

## Effect of Diurnally Cyclic Temperature on the Performance of a Continuous Mix Anaerobic Digester

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**Abstract: Problem statement:** Concentrated livestock production is a major contributor to environmental problems through the production of large quantity of husks on relatively small land area. Anaerobic digestion represents a valuable means of cover by these husks into methane while reducing manure pollution problems. **Methodology:** An experimental apparatus, including data acquisition and control system, was developed and used to investigate the effects of two diurnally cyclic temperature ranges (20-40 and 15-25°C) and four levels of hydraulic retention times (25, 20, 15 and 10 d) on the performance of anaerobic reactors operated on screened dairy manure. **Results:** The reactor temperature exhibited a lag relative to the chamber temperature. For the 20-40°C temperature cycles, the average lag at the maximum chamber temperature was 3.75 h while the lag at the minimum chamber temperature was 4.37 h. For the 15-25°C temperature cycle, the average lag at maximum chamber temperatures was 3.61 while the lag of the minimum chamber temperature was 4.34 h. The effluent solids content, total Kjeldahl nitrogen and ammonium nitrogen concentrations were not adversely affected by the reactor diurnally cyclic temperature. The observed values of these parameters compared fairly well with the values obtained by other researchers. The effluent total solids, volatile suspended solids, TKN, NH<sub>4</sub>-N and methane content of the biogas diurnally cyclic patterns were out of phase with the diurnally cyclic pattern of the reactor temperature by about 12 h under most of the investigated operating conditions. The pH and the carbon dioxide content of the biogas all exhibited a diurnally cyclic pattern which was in phase with the reactor diurnally cyclic temperature. The reductions in total solids, total suspended solids, fixed suspended solids, total Kjeldahl nitrogen, ammonium nitrogen and methane yield were all significantly affected by the diurnal temperature range and hydraulic retention time. **Conclusion:** The measured reactor pH followed a diurnally cyclic pattern which was in phase with the reactor temperature. At the operating temperature cycle of 20-40°C, the reactor pH ranged from 6.80-7.54 while VFA concentration ranged from 44.7-154.8 mg L<sup>-1</sup>. At the operating temperature cycle of 15-25°C, the pH ranged from 6.30-6.60 while the VFA concentration ranged from 151.0-1187.0 mg L<sup>-1</sup>.

**Key words:** Anaerobic digestion, dairy manure, continuous mix, diurnal temperature, solids, nitrogen, volatile fatty acids, biogas, methane, livestock production

### INTRODUCTION

Concentrated livestock production is a major contributor to environmental pollution problems through the production of large quantities of wastes on a relatively small land area. When exposed to surface waters, animal manure leads to: (a) an over-enrichment of nutrients causing eutrophication problems (Mogensen *et al.*, 2009), (b) high organic matter content resulting in the exertion of high Biochemical Oxygen Demand (BOD) and causing an ecological imbalance (Dieu, 2009), (c) high pathogen content

causing numerous human and animal diseases (Pimentel *et al.*, 2008a) and (d) high air contamination by obnoxious odorous compounds causing widespread health problems (Bradford *et al.*, 2009). In addition, when manure is decomposed under anaerobic conditions, it releases heat trapping gases such as methane (CH<sub>4</sub>) and Nitrous Oxide (N<sub>2</sub>O) which contribute to climate change (Izaurrealde, 2009).

Modern systems of farming have also resulted in an increased demand of energy. Efforts to increase the quantity of food produced, to meet the needs of a growing population, have led to large mechanical

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energy inputs and increased use of fertilizers and other chemicals which resulted in an increased competition for available energy supplies (Pimentel and Pimentel, 2008). Unfortunately, man has depended for a long time on the burning of finite and non-renewable fossil fuels for meeting his energy needs (Andres *et al.*, 1999). It was not until the energy crises, caused by the wars in the Middle East in the 1970s and 1990s which clearly dramatized the vulnerability of a fossil-fuel based economy, that serious awareness was created over the need for intensified effort at finding alternative energy sources (Cleveland, 1995). Among the various alternative energy sources, biomass (a general term that refers to plant and animal materials) is perhaps the only energy source which is available and affordable to the third world population (Legros *et al.*, 2009). Many chemical and biological conversion processes are available for the release of energy stored in these materials. Among them, anaerobic digestion represents a valuable means of converting biomass to methane (a more efficient and versatile fuel) while acting as a vital means of reducing animal manure pollution problems (Macias-Corral *et al.*, 2008; Riano *et al.*, 2011).

Anaerobic digestion is a biological process in which organic materials are decomposed in the absence of free oxygen to yield methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and small quantities of other gases (H<sub>2</sub>S, N<sub>2</sub> and H<sub>2</sub>O). The process requires the concerted actions of a symbiotic population of three groups of facultative and obligate anaerobic bacteria to: (a) degrade carbohydrates, lipids and proteins into alcohols and long chain fatty acids, (b) produce acetate, carbon dioxide and hydrogen from the end products of the fermentation of organic materials and (c) produce methane and carbon dioxide from the fermentation of acetate as shown in Fig. 1 (Ghaly *et al.* 2000).

Compared to other biological treatment processes, anaerobic digestion has several advantages including: (a) production of usable biogas that is about 60-80% methane with a fuel value of 17-23.9 MJ m<sup>-3</sup> (Macias-Corral *et al.*, 2008; Pimentel *et al.*, 2008b; Porpatham *et al.*, 2008), (b) the digested residue is almost odourless with reduced solids content (Burke, 2001; Dieu, 2009), (c) the inorganic nutrients are conserved in the digestion process resulting in the enhancement of the fertilizer value of the digested sludge (Iannotti *et al.*, 1979) and (d) pathogenic microorganisms such as *Salmonella* Sp. and *Brucella* Sp. as well as weed seeds are destroyed during the anaerobic digestion process (Pyle, 1978; Jeyanayagam and Collins, 1984; El-Mashad *et al.*, 2003; Masse *et al.*, 2011). The latter implies that livestock can be grazed on pastures which have been spread with sludge from the anaerobic digester sooner than would be acceptable if raw manure was used (Blanchard and Gill, 1987).

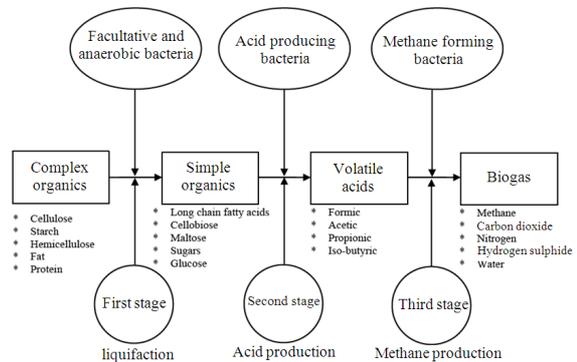


Fig. 1: Three stage anaerobