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Research Article

Comparative evaluation of biogas production from dairy manure and co-digestion with maize silage by CSTR and new anaerobic hybrid reactor

This study aimed to investigate potential methane production through anaerobic digestion of dairy manure and co-digestion with maize silage. Two different anaerobic reactor configurations (single-stage continuously stirred tank reactor [CSTR] and hybrid anaerobic digester) were used and biogas production performances for each reactor were compared. The HR was planned to enable phase separation in order to improve process stability and biogas production under higher total solids loadings ($\geq 4\%$). The systems were tested under six different organic loading rates increased steadily from 1.1 to 5.4 g VS/L.d. The CSTR exhibited lower system stability and biomass conversion efficiency than the HR. The specific biogas production of the hybrid system was between 440 and 320 mL/gVS with 81–65% volatile solids (VS) destruction. The hybrid system provided 116% increase in specific biogas production and VS destruction improved by more than 14%. When MS was co-digested together with dairy manure, specific biogas production rates increased about 1.2-fold. Co-digestion was more beneficial than mono-material digestion. The hybrid system allowed for generating methane enriched biogas ($>75\%$ methane) by enabling phase separation in the reactor. It was observed that acidogenic conditions prevailed in the first two compartments and the following two segments as methanogenic conditions were observed. The pH of the acidogenic part ranged between 4.7 and 5.5 and the methanogenic part was between 6.8 and 7.2.

Keywords: Anaerobic co-digestion / Biogas production / Dairy manure / Hybrid reactor / Maize silage

Received: December 23, 2015; *revised:* August 5, 2016; *accepted:* September 19, 2016

DOI: 10.1002/elsc.201500187

1 Introduction

Increase in dairy population results in high amount of dairy manure, which needs to be managed. If animal manure is untreated or poorly managed, it can cause air and water pollution as well as the emissions of CH_4 that cause global warming [1]. However, when handled properly, manure can be used as a renewable energy source [2].

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Abbreviations: CSTR, continuously stirred tank reactor; CM, dairy cattle manure; C/N, carbon to nitrogen ratio; HR, hybrid reactor; HRT, hydraulic retention time; OLR, organic loading rate; MS, maize silage; SBP, specific biogas production; TS, total solids; VBPR, volumetric biogas production rate; VFA, volatile fatty acids; VS, volatile solids

Anaerobic digestion process serves as a waste stabilization while simultaneously generating renewable energy, thus acts as an important part of sustainable waste management. Anaerobic digestion plays an important role in the disposal routes for biomass waste due to its ability to convert the biomass into methane rich biogas [3]. By this way anaerobic digestion provides the chance to reduce our dependence on fossil fuels. The anaerobic digestion process precedes under three sequential stages of hydrolysis: acidogenesis, acetogenesis and methanogenesis. Hydrolysis is the breakdown of complex compounds into simple compounds. During hydrolysis polymers are converted to monomers such as glucose and amino acids. Acidogenic bacteria convert these monomers into alcohols, acetic acid, volatile fatty acids (VFAs), and H_2 and CO_2 . In the following stage, VFAs (butyric acid and propionic acid) are converted to hydrogen and acetic acid by acetogenic bacteria. In the methanogenic stage, hydrogen, carbon dioxide and acetate are then broken down

to mainly CH₄ (60–70%) and CO₂ (30–40%) by methanogenic bacteria [4].

Poor biodegradability (40–50%) of fibrous materials present in dairy manure is reported in [5]. This may lead lower methane production (0.2–0.25 m³/kgVS) than the theoretical yield (0.40–0.45 m³/kgVS) [6]. Dairy manure contains relatively high concentrations of total nitrogen (0.35%) which result in low carbon to nitrogen ratio (C/N) ratio [7]. High lignocellulosic material content of the substrates requires longer hydraulic retention times (HRT). Typical HRT for anaerobic digestion ranges between 15 and 30 days [8]. The C/N ratio is an important indicator for controlling biological treatment systems. Higher C/N ratios result rapid N consumption by methanogens, which results in nutrient deficiency and lower methane yields. Low C/N ratios lead the accumulation of ammonia and increase in pH, which are toxic to methanogenic bacteria. In anaerobic digestion process, the recommended range for C/N ratio is between 15 and 30 and C/N ratio of 25 is used commonly [7, 9–11]. C/N ratio of a substrate shows its nutrient levels. In order to obtain a proper C/N ratio, residues containing low levels of nitrogen (high C/N ratio) can be mixed with residues with high levels of nitrogen (low C/N ratio). Otherwise it is possible to struggle with either VFA accumulation or ammonia inhibition. Thus, co-digestion can improve methane yield and process stability by providing better nutrient balance.

In order to improve biogas production different pretreatment methods, co-digestion alternatives with other substrates and different reactor configurations are required. Co-digestion is defined as the digestion of mixtures of at least two waste materials for improving anaerobic digestion efficiency [12]. Different organic substrates can be mixed in order to increase process performance. In the recent years it has been shown that co-digestion provided more benefits than single material digestion. Co-digestion process helps optimizing feed composition, balancing several parameters in the co-substrate mixture: macro and micronutrients, carbon to nitrogen (C/N) ratio, pH, inhibitors/toxic compounds, biodegradable organic matter and dry matter [7, 13]. Mata-Alvarez et al. [14] showed that anaerobic co-digestion can increase CH₄ production by 50–200% depending on the operating conditions and co-substrates used. Agricultural wastes such as wheat straws, rice straws, and MS can be used as a valuable alternative feedstock for biogas production [15]. Co-digestion of agricultural residues with animal manure is considered as a more cost-effective method for nutritional balance compared with the addition of nitrogen-containing chemicals since these wastes contain considerable amount of carbon.

The continuously stirred tank reactor (CSTR) is the most commonly used reactor configuration for biogas production. In the CSTR hydrolysis, acidification, acetic acid formation and methanogenesis are carried out simultaneously in the same reactor. However, in two-stage systems hydrolysis and acidogenesis are carried out in the first reactor, acetogenesis and methanogenesis proceed in the second reactor. These systems are reported to improve volatile solids (VS) conversion efficiency and thus biogas yield and provide better system stability.

In this study, the effects of co-digestion and reactor configurations on biogas production were investigated to determine optimal methanogenic activity. For this purpose, the system performances of single-stage CSTR and newly developed horizontal

Table 1. Characteristics of the substrates used

Parameter (w/w%)	Dairy cattle manure	Maize silage
Dry matter	13.4	28
Organic matter of Dry matter	82.2	94
Dry organic matter	11	26.6
C/N Ratio	13.5	37
TKN	2.2	0.8
TN _{organic}	1.8	0.5
NH ₄ -N	0.4	0.3
P ₂ O ₅	2.7	0.4
K ₂ O	0.4	0.15

hybrid reactor (HR) with phase separation were compared in terms of biogas production from dairy cattle manure (CM). In order to balance the C/N ratio of the feed, co-digestion with maize silage (MS) was also tested in both systems.

2 Materials and methods

2.1 Substrates

In this study, dairy manure and MS having low protein and lipid contents were used as substrates. Dairy cattle manure was diluted with tap water to obtain the desired total solid (TS) concentration of approximately 4 and 10%. The organic fraction (VS) of the dairy manure was 82%. The manure was then stored in the freezer (−18°C) and defrosted at room temperature prior to use. Generally, CM contains high total nitrogen (TN), which results in low C/N ratios (about 15–25). The C/N ratio is lower than the recommended range for anaerobic digestion (25–30) [16]. MS has low nitrogen content which has much higher C/N ratio compared with dairy manure. In the second part of the study, co-digestion with MS was investigated in order to balance the nutrient level (hence the C/N ratio). MS was selected as co-substrate due to its high biomass yield (21–30 kg TS ha^{−1}) and high methane production potential. The MS was dried at 100°C, grounded and stored at room temperature. The characterization of dairy manure and MS are given in Table 1. The organic content of the dairy manure and MS mixture was 84%. The study intended to evaluate methane production potential of dairy manure and co-digestion with MS through several different total solids concentrations, including 4, 6, 8 and 10% TS. The system performances were tested and compared under similar conditions. The reactors were operated under seven different organic loading rates (OLRs) when used dairy manure only (OLR); 1.1, 1.6, 2.2, 2.6, 3.3, 4.1 and 5.4 gVS/L.day. Anaerobic co-digestion with MS (in a ratio of 4:1w/w) was carried out at OLRs 1.1, 1.7, 2.3, 2.7, 3.4, 4.2 and 5.6 gVS/L.day.

