Full Length Research Paper

Assessment of the effects of dry anaerobic codigestion of cow dung with waste water sludge on biogas yield and biodegradability

Jianzheng Li¹*, Ajay Kumar Jha^{1, 2}, Junguo He¹, Qiaoying Ban¹, Sheng Chang¹ and Peng Wang¹

¹State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, P. R. China.

²Mechanical Department, Kathmandu Engineering College, Tribhuvan University, Kathmandu, Nepal.

Accepted 21 June, 2011

Dry anaerobic digestion has been treated as feasible process for potential renewable energy recovery with nutrient-rich fertilizer and sustainable solid waste management. Dry methane fermentation of undiluted cow manure (CM), waste water sludge (WWS) and their mixtures into different ratios were conducted at 35 °C in the laboratory-scale single-stage batch reactors for 63 days. The specific biogas production obtained for the CM/WWS ratios of 1:0, 4:1, 3:2, 2:3, 1:4 and 0:1 were 56.94, 58.51, 61.64, 63.12, 59.30 and 55.39 L/kg, with methane yield were 32.01, 33.14, 35.31, 36.91, 34.76 and 32.63 L/kg respectively. The experimental results showed that the co-digestion with CM/WWS ratio of 2:3 obtained highest total biogas production of 63.12 L/kg, methane yield of 0.328 m³/kgVS and total solid (TS), volatile solids (VS), chemical oxygen demand (COD), total organic carbon (TOC) reductions of 34.24, 54.80, 55.22 and 70.71% compared to the other co-digestion ratios and single digestions. It was also revealed that co-digestion resulted in 3.11-13.99% higher methane gas yields, due to synergistic effect. The synergistic effect is mainly attributed to more balanced nutrients and increased buffering capacity.

Key words: Dry anaerobic digestion process, co-digestion, specific energy production, methane.

INTRODUCTION

During the last few decades, anaerobic digestion of organic matters has been regarded as an appropriate technology for potential renewable energy recovery with nutrient rich fertilizer and sustainable waste management (McCarty, 2001). The anaerobic digestion produces less greenhouse gases than other waste treatment techniques like incineration (Oliveira and Rosa, 2003), composting (Walker et al., 2009) and landfilling (Lou and Nair, 2009). The anaerobic digestion technology is mainly used for stabilization of organic wastes and production of energy from biogas combustion (Lema and Omil, 2001). In an oxygen free environment, anaerobic microbes such as, methanogenic bacteria, acetogenic bacteria and fermentative bacteria, digest biodegradable matter into biogas with methane as potential energy content, carbon dioxide and other gases in small amount. This process is highly complex, and involves a number of sequential and parallel steps (McInerney and Bryant, 1981; Pavlostathis and Giraldogomez, 1991; Rittmann and McCarty, 2001).

^{*}Corresponding author. E-mail: ljz6677@163.com. Tel: 0086 451 86283761.

Abbreviations: CM, Cow manure; WWS, waste water sludge; VFAs, volatile fatty acids; COD, chemical oxygen demand; SCOD, soluble chemical oxygen demand; TOC, total organic carbon; TS, total solids; VS, volatile solids; TKN, total Kjeldahl nitrogen; NH₃-N, ammonia nitrogen; TP, total phosphorus; TS, total solid.

The anaerobic digestion of organic material basically follows: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Ofoefule et al., 2009; Veeken et al., 2000). The conversion process begins with bacteria complex organic polymers such as hydrolyzing carbohydrates, proteins, lipids and fats, into simple monomeric carbohydrates, amino acids, sugars and long chain fatty acids. The reduced compounds are then converted by fermentative bacteria into a mixture of short chain volatile fatty acids (VFAs) and other minor products such as carbon dioxide, hydrogen and alcohol. These organic acids are further breakdown during acetogenesis to acetate, carbon dioxide, and hydrogen (Gerardi, 2003). In the final stage, methanogenesis takes place by two groups of bacteria: acetoclastic and hydrogenotrophic methanogens. Acetoclastic methanogens split acetate into methane and carbon dioxide (approx. 70%) while hydrogenotrophic methanogens uses hydrogen as electron donor and carbon dioxide as electron acceptor to produce methane (approx. 30%) (Gerardi, 2003; Zinder, 1993).

