 ± 0.4	78.1 ± 3.1	58.7 ± 0.2
C (%) <sup>b</sup>	44.2 ± 1.7	36.2 ± 1.3	34.3 ± 4.2
H (%) <sup>b</sup>	$6.0 \pm 0.3$	$5.2 \pm 0.3$	4.9 ± 1.1
O (%) <sup>b</sup>	44.6 ± 0.3	29.9 ± 0.5	ND
N (%) <sup>b</sup>	$0.7 \pm 0.1$	3.6 ± 1.1	3.8 ± 1.1
C/N	63.2 ± 8.5	10.1 ± 2.9	9.3 ± 1.6
pH	ND	9.3 ± 0.2	$7.6 \pm 0.2$
Total alkalinity (g CaCO <sub>3</sub> /kg)	ND	$10.0 \pm 1.0$	$7.3 \pm 0.7$
VFAs (g/kg)	ND	$0.9 \pm 0.4$	$0.4 \pm 0.1$
NH <sub>3</sub> -N (g/kg)	ND	$2.8 \pm 0.3$	ND
Cellulose (%) <sup>b</sup>	42.3 ± 1.3	$20.0 \pm 0.9$	ND
Hemicelluloses (%) <sup>b</sup>	29.8 ± 1.2	$23.2 \pm 0.8$	ND
Lignin (%) <sup>b</sup>	9.4 ± 1.1	$2.3 \pm 0.5$	ND
Protein (%) <sup>b</sup>	$4.4 \pm 0.9$	15.6 ± 5.3	ND
Lipids (%) <sup>b</sup>	$0.0 \pm 0.0$	$0.0 \pm 0.0$	ND
Non-structural carbohydrates (%) <sup>b</sup>	8.5 ± 4.8	17.1 ± 8.7	ND
Ash (%) <sup>b</sup>	$5.9 \pm 0.4$	$21.9 \pm 3.1$	41.3 ± 0.2

ND: not determined; CS: corn stover; CM: chicken manure.

<sup>a</sup> As total weight of sample.

<sup>b</sup> As TS of sample.

chicken manure (CS:CM) ratios, based on VS, were 1:0, 3:1, 1:1, 1:3, and 0:1. The corresponding substrate to inoculum (S/I) ratio of each digester was 0.5, on a VS basis (Chynoweth et al., 1993). It was assumed that basic nutrient requirements for anaerobic microorganisms were provided by the inoculum (Labatut et al., 2011). Therefore, no additional nutrients/trace elements were added to simplify the BMP assay. Three blank digesters which contained the same amount of inoculum and water were also used as corrections. All digesters were manually shaken twice a day for about 1 min. More details about the BMP assay were presented by Li et al. (2013b).

#### 2.3. Wet, hemi-solid, and solid state anaerobic digestions

Both feedstocks were mixed with tap water and inoculum to obtain a mixture with a total solids of 5.1–5.6% for W-AD; 10.1–11.2% for the HSS-AD; and 20.1–22.4% for SS-AD. An S/I ratio of 3, based on VS, was applied in all experiments. The corresponding initial volatile solids of feedstocks were 30, 60, and 120 g VS/L for W-AD, HSS-AD, and SS-AD, respectively. All tests were carried out for different mixtures of CS and CM (CS:CM) of 1:0, 3:1, 1:1, 1:3, and 0:1 (on VS basis). The mixtures were loaded in 1-L glass bottles and incubated in an incubator (YIHENG, China) maintained at 37 °C. Duplicate reactors were used for each condition. Inoculum and water without any feedstock addition was used as a blank. Biogas composition and volume were measured every 1–3 days for 30 days. All digesters were manually shaken twice a day for about 1 min.

#### 2.4. Theoretical methane yield and biodegradability

Theoretical methane yields (TMY) of CS and CM were calculated according to the reported formula (Buswell and Mueller, 1952; Li et al., 2013a) as shown in Eqs. (1) and (2):

$$C_{n}H_{a}O_{b}N_{c} + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4}\right)H_{2}O$$
  
$$\rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)CH_{4} + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8}\right)CO_{2} + cNH_{3}$$
(1)

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