2.2 Reactor configurations

In this study, two different semi continuous types of reactors were used; a conventional continuous flow stirred tank (CSTR)

reactor and a horizontal HR, in order to compare the system performances on biogas production.

2.2.1 CSTR

The digester used for single-stage anaerobic CSTR has total volume of 7 L and working volume of 5 L (BioFlo200 Fermenter, New Brunswick). The reactor temperature was kept at $37 \pm 2^\circ\text{C}$ by a water jacket around the reactor. The reactor was covered in order to prevent photosynthetic growth. The complete mixing was provided by a propeller type of mixer at a rate of 60–80 rpm. The system was mixed continuously to provide a homogeneous substrate in the reactor and prevent settling. Therefore, better substrate and microorganism contact was provided. The pH was monitored continuously and corrected automatically by an acid or a base when necessary.

2.2.2 HR

A new HR was designed for the anaerobic digestion of wastes with high TS values ($\text{TS} > 5\%$). The HR is a horizontal type reactor with four compartments in it each having different volumes (Fig. 1). The system was mixed by the paddles in the middle of the reactors mounted on a shaft. Therefore, each compartment was a conventional stirred tank. The liquid was flowing upwards between compartment partitions. The total volume of the reactor was 45 L, active volume being 32 L. The volumes of the four compartments were 4.8, 4.8, 9.6 and 12.8 L.

The system was tested under total HRT of 30, 25, 20 and 15 days as that of single-stage CSTR by feeding from the first compartment and removing 1.05 to 2.13 L daily (depending on desired HRT) from the last compartment (Fig. 1). The corresponding HRTs for the first and second compartments changed between 2.25 and 4.5 days, third compartment being between 4.5 and 9 days and last compartment being between 6 and 12 days. After reaching stationary conditions, the operational conditions were maintained at least two HRTs before applying different conditions. The variation of pH and temperature of each compartment were continuously measured. The system control was provided by an automation system. Heating was provided by a thermocouple located on the shaft and temperature in the reactor was kept at $37 \pm 2^\circ\text{C}$. During the operational period, the volumes of biogas produced from each compartment were measured daily by water displacement.

Anaerobic conditions were provided by flushing nitrogen gas in order to remove oxygen before closing both reactors. The biogas produced from the system was measured by water displacement and expressed under standard temperature and pressure (STP). In this study, HRT of the reactor changed between 15 and 30 days. The system was fed daily by removing appropriate amount of mixed liquor depending on HRT, by using a plastic syringe, which was replaced by the same amount of fresh feed manually to keep the effective volume constant. Samples were taken from the surplus digestate. All the system controls were done by monitoring the parameters; TS, VS, pH and biogas volume. CH_4 content was measured by using methane gas composition analyzer.

3 Results and discussion

3.1 Biogas production from dairy manure

In the anaerobic digestion of the waste, organic fraction is first hydrolyzed which is followed by acidogenesis, acetogenesis and methanogenesis. The conventional single-stage continuous stirred tank reactors are simple to operate but are considered as less efficient with low VS loadings and low removal rates which also requires long HRTs [3]. By applying phase separation, the acidogenic and methanogenic processes proceed separately and provide better system control for different groups of microorganisms and reduce byproduct inhibition. The material passing from the first stage to the second stage has become homogenized and can be considered as more stable [17].

The performance of anaerobic digestion was determined by the amount of the VS converted into biogas (specific biogas production, SBP) and biogas produced per reactor volume (volumetric biogas production rate, VBPR), and methane content. SBP is an indicator of substrate utilization efficiency, whereas VBPR is an indicator of efficiency of the reactor [18]. The digestibility and composition of substrates affect the maximum methane yield. It was revealed that several factors that influence methane yields were biodegradability, VS loading rate, %TS concentration and HRT. TSs and/or VSs were typically used for expressing the organic material loaded into the reactors.

Dairy manure and MS were processed through anaerobic digestion to generate biogas. The studies were conducted by using two different reactor configurations. The digestion of dairy manure was carried out under 15 to 30 days of HRT and using CSTR and horizontal HR. The two systems were operated under seven different sets with different HRT and TS loadings when dairy manure was used as a sole substrate (OLR); 1.1, 1.6, 2.2, 2.6, 3.3, 4.1 and 5.4 gVS/L.d. The corresponding SBP of the CSTR was 360, 380, 370, 350, 320, 240, 150 mL/VS.d, respectively; and for the HR 410, 420, 440, 425, 395, 380, 320 mL/VS.d, respectively.