Jha et al. (2010b), Kuroshima et al. (2001) and Pavan et al. (2000) noted the following advantages of dry anaerobic treatment when compared to liquid anaerobic digestion: higher organic loading rate, lower energy requirements for heating, no process energy for stirring, reduced nutrient run off during storage and distribution of residues and limited environmental consequences. In addition, De Baere (2000) stated that, dry anaerobic processes have a more energetically effective performance since they require less pre-treatment and added water. Mainly due to its reduced cost in digesters and slurry handling problems, the dry anaerobic digestion process has attracted increased attention all around the world recently. However, the high-solids anaerobic digestion is known to suffer from many inhibition problems (Liu et al., 2006) and the process is also harder to control. The major disadvantages of solid state anaerobic digestion are the requirement of larger amount of inocula and much longer retention time (Li et al., 2010). Jha et al. (2010a) has presented that the dry methane fermentation of cow manure took relatively longer retention time than wet fermentation to produce same amount of biogas. Furthermore, dry anaerobic digestion exhibits a poor start-up performance, while the conversion of acetate to methane is generally considered as rate limiting due to slow growth of methanogens (Zinder, 1993). Also, the accumulation of VFAs is known to restrict the biogas yield (Guendouz et al., 2010). Moreover, complete mixing is difficult to achieve. Hence, this technology needs enhancement of reliability in operation to become more sustainable (De Baere, 2006).

An option for significantly improving yields of anaerobic digestion of solid wastes is the co-digestion of multiple substrates (Adelekan and Bamgboye, 2009; Li et al.,

2009; Kuroshima et al., 2001). Co-digestion enhances the methane yield due to positive synergisms established in the digestion medium, bacterial diversities in different wastes and the supply of missing nutrients by the cosubstrates. Animal manure contains rumen microorganisms that assists to carry out anaerobic digestion faster (Uzodinma et al., 2008) and cattle manure based biogas plants are successful in the rural area of many developing countries but they are affected due to the continuous increasing scarcity of feedstocks. The codigestion process can assist to solve the feedstocks scarcity dilemma. The manure and solid sludge have good biogas potential as they contain high percentage of biodegradable organic carbon. The mixing of manure with the solid sludge gives homogeneous mixture and their simultaneous digestion might provide additional energy. The wet bio-methanation process of the mixture of different wastes is relatively well understood and documented, however, limited research reports were found about the dry anaerobic co-digestion of organic wastes including the co-digestion of manure and the sludge. The aim of this study was to assess the feasibility of dry anaerobic co-digestion of cow manure with solid sludge using batch digesters under mesophilic condition. Biogas and methane yields, chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD), total organic carbon (TOC), total solids (TS) and volatile solids (VS) degradation, and VFAs and ammonia accumulation and degradation are considered for comparisons.

MATERIALS AND METHODS

Experimental set up and procedure

The single-stage batch dry anaerobic digestion consists of a process in which the substrates remain in solid state and static conditions. The experiments were carried out in six batch labreactors of 2.5 L effective volume with an internal diameter of 13 cm and height of 25 cm. The capped reactors were kept in a water bath of operational temperature 35 ± 1 °C, the optimum temperature for mesophilic range. Each reactor was fitted with four ports. The two ports were fitted on the cover while other two ports were fitted on the side. One of the cover ports was used for measuring biogas production. The sample for analysis of biogas quality was also taken out from the same port. The other cover port was used to add 6 nmol NaOH or 6 nmol HCl to maintain pH in between 6.8 to 7.6. One of the side ports was kept above 5 cm from the bottom. This port was used to take out the sample for the analysis of various parameters while pH meter was set up at the other side port. The samples were stored at - 4 °C in a freezer before analysis. The analysis was generally performed within one week.

Characteristics of feed stocks

The study was conducted to evaluate the mesophilic dry anaerobic digestion of undiluted and unscreened cow manure, solid fraction of waste water sludge and their mixtures into various ratios. The digesters, R_1 to R_6 , filled with the manure and the solid sludge

Table 1. Characteristics of substrates and inoculants.

Substrates	Cow manure	Sludge	Inoculants	
рН	7.84	8.03	7.93	
Total solid (TS), g/kg	162.78	178.54	87.50	
Volatile solids (VS), % of TS	86.73	62.28	66.20	
Chemical oxygen demand (COD), g/kg	160.86	139.34	67.58	
Soluble COD, g/kg	73.12	68.54	20.44	
Total organic carbon (TOC), g/kg	38.48	40.22	12.35	
Total phosphorus (TP), g/kg	1.28	1.51	1.02	
Total Kjeldahl Nitrogen (TKN), g/kg	2.62	3.55	1.6	
Ammonia nitrogen (NH ₃ N), g/kg	1.07	1.36	0.96	
Alkalinity, gCaCO ₃ /L	4.22	4.35		

Table 2. Composition and condition of six reactors utilized for the experiments.