It was found that SBP decreases when increasing the OLR beyond 2.3 gVS/L.d and decreasing HRT (Fig. 2). The SBP for the CSTR system was 10–15% lower than the HR when OLR was ≤ 2.6 gVS/L day. However, when the OLR was further increased to 2.6 gVS/L.d and then to 5.4 gVS/L.d, the SBP of CSTR decreased sharply compared with the hybrid system. The discrepancy in the SBP rate was higher, especially at the higher OLRs. The biogas production rate decreased when OLR was increased by reducing HRT from 25 days to 20 days under the same %TS loading. This shows that HRT is an important operational parameter that significantly affects the anaerobic digestion. The optimum HRT for the CSTR is suggested as 25 days. Specific biogas yield peaked at the OLR of 2.2g VS/L.d in the CSTR. CSTR was not capable of converting organic loads at shorter HRT above 2.6 gVS/L.day showing possibility of inhibition (Fig. 4).

The hybrid system produced 116% higher biogas than the CSTR at the highest OLR applied under shorter HRT (15 days). The SBPR increased with increasing TS loading. No breakthrough was observed in the HR at the loading rates applied. This shows a great advantage of hybrid system for

Figure 1. Anaerobic HR with compartments (developed by Ugurlu A. and Varol A.).

reducing reactor sizes for the real size applications. The separation of the hydrolysis/acidogenesis and acetogenesis/methanogenesis processes in the HR (having four separate CSTRs within) provided better system performance than the completely mixed CSTR system.

When the VBPRs of the reactors were compared it increased up to 1.1 mL/L/d in the CSTR when OLR was 3.3 gVS/L.d. It dropped to 0.8 mL/L.d when VS loading was further increased to 5.4. gVS/L.d (Fig. 3). On the other hand, the VBPR increased consistently in the HR and reached 1.73 mL/L/d at the highest

Figure 2. Variation of SBP rate with respect to OLR during digestion of cattle manure.

Figure 3. Change of VBPR with respect to OLR during digestion of cattle manure.

loading applied which is about 129% than that of in the CSTR. This study showed that dairy manure could be more efficiently degraded to methane in the HR than the single-stage CSTR. It was observed that at higher % TS loadings HR could be operated with higher system stability and with little or no effect of inhibition.

Organic matter removal (VS degradation) is shown in Table 2. The results revealed that the higher VS removals were obtained at lower OLR. At 1.1 gVS/L.d, 66% VS conversion was observed in CSTR, where it decreased to 38% when VS loading was 5.4 gVS/L.d. The single-stage CSTR reactor exhibited lower system stability and biomass conversion efficiency than that of the HR, especially at higher loading rates. The data obtained from the HR showed that the VS (organic) conversion rate (% VS removed/VS added) were higher than the results obtained in the previous studies and from the single-stage studies. The system achieved 80% VS conversion with 410–300 mL biogas/g VS added, which is about 89% of the theoretical amount [6]. The VS conversion rate decreased depending on increase in OLR and TS% and decrease in HRT. At the highest OLR applied (5.4 gVS/L.d, 15d of HRT and 10% TS) the conversion rate decreased to 62% (Fig. 2). When VS conversions of both reactors were compared, the lower conversion rates were achieved in the CSTR than the hybrid system at all loading rates applied at higher loadings the effect of phase separation was more pronounced. The VS conversion of the hybrid system also decreased with

increasing VS loading rate and varied between 80 and 62%. It is reported that phase separated reactors are capable of reliable activity under C:N ratios less than 20 compared with the single-stage systems [17, 19]. It was shown in the previous studies that under low C:N ratios (5–10) growth of microorganisms was not limited [16]. During high substrate loadings (TS) faster bacterial growth and reaction rates resulted in higher biogas productions at the beginning of these sets.

Higher CH₄ content was observed in biogas at lower loading rates (60%) in the CSTR. The biogas produced from compartments 1 and 2 of HR had lower methane content which was about 35–41%. This was expected as methanogenesis proceeded in the last compartments. Higher biogas amounts with higher methane content of 65 to 76% were produced from these compartments. High CH₄ content of the biogas shows that methanogenesis was performed optimally. In the HR, biogas containing high amounts of CO₂ produced during hydrolysis and acidogenesis (compartments 1 and 2) was collected separately from biogas produced in the other compartments (3, 4). By this way, CH₄ composition of biogas was increased substantially, since most of the methane was produced in the methanogenic phase. Separate collection of biogas from the compartments will help CH₄ enrichment of biogas in the pilot or real scale applications. Möller et al. [1] found theoretical methane productivity in dairy manure as 469 L/kg VS. As can be seen the amount of methane production obtained by CSTR is much lower than ultimate methane yield (220 to 75 L/kg VS). This is mainly due to use of certain amount of substrate for bacterial synthesis, presence of lignin-containing compounds which can be degraded to a limited degree and presence of inhibitory compounds such as ammonia and VFA [1].

Methanogens are active at pH between 6.2 and 8, with an optimal range of pH to obtain maximal biogas yield in anaerobic digestion is of 7.0–7.2, but the optimal value of pH varies with substrate and digestion technique [20]. The pH of the CSTR ranged from 6.9 to 7.2 during the OLR of the system was between 1.1 and 2.6 gVS/L.day. However, pH decreased below 6.5 when OLR was increased to 3.3 gVS/L.day and above. Therefore, pH correction was done using a base (NaOH-8M) to bring pH to neutrality in the last 3 Sets to prevent inhibition of methanogens. This can be an indication of lower gas production caused by acid accumulation in the CSTR. The segments in the hybrid system provided phase separation giving different pH values in the compartments and biogas/methane productions. It was observed that hydrolysis and acidogenesis took place in the first and second compartments. The last two compartments acted as methanogenic reactor. The average pH was measured between 4.8 and 5.4 in the first two compartments. It was observed that pH of the last compartments of the HR ran in the optimum pH range for anaerobic digestion (6.8–7.1). No pH correction was required during the operational period of HR.

As shown in Fig. 2, HR operated at 10% TS still performed better compared with CSTR. The HR converted higher amount of organic matter (62–81% VS) into biogas than the single-stage CSTR (38–67% VS). The hybrid system was capable of producing higher SBP at higher OLR.

In single substrate digestion studies, the stable biogas production and stable reactor operation was observed at the HRT of 20 days (OLR: 3.3 g VS/L.d) which was the minimum HRT tolerated by the CSTR system. Therefore, HRTs shorter than 20 days

Table 2. Steady-state results of CSTR and HR from dairy cattle manure obtained at different organic influent rate

	HRT (30 d)		HRT (30 d)		HRT (30 d)		HRT (25 d)		HRT (20 d)		HRT (15 d)	
	TS (4%)		TS (6%)		TS (8%)		TS (8%)		TS (10%)		TS (10%)	
	CSTR	HR	CSTR	HR	CSTR	HR	CSTR	HR	CSTR	HR	CSTR	HR
Total influent rate (g VS/L/day)	1.1	1.1	1.6	1.6	2.2	2.2	2.6	2.6	3.3	3.3	4.1	5.4
SBP (mL/ g VS)	360	410	380	420	370	440	350	425	320	395	240	150
VBPR (L/L/day)	0.40	0.45	0.61	0.67	0.81	0.97	0.91	1.10	1.10	1.30	0.98	0.80
Biogas methane content (%)	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4	Sec. Sec. 3.4
	1.2	37	75	60	35	76	81	67	59	41	75	38
VS conversion (%)	61	37	75	60	35	76	81	67	59	41	75	38
pH change (*pH neutralization)	66	80	80	67	65	75	59	72	51	68	42	62
	2	4	2	4	2	4	2	4	2	4	2	4
	6.9-7.2	5.4	7.1	6.9-7.3	5.5	7.2	6.8-7.2	5.1	7.2	6.6-7.2*	4.9	6.9

were not sufficient for VS degradation. However, HR allowed decreasing the HRT until 15 days.

3.2 Co-digestion with MS

Dairy manure is helpful to achieve a suitable pH during anaerobic fermentation with the production of ammonia. The C/N ratio of dairy manure is low resulting in high ammonia concentrations. The produced ammonia can inhibit the system and lower biogas production. This problem may be resolved by co-digestion with a high C/N ratio material. MS is most preferred additional feedstock in biogas plants fed with dairy manure since MS has high carbohydrate composition that can balance dairy manure in terms of C/N ratio and can increase biogas yield. Therefore, the effect of co-digestion with MS was studied to investigate the effect on system stability and biogas production. The presence of MS contributed to decreasing the amounts of nutrients in the mixtures containing higher proportions of the dairy manure.