Reactors	Feed stocks	Inoculants	рН	TS (%)	TS (g/kg)	VS (% TS)
R ₁	1000 g manure	200 g	7.91	15.01	150.13	84.82
R ₂	800 g manure + 200 g sludge	200 g	7.94	15.30	152.99	80.09
R ₃	600 g manure + 400 g sludge	200 g	7.96	15.53	155.26	75.49
R ₄	400 g manure + 600 g sludge	200 g	7.99	15.80	158.04	71.29
R ₅	200 g manure + 800 g sludge	200 g	8.01	16.05	160.48	67.13
R ₆	1000 g sludge	200 g	8.03	16.35	163.49	62.50

mixtures in the ratios of 1:0, 1:4, 2:3, 3:2, 4:1 and 0:1 on weight basis. It means each reactor contained 1 kg wet substrate and 200 g digested slurry as inoculants. The digested slurry from previous dry anaerobic digestion experiment of cow manure was utilized as inoculums. No other nutrients, chemicals or water was fed into the reactors. The average values of the characteristics of the manure and the sludge for each reactor are shown in Table 1. The manure was obtained from a livestock farm of Harbin, China while the sludge from the municipal waste water treatment plant at State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, P. R. China. Both cow manure and solid sludge were thick slurries. In the fermentation process, the substrates were pretreated and fed into air tight digester under specified environmental conditions for 63 days without dilution. Pretreatment means separation of substrates from foreign materials like stones, woods, metals and other inorganic materials, and the addition of inoculants into the feedstocks. The visible straw and feathers were removed by hand. Table 2 shows the composition of the substrates and inoculants in each reactor and the mean values of their physical-chemical characteristics. Each digester was purged with nitrogen for 15-20 min to create complete anaerobic environment. The contents of the reactors were slowly shaken once daily for 2-3 min to create homogeneous substrate preventing stratification and formation of a surface crust and distributing microorganisms throughout the digester.

Analytical methods

The parameters analyzed were temperature, pH, TS, VS, COD, SCOD, VFAs, TOC, total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3 -N). All the analytical determinations were performed

according to the standard methods (APHA, 1995). The pH of the mixtures was measured with a digital pH meter (Model 526, Germany). The yielded biogas was measured per day by downward water displacement method at atmospheric pressure using calibrated 1 or 2 L cylindrical jar for each reactor. The constituents $(CH_4, CO_2 \text{ and } H_2)$ of the biogas were determined using Gas Chromatography (SC-7, Shandong Lunan Instrument Factory) equipped with a thermal conductivity detector and a 2 m stainless column packed with Porapak TDS201 (60-80 mesh). Nitrogen was employed as the carrier gas at a flow rate of 40 mL/min. The operation temperatures for the injection port, oven and detector all were 80 °C. The cumulative methane production for each test was determined by summing daily methane production, which was calculated by timing daily biogas production with corresponding methane content minus the methane produced due to inoculums source. The samples taken from the batch culture reactor were centrifuged at 6,000 rpm for 15 min, and then acidified with analysis of VFAs and ethanol. The concentrations of the VFAs and ethanol were determined using a second gas chromatograph (Model GC122, Shanghai Analysis Instrument Factory) equipped with a flame ionization detector and a 2 m stainless (5 mm inside diameter) column packed with Porapak GDX-103 (60/80 mesh). The operational temperatures of the injection port, the column and the detector were 220, 190 and 220 °C respectively. Nitrogen was used as carrier gas at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Six lab-batch reactors were tested during a period of 63 days to assess the dry anaerobic digestion of cow manure

with the solid sludge and evaluate the effect of their codigestion at the optimal mesophilic digestion temperature. The co-digestion of the manure and the sludge could provide balanced nutrients, buffering capacity, appropriate C/N ratio and sufficient anaerobic microorganisms.

pH and alkalinity

The pH of cow manure and the sludge were initially around 7.84 and 8.03 respectively. It was decreased swiftly during start up phase of each experiment due to the increase in VFAs production by acidogenic bacteria. The easily digestible fraction of organic matter was hydrolyzed and converted to fatty acids rapidly. The pH began to rise gradually as the VFAs were consumed by methanogens and transferred to the methane. In this study, pH was maintained constant in between 6.8 to 7.6 by adding 6 nmol NaOH or 6 nmol HCl during the digestion period. It was also observed that there was stable pH after 2 weeks in all the reactors. The substrates were able to buffer theirselves and prevent the acidification occurrence during digestion due to proper alkalinity of cattle manure (4.22 gCaCO3/L) and solid sludge (4.35 gCaCO3/L), which is a pre-requisite for proper biogas production. The alkalinity was adequate to maintain optimal biological activity and stability of the anaerobic digestion system.

Total nitrogen (TN), total phosphorus (TP), NH_4^+-N accumulation and degradation

The values for carbon, nitrogen and phosphorus for the manure and the sludge were around 34.96, 2.43, 1.23 g/kg and 36.25, 3.43, 1.46 g/kg, respectively, which are sufficient to satisfy the cell growth requirements during biogas production. The NH₃-N was noted less than 1.3 g/kg during the fermentation period in all the reactors. Free ammonia is the active component causing ammonia inhibition (Angelidaki and Ahring, 1993). Free ammonia was calculated using Hansen et al. (1998):

$$\frac{[\mathbf{NH}_3]}{[\mathbf{TNH}_3]} = \left(1 + \frac{10^{-pH}}{10^{-\left(0.09018 + \frac{2729.02}{T(K)}\right)}}\right)^{-1}$$