The change of daily biogas production rate by the co-digestion of dairy manure and MS was recorded between 4 and 10% TS concentrations. The organic content of the dairy manure and MS mixture was 84%. Both reactors were fed with 4:1 (w/w) dairy manure/MS blend.

This study revealed that the co-digestion of dairy manure and MS significantly enhanced the SBP and VBPR performance of the both reactors. The SBP rates of dairy manure and co-digestion with MS exhibited similar trends, initially increasing and subsequently decreasing with respect to increasing VS loading rate. The SBP of CSTR system was 425, 450, 455, 420, 380, 270 and 170 mL/gVS_{added}/day for OLRs 1.1, 1.7, 2.3, 2.7, 3.4, 4.2 and 5.6 gVS/L.d, respectively. This shows that SBP was improved by 13–23% compared with single substrate digestion. On the other hand, during co-digestion, SBP from the HR was 490, 505, 520, 490, 460, 450 and 390 mL/gVS_{added}/d for OLRs 1.1, 1.7, 2.3, 2.7, 3.4, 4.2 and 5.6 gVS/L.d, respectively. The improvement SBP was between 15 and 22% compared with single substrate degradation (Tables 2 and 3). The VBPR increased by about 20 to 36% (2.18 mL/L.d vs. 1.73 mL/L.d) from 4:1 dairy manure/MS blend compared with the anaerobic digestion of pure dairy manure from HR. Higher organic conversion rates were observed with the co-digestion of CM with MS in both reactors. The corresponding organic conversion rates were between 67 and 39% VS/V_S added for the CSTR. The organic conversion of CM and MS mixture was much higher in the HR (80 to 62% VS/V_S added). The average methane content of biogas produced from CSTR was between 60 and 50%. The methane content of the biogas produced from the last two compartments of the HR was between 75 and 71%. It can be seen easily that the performance of the HR was significantly higher than the CSTR at the higher OLRs.

Higher SMPR and VBPR were achieved during co-digestion studies than the mono substrate digestion under the same TS loadings for both reactors (Figs. 4 and 5). It was observed that CSTR co-digesting dairy manure and MS can be operated with higher OLR and shorter HRT than the single substrate digestion. Maximum SBP was obtained during co-digestion with maize at 2.3 gVS/L.d as 455 mL/gVS.d compared with 370 mL/gVS.d during single-stage digestion. The effect of co-digestion was more pronounced with the HR. The SBP increased from 440 to 520

mL/gVS.d from the HR during co-digestion studies. Methane production of the co-digestion of maize with dairy manure was found as 267 L/kg of VS_{added} was obtained by Kalamaras and Kotsopoulos [21] in batch studies. The results obtained by the CSTR is comparable with this study (284–294 L methane/kg of VS_{added}), while higher values were obtained by the HR. The maximum VBPR achieved from the HR on the other hand was 1.73 L/L.d at the highest OLR applied during single substrate feeding. It increased up to 2.18 L/L.d when during co-digestion studies. In order to maximize methane yield, higher system stability is essential in a reactor. The results indicated that co-digestion improved the SBP and VBPR, thereby facilitating the application of higher OLRs and shortening digestion times.

The optimum operational conditions for the CSTR can be proposed as 8% TS loading (3.3 to 3.4 gVS/L.d) with 20 days of HRT for both single substrate (CM) digestion and co-digestion by considering VBPR. The organic conversion rate decreased with increasing TS% (OLR) in both reactors. The organic conversion was between 61 and 50% for the CSTR. HR was capable of converting higher volatile organics into methane (62–80%) even at 10% of TS. Figure 3 showed that HR operated at 10% TS produced biogas around 2.2 times that of CSTR reactor without any sign of inhibition.

Moreover, the co-digestion of CM and MS showed relative higher process stability with regard to single substrate digestion and no process inhibition was observed. Co-digestion also reduced the retention time. HR achieved higher SBP and VS conversion rates when HRT was longer than 15 days.

High ammonia content of dairy manure results in ammonia production. When only dairy manure was utilized in the reactors, the stability of CSTR was low, especially during the higher organic loadings. Thus, the byproducts of anaerobic digestion (produced ammonia) may have inhibited the anaerobic bacteria, which would lead to lower VS conversion and methane production. SBP from HR fed with dairy manure and MS (co-digestion) increased from 1.29 L/Lreactor.d (which was the maximum rate achieved in CSTR) to 2.18 L/Lreactor.d due to higher organic conversion and high loading rate. Furthermore, VBPR for HR fed with only dairy manure was increased from 1.1 L/Lreactor.d (which is maximum rate for CSTR) to 1.73 L/Lreactor.d by adding a co-substrate. When the acceptable biogas production rate which is 1 L/Lreactor.d is taken into account, it can be concluded that VBP rate was significantly enhanced by the HR. The higher production of biogas obtained from co-digestion than the single substrate digestion under the similar OLRs can be explained by the higher system stability conditions arising from the balanced nutrient levels during co-digestion.

Li et al. [22] studied anaerobic semi-continuous co-digestion of cow manure with three types of straws under five mixing ratios. The biogas production rate was observed between 101 and 576 mL/L.d and obtained a high CH₄ content and VS reduction when mass mixing ratio of cow manure to crop of 1:9. However, in this study higher results were obtained by both CSTR and HR at a mixing ratio of 4:1 with MS. In another study, Giuliano et al. [23] investigated the biogas yield from anaerobic co-digestion of manures and energy crops in four pilot scale CSTRs. They obtained the highest SBP at an OLR of 2 kg TVS/m³ consisting of 50% manure, 25% energy crops and 25% agro-waste on VS basis as 0.54 m³/kg VS_{fed}.

Table 3. Steady-state results of CSTR and HR from co-digestion of dairy cattle manure and MS

	HRT (30 d)		HRT (30 d)		HRT (30 d)		HRT (25 d)		HRT (20 d)		HRT (20 d)		HRT (15 d)	
	TS (4%)		TS (6%)		TS (8%)		TS (8%)		TS (8%)		TS (10%)		TS (10%)	
	CSTR	HR	CSTR	HR	CSTR	HR	CSTR	HR	CSTR	HR	CSTR	HR	CSTR	HR
Total influent rate (g VS/L/day)	1.1	1.1	1.7	1.7	2.3	2.3	2.7	2.7	3.4	3.4	4.2	4.2	5.6	5.6
Specific biogas production (mL/g VS)	425	490	450	505	455	520	420	490	380	460	270	450	170	390
VBPR (L/L/day)	0.47	0.54	0.77	0.86	1.10	1.20	1.13	1.32	1.29	1.56	1.13	1.90	0.95	2.18
Biogas methane content (%)	60	74	59	73	59	75	57	72	55	72	52	71	50	72
Volatile solid conversion (%)	67	78	66	79	64	74	55	69	52	66	44	63	39	62
pH change (*pH neutralization)	6.9–7.2	5.5	6.8–7.1	5.3	6.7–7.0	4.9	6.8–7.1	4.9	6.6–7.1*	4.7	6.5–7.2*	4.8	6.7–7.1*	4.6
		2	4	2	4	2	4	2	4	2	4	2	4	2
		5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9	4.6
		Sec.	Sec.	Sec.	Sec.	Sec.	Sec.	Sec.	Sec.	Sec.	Sec.	Sec.	Sec.	Sec.
		Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4	Sec. 3.4
		1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
		35	38	38	73	59	42	75	40	72	41	38	71	36
		60	74	59	73	64	74	55	69	66	44	63	39	62
		67	78	66	79	64	74	55	69	66	44	63	39	62
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
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		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
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		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
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		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.3	7.3	4.9	7.1	4.9	7.1	4.7	7.0	4.8	6.9
		6.9–7.2	5.5	7.2	5.

Figure 4. Variation of SBP rate with respect to OLR during co-digestion with MS.

Figure 5. Change of VBPR with respect to OLR during co-digestion with MS.

No significant differences were observed in pH of the reactors during single-substrate digestion and co-digestion studies. The both systems digesting MS and dairy manure showed no deterioration in performance or stability throughout the co-digestion period. However, pH of the CSTR decreased below the optimum range for anaerobic digestion when loading rate was $\geq 3.4 \text{ g VS/L.d}$ and pH was increased by using a base solution. At this OLR decreases in SBP and VBPR were observed (Fig. 4) can be the indication of inhibition. In the HR, on the other hand, pH varied between 5.5 and 4.7 in the first two compartments and 6.9 to 7.3 at the last two compartments as in the case of single substrate digestion as it was in the digestion of solely dairy manure.