Where $[NH_3]$ is the free ammonia concentration, $[TNH_3]$ is the concentration of total ammonia and T is the temperature in Kelvin. Calculated free NH_3 ranged from 0.025 to 0.035 g/kg in all the reactors. The value obtained was not supposed to be high enough to create inhibition as though ammonia can inhibit anaerobic digestion; the total ammonia concentration that can be tolerated was relatively high. The critical ammonia concentration to inhibit the anaerobic digestion is 2.8 g/kg NH_3 -N (Poggi-Varaldo et al., 1997). Liu and Sung (2002) reported that the ammonia concentrations below 2 g/L are beneficial to anaerobic process since nitrogen is an essential nutrient for anaerobic microorganisms. The maintained environmental condition and obtained results were indicative of strong microbial activities but partial inhibition might be possible due to presence of free ammonia at higher pH (McCarty, 1964).

Volatile fatty acids accumulation and degradation

Volatile fatty acids are usually produced due to the degradation of the complex organic polymers during hydrolysis and acidogenic stages. The conversion of intermediate products - VFAs - has been treated as an indicator of the digestion efficiency but the high concentration of VFAs results in decrease of pH, inhibit acidification, destroy methanogenic bacteria activity and leading to failure of digester ultimately. In this study, all the reactors showed high volatile fatty acids concentrations in the start up phase (Figure 1) due to higher acidogenesis and lower methanogenic activities. The principal volatile acids formed were acetic, butyric and propionic acids. Acetic acid was the dominant volatile fatty acids. The share of propionic and butyric acids was observed low because of the sufficient propionate- and butyric-degrading syntrophs which could rapidly convert propionic acid and butyric acid to acetic acid (Montero et al., 2008). The VFAs were increased rapidly after starting the test and reached a maximum of 16.72, 16.42, 17.84, 17.73, 18.27 and 17.55 g/L within 1 to 2 weeks. During this period, the acetic acid production rate was apparently higher than the acetic acid consumption rate. The degradation of propionate and butyrate by syntrophic acetogenic bacteria (for example, syntropher wolinii, syntrophomonas wolfei) produced acetic acid that was subsequently degraded into methane and CO₂ by acetoclastic methanogens (Montero et al., 2008). During methanogenic stage, acetic acid was started to convert into biogas such as methane and carbon dioxide. Thus, as methanogenesis and methane gas yield have increased, the VFAs concentrations were decreased. No high VFAs accumulation was detected due to perhaps acetatoclastic methanogens could consume acetate quickly in the digesters to yield methane and carbon dioxide. At the end of the processes, VFAs contents decreased below 1.3 g/L. No inhibitory concentration of VFAs was noted during the experiment as according to Ahring et al. (1995), the inhibitory concentration for methanogenesis is 3.5 g/L.

Biogas generation and methane content

The energy contained in biogas is determined by both biogas volume and methane content. The total biogas and

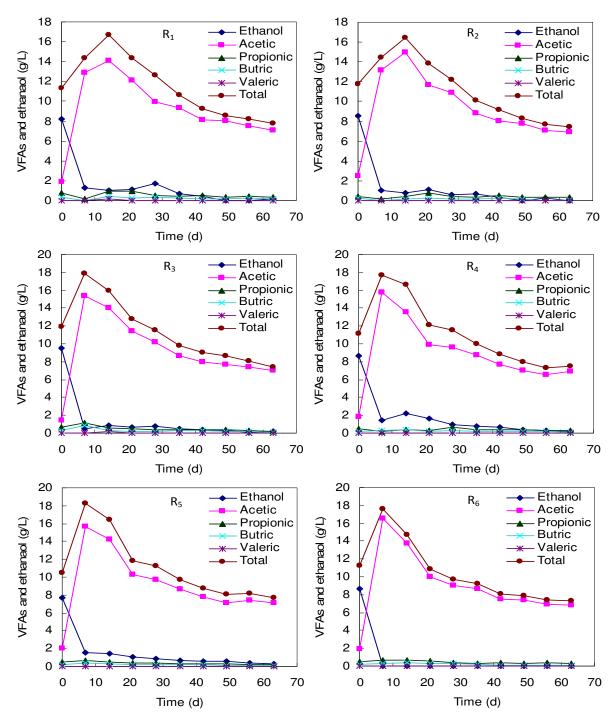


Figure 1. VFAs accumulation and degradation.

methane productions were calculated by summing daily biogas and methane production respectively. The daily methane yield was computed by timing daily biogas production with corresponding methane content. The daily biogas production, total biogas generation and cumulative methane yield for each test are shown in Figures 2 and 3. The rapid initial biogas production was due to readily biodegradable organic matter in all the substrates and presence of high content of the methanogens. Similar trends of daily biogas and methane

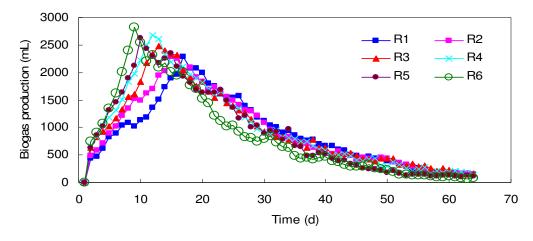


Figure 2. Daily biogas production.

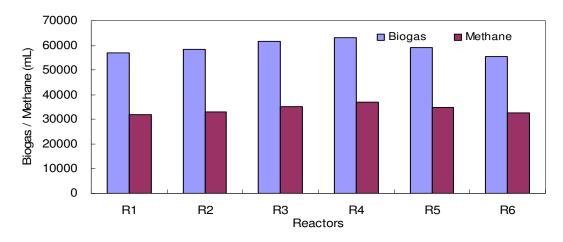


Figure 3. Total biogas and methane yield.

yield were observed for all the tests. The biogas generation started after seeding, kept increasing until reaching the peak, and then began to decline. It was not observed several peaks during the digestion process as reported by Li et al. (2009), since both co-substrates were highly biodegradable. The biogas started generating earlier and obtained the peak value (2.82 L) swiftly on day 8 in the case of the pure sludge. The daily biogas yield reached a peak value of 2.29 L on day 16 and decreased slowly for pure manure. It was also detected that the addition of sludge into cow manure has prompted the start up period with early generation of biogas and biodegradability as the sludge has more soluble COD, relatively high biodegradable matter and might contain more anaerobic microorganisms. The initial methane contents in the yielded biogas has increased and exceeded 50% after one week in all the functional

reactors and obtained stable phase of the digestion. The percentage of carbon dioxide has increased and stabilized in between 25 to 40%. Hydrogen gas was detected in very small percentage (<1%) during start up phase and then decreased. Negligible percentage (<0.3%) of Hydrogen gas was usually detected during rest of the digestion period in all the tests. This might be happened due to the fact that, all the available hydrogen gas rapidly combined with CO₂ to produce methane by hydrogenotrophic methanogens and presence of high percentage of H₂-utilising methanogens. There were variations of methane content among different treatments. The maximum methane percentage was found in reactor R_6 followed by R_5 , R_4 , R_3 , R_2 and R_1 ; which were 67.04, 66.08, 65.17, 63.46, 63.02 and 60.73% respectively. The average methane content had also same trends; which were 58.91, 58.62, 58.48, 57.29, 56.63 and 56.22%

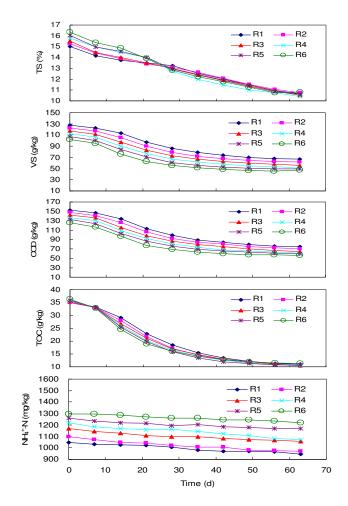


Figure 4. TS, VS, COD, TOC and NH₄⁺-N degradation.

respectively. The co-digestion could not improve the biogas guality (methane content in the biogas). The cumulative specific biogas generation of the reactors R_1 , R₂, R₃, R₄, R₅ and R₆ measured were 56.94, 58.51, 61.00, 63.12, 59.30, and 55.39 L/kg with 32.01, 33.13, 34.96, 36.91, 34.76, and 32.63 L/kg methane contents, respectively. As previous studies Jha et al. (2010a) and Luning et al. (2003) pointed out that, the quality of biogas and the specific gas production were identical to the digestion liquid anaerobic processes. Several researchers like De Baere (2006) and Li et al. (2010) have pointed out also that higher inoculum are required for dry anaerobic digestion. This study revealed that dry anaerobic digestions of manure, solid sludge and their mixtures were feasible using 20% digested slurry as inoculum.

In 28th day, the cumulatative methane production from the reactor R_6 containing pure sludge was 81% of the total methane yield while the reactor R_1 having pure manure produced 69% of the cumulative methane and

the mixtures yielded 72 to 79% of the computed methane. It was also calculated that 35 days was needed to obtain 81% of the cumulative methane production in the reactor R_1 . It means that the sludge required relatively less digestion time and the addition of the sludge prompted the digestion efficiency of the manure.