According to Figs. 4 and 5, HR mainly designed for digesting higher organic loadings was found to be superior to single-stage CSTR model in terms of efficiency and performance. It was observed that the HR achieved higher organic matter conversion and also tolerated higher OLRs. Phase separation provided by compartments prevented inhibition of ammonia due to low C/N ratio of dairy manure at higher OLRs. This resulted in higher SBP and VBPR. In addition, biogas was collected in one compartment in single-stage CSTR. The hydrolysis of dairy manure is difficult and long lasting when compared with other organic wastes since dairy manure consists of high cellulose and hemicel-

lulose content in addition to lignocellulosic content. Therefore, it requires higher retention time for one-stage CSTR. However, in the HR, especially in the first and second compartments, low pH and higher bacterial activity in hydrolysis provided higher VS destruction and lower retention time.

In their study Seppälä et al. [24] investigated the biomethane production from maize and liquid cow manure and the highest methane yield $0.259 \text{ Nm}^3 \text{ CH}_4/\text{kg VS}$ was achieved when the MS was 40% of the feed and the OLR was $2 \text{ kg VS/m}^3.\text{d}$. The present study showed that substrates worked could be digested at a shorter HRT (15 d) in the HR. Aboudi et al. [25] also applied 15 days of HRT (OLR: $4.97 \text{ g VS/L.reactor.d}$) and achieved 32% higher biogas generation during co-digestion of sugar beet byproduct with cow manure compared with mono-digestion. The methane yield from anaerobic digestion of dairy manure was reported as between 0.10 to $0.37 \text{ m}^3/\text{kg VS}$ [26] and for MS between 0.6 and $0.65 \text{ m}^3/\text{kg VS}$ [27]. These results are in agreement with the present study that addition of MS as co-digestate is beneficial for system stability and for increasing biomethane production potential. The performance of the reactors was also evaluated depending on OLR. The study reveals that the optimum OLR is approximately 2.2 g VS/L.d for both of the reactors according to the specific biogas yields. When the VBPRs were compared the optimum OLR for the CSTR was 2.3 g VS/L.d , where after the VBPR decreased with increasing OLR. However, the breakthrough was not observed for the HR although the system was loaded up to 5.4 g VS/L.d . It is supposed that the HR can perform at higher OLR values during single substrate digestion and co-digestion studies. Higher OLR and $<5 \text{ TS } \%$ was inhibitory for anaerobic digestion in the CSTR. VFAs accumulate at higher OLR values whereas lower moisture content at $10\text{--}20\% \text{ TS}$ results in slower acidification in the single-stage reactors [28]. The phase separation in the HR provided better system stability and higher SBP compared with single-stage CSTR. Boe and Angelidaki [5] obtained similar results when they operated single and serial CSTR. They attributed the higher biogas yields in the serial CSTR to better conversion of readily degradable organics compared with the single CSTR. In another study with serial digestion of manure 16.4 to 17.8% higher biogas production was obtained compared with one-step CSTR [29]. However, in contrast to our study, they did not observe phase separation with $30/70\%$ and $13/87\%$ reactor volume distributions. This could be due to $15/15/30/40\%$ volume distribution in the HR.

4 Concluding remarks

The study explored the production of biogas from dairy manure and co-digestion with MS by using CSTR and horizontal HR. It was found that single-stage CSTR was less efficient in terms of VS conversion and methane production efficiency compared with the newly designed horizontal reactor with phase separation, especially at higher loadings. The HR provided better VS removal under shorter HRT's than the single-stage CSTR. This study has shown that the biogas production from dairy manure could be improved by co-digestion with MS. The co-digestion of CM and MS in the HR provided relatively

better fermentation stability with regard to mono substrate digestion and no process inhibition was observed.

Practical application

The horizontal HR was developed to overcome operational problems of anaerobic digestion, especially during higher loading rates. The HR has phase separation which provides higher system stability. The pH of the one stage CSTR decreased below the optimum value at higher loadings, while the pH in the hybrid system was always in the recommended range for anaerobic digestion. The hybrid system also enables high VS conversion and VBPR at shorter HRT values which help reducing reactor volumes. The anaerobic co-digestion of animal manure with MS provided higher SBP rates compared with single-stage CSTR with mono and co-digestion. Therefore, practical application of the HR will provide higher biogas yields and stability under higher OLR and % TS loadings. The difference in the system performances were more pronounced at higher loading rates.

5 References

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