Total solids (TS), volatile solids (VS), chemical oxygen demand (COD) and total organic carbon (TOC) removal

Biogas is generated from the biological conversion of the substrates. The efficiency of solid-state anaerobic digestion was evaluated in terms of TS, VS, COD and TOC reduction as the amount of dry matter and organic compounds of the substrates represented the above mentioned parameters. Figure 4 and Table 3 present the removal percentage of TS, VS, COD, SCOD and TOC, and methane yield per gVS and gCOD in bio-methanization

	Organic matter and its removal							Methane yield		
Reactors	VS _i (g/kg)	VS _r (%)	COD _i (g/kg)	COD _r (%)	SCOD _i (g/kg)	SCOD _r (%)	TOC _i (g/kg)	TOC _r (%)	CH₄/gVS (L)	CH₄/gCO D (L)
R ₁	127.34	47.52	152.4	51.13	65.36	72.15	34.96	68.39	0.251	0.210
R ₂	122.53	49.91	147.84	52.27	63.21	73.68	35.10	69.94	0.270	0.224
R₃	117.21	52.77	142.08	54.23	62.48	75.59	35.35	70.27	0.301	0.249
R ₄	112.67	54.80	136.77	55.22	63.02	77.98	35.68	70.71	0.328	0.270
R_5	107.74	53.73	132.67	55.02	61.84	77.75	35.94	70.17	0.323	0.262
R_6	102.18	53.74	126.18	55.10	61.12	77.70	36.25	68.52	0.319	0.259

Table 3. Organic matter degradation and methane yield in each reactor.

R, reactors; I, initial; r, removal.

Table 4. Synergistic effect of co-digestion of cow manure and solid sludge.

Reactors	CM/WWS ratio	Biogas						
		Co-digestion (mL)	Manure (mL)	Sludge (mL)	Increase (mL)	Increase (%)		
R ₁	1:0		32011.91	0.00				
R ₂	4:1	33136.27	25609.53	6526.16	1000.58	3.11		
R ₃	3:2	35314.12	19207.15	13052.32	3054.66	9.47		
R ₄	2:3	36912.63	12804.76	19578.47	4529.40	13.99		
R ₅	1:4	34760.71	6402.38	26104.63	2253.70	6.93		
R ₆	0:1		0.00	32630.79				

processes of cow dung with the solid sludge at 35 °C. These values were high in the beginning and gradually decreased due to consumption by fermenting and methanogenic bacteria. The specific methane generation was found to be 0.251, 0.27, 0.301, 0.328, 0.323 and 0.319 m³/kgVS in the functional digesters R_{1} - R_{6} while in terms of m³/kgCOD were 0.21, 0.224, 0.249, 0.269, 0.262 and 0.256, respectively. There were close relationships between biogas yield and TS, VS, COD and TOC removal. As presented by Bhattacharya and Mishra (2005) and Jha et al. (2010a), the current study also shows that the biogas yield and biodegradation of undiluted substrates were comparable with that of the diluted anaerobic digestion. It can be observed that the highest efficiency of TS (34.24%), VS (54.80%), COD (55.22%) and TOC (70.71%) removals and methane yield $(0.328 \text{ m}^3/\text{kgVS}; 0.269 \text{ m}^3/\text{kgCOD})$ were found in R₄ compared to the other co-digestion ratios and the controls. The results imply that the methane yield and the biodegradability were improved by co-digesting cow manure with the sludge. It was also noted that 84% VS, 83% COD and 81% TOC degradation of the computed degradation for the pure sludge were achieved in four weeks while the degraded VS, COD and TOC were 68, 69 and 69% of the total degradation in the case of pure manure during the same digestion time. The values for the mixtures were determined in between 72 - 80% for VS, 72 - 80% for COD and 73 - 80% for TOC. It reveals that the sludge was more biodegradable than the manure and helped to increase the biodegradability of the manure.

Co-digestion performance and synergistic effect

The co-digestion of the organic wastes involves the mixing of the various substrates in varying proportions. Four co-digestion CM/WWS ratios of 1:4, 2:3, 3:2 and 4:1 were utilized and tested against pure manure and solid sludge as the controls. The co-digestions improved waste treatment efficiencies and achieved higher cumulative biogas production and methane yield due to synergistic effect. The synergistic effect is mainly attributed to more balanced nutrients, increased buffering capacity, decreased effect of toxic compounds and the structural changes of the fibers in co-digestion. More balanced nutrients in co-digestion would support microbial growth for efficient digestion, while increased buffering capacity would help maintain the stability of the anaerobic digestion system. Table 4 illustrates the synergistic effect of co-digestion of cow manure and solid sludge. It was found that compared to the single-digestions, the codigestions at four CM/WWS ratios achieved 3.11 to 13.99% additional biogas production. This means that based on the same amount of manure and sludge feedback, supplementary bio-energy can be generated when the co-digestion process is applied. This result is consistent with other research (Li et al., 2009; Mata-Alvarez et al., 2000; Naomichi and Yutaka, 2007) who have stated that digestion of more than one kind of substrate could establish positive synergism in the digester. The CM/WWS ratios of 3:2 and 2:3 might provide more balanced nutrients and buffering capacity and thus enhance the anaerobic digestion process and bio-energy production.

Organic fertilizer

Apart from biogas, the dry anaerobic digestion process results in a lower outcome of leachate and produces byproduct (digested residual) which can have a value as a fertilizer or soil amendment. The bio-fertilizer enriches soil with no detrimental effects on the environment (Ivagba et al., 2009; Uzodinma et al., 2008). The weight and volume reductions, compared to initial values of the substrates, were found approximately 10 - 20%. The nutrients, mainly Nitrogen (1.67 to 2.49 g/kg) and Phosphorus (0.95 to 1.13 g/kg), in the digestate were observed high. In addition, the handling of the digested residues (TS: 10.5 to 10.8%) that could be further treated by composting process or be used as fertilizer is easier than that of obtained in the liquid digestion (Brummeler, 2000). Bio-fertilizers which increase crop productivity are more cost-effective and eco-friendly supplements than chemical fertilizers.

Conclusions

Dry anaerobic digestions of cow manure and solid sludge are feasible and stable processes. Dry anaerobic codigestion of cow dung with the sludge boosted biogas production and achieved stable performances of anaerobic digestions. The co-digestions persuaded a better nutrient balance and therefore better digester performance and higher biogas yields. The specific methane generation for the digesters R₁-R₆ was found to be 0.251, 0.27, 0.301, 0.328, 0.323 and 0.319 m³/kg VS while in terms of m³/kgCOD were 0.21, 0.224, 0.249, 0.269, 0.262 and 0.256, respectively. The biogas generation and biodegradation of the substrate as started early in the case of the sludge followed by co-digested substrates than single manure. The co-digestion of the manure with the sludge in the ratio of 2:3 achieved the highest biogas production, methane yield, biodegradeability and TS, VS, COD, SCOD, TOC reductions, which are 63.12 L/kg, 36.91 L/kg, 0.328 m³/kgVS, 0.269 m³/kgCOD, 34.24, 54.80, 55.22, 77.98 and 70.71%, respectively. Compared to single-digestions, 3.11 to 13.99%

more biogas productions were obtained in the case of codigestions due to the synergistic effect. The synergistic effect is mainly attributed to more balanced nutrients and increased buffering capacity. The results showed that codigestion of cow manure with the sludge could be one of the options for efficient biogas production and sustainable waste management.

ACKNOWLEDGEMENTS

The authors would like to thank the State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (Grant No. 2010DX06), National S and T Major Projects (Grant No. 2008ZX07207-005-02), and Harbin Science and Technology Bureau (Grant No. 2009RFXXS004) for their support for this study.

REFERENCES

- Adelekan BA, Bamgboye AI (2009). Comparison of biogas productivity of cassava peels mixed in selected ratios with major livestock waste types. Afr. J. Agric. Res., 4 (7): 571-577.
- Ahring M, Sandberg I, Angelidaki I (1995). Volatile fatty acids as indicators of process imbalance in anaerobic digestors. Appl. Microbiol. Biotechnol., 41: 559–565.
- Angelidaki I, Ahring B (1993). Thermophilic anaerobic digestion of livestock waste: the effect of ammonia. Appl. Microbol. Biotechnol., 38: 560-564.
- APHA (1995). Standard Methods for the Examination of Water and Wastewater [J]. 19th ed., American Public Health Association; Washington, DC.
- Bhattacharya TK, Mishra TN (2005). Biodegradability of dairy cattle manure under dry anaerobic fermentation process. J. Inst. Engineers (India): Agric. Eng. Div., 84: 9-11.
- Brummeler ET (2000). Full scale experience with the BIOCEL process. Water Sci. Technol., 41: 299-304.
- De Baere L (2000). Anaerobic digestion of solid waste: state-of-the-art. Water Sci. Technol., 41 (3): 283-290.
- De Baere L (2006). Will anaerobic digestion of solid waste survive in the future? Water Sci. Technol., 53 (8): 187–194.
- Gerardi MH (2003). The Microbiology of Anaerobic Digesters. New York: Wiley, John & Sons.
- Guendouz J, Buffière P, Cacho J, Carrère M, Delgenes JP (2010). Dry anaerobic digestion in batch mode: Design and operation of a laboratory-scale, completely mixed reactor. Waste Manage., 30: 1768–1771.
- Hansen KH, Angelidaki I, Ahring BK (1998). Anaerobic digestion of swine manure: inhibition by ammonia. Water Res., 32: 5-12.
- Iyagba EI, Mangibo IA, Mohammad YS (2009). The study of cow dung as co-substrate with rice husk in biogas production. Sci. Res. Essays. 4 (9): 861-866.
- Jha AK, He J, Li J, Zheng G (2010^a). Effect of substrate concentration on methane fermentation of cattle dung. In: Proceedings of international conference on challenges in environmental science and computer engineering. Wuhan, P. R. China. March 6-7. Part. 1: 512-515.
- Jha AK, Li J, He J, Chang S (2010^b) Optimization of Dry Anaerobic Fermentation of Solid Organic Wastes. Adv. Mat. Res., 113-114: 740-743.
- Kuroshima M, Misaki T, Ishibashi T (2001). Dry anaerobic treatment of livestock waste together with municipal solid waste [C]. In: Proceedings of 9th World Congress, Antwerpen, Belgium (Velse AFM,

Verstratete WH, ed.), Part. 1: 375–380.

- Lema JM, Omil F (2001). Anaerobic treatment: a key technology for a sustainable management of wastes in Europe, Water Sci. Technol., 44: 133–140.
- Li D, Yuan Z, Sun Y (2010). Semi-dry mesophilic anaerobic digestion of water sorted organic fraction of municipal solid waste (WS-OFMSW). Biores. Technol., 101: 2722–2728.
- Li X, Li L, Zheng M, Fu G, Lar JS (2009). Anaerobic co-digestion of cattle manure with corn stover pretreated by sodium hydroxide for efficient biogas production. Energy Fuels, 23: 4635-4639.
- Liu T, Sung S (2002). Ammonia inhibition on thermophilic aceticlastic methanogens. Water Sci. Technol., 45: 113–120.
- Liu GT, Peng XY, Long TR (2006). Advance in high-solid anaerobic digestion of organic fraction of municipal solid waste. J. Cent. South Univ. Technol., 13: 151–157.
- Lou XF, Nair J (2009). The Impact of Landfilling and Composting on Greenhouse Gas Emissions–A Review. Bioresour. Technol., 100(16): 3792-3798.
- Luning L, VanZundert EH, Brinkmann AJ (2003). Comparison of dry and wet digestion for solid waste. Water Sci. Technol., 48(4): 15-20.
- Mata-Alvarez J, Mace S, Labres P (2000). Anaerobic digestion of organic solid wastes: An overview of research achievements and perspectives. Biores. Technol., 74(1): 3-16.
- McCarty PL (1964). Anaerobic waste treatment fundamentals III. Publ. Wks., 95: 91-94.
- McCarty PL (2001). The development of anaerobic treatment and its future, Water Sci. Technol. 44: 149–156.
- McInerney MJ, Bryant MP (1981). In: Fuel Gas Production from Biomass (ed. Wise DL), Chemical Rubber Co. Press Inc., West Palm Beach, Florida, pp. 26–40.
- Montero B, Garcia-Morales JL, Sales D, Solera R (2008). Evolution of microorganisms in thermophilic-dry anaerobic digestion. Biores. Technol., 99 (8): 3233–3243.
- Naomichi N, Yutaka N (2007). Recent development of anaerobic digestion processes for energy recovery from wastes. J. Biosci. Bioeng., 103(2): 105–112.

- Ofoefule AU, Uzodinma EO, Onukwuli OD (2009). Comparative study of the effect of different pretreatment methods on biogas yield from water Hyacinth (*Eichhornia crassipes*). Int. J. Phys. Sci., 4(8): 535 -539.
- Oliveira LB, Rosa LP (2003). Brazilian waste potential: energy, environmental, social and economic benefits. Energy Policy, 31: 1481-1491.
- Pavan P, Battistoni P, Mata-Alvarez J, Cecchi F (2000). Performance of thermophilic semi-dry anaerobic digestion process changing the feed biodegradability. Water Sci. Technol., 41(3): 75–81.
- Pavlostathis SG, Giraldogomez E (1991). Kinetics of anaerobic treatment. Water Sci. Technol., 24(8): 35–59.
- Poggi-Varaldo HM, Rodriguez-Vazquez R, Fernandez-Villagomez G, Esparza-Garcia F (1997). Inhibition of mesophilic solid-substrate anaerobic digestion by ammonia nitrogen. Appl. Microbial. Biotechnol., 47: 284-291.
- Rittman BE, McCarty PL (2001). Environmental Biotechnology: Principles and Applications. McGraw-Hill. New York.
- Uzodinma EO, Ofoefule AU, Eze JI, Mbaeyi I, Onwuka ND (2008). Effect of some organic wastes on the biogas yield from carbonated soft drink sludge. Sci. Res. Essays. 3 (9): 401-405.
- Veeken A, Kalyuzhnyi S, Scharff H, Hamelers B (2000). Effect of pH and VFA on hydrolysis of organic solid waste. J. Environ. Eng. ASCE. 126: 1076–1081.
- Walker L, Charles W, Cord-Ruwisch R (2009). Comparison of static, invessel composting of MSW with thermophilic anaerobic digestion and combinations of the two processes. Biores. Technol., 100(16): 3799-3807.
- Zinder SH (1993). Physiological ecology of methanogens. In: Ferry JG (Ed.), Methanogenesis: Ecology, Physiology, Biochemistry and Genetic. Chapman & Hall, New York, pp. 128-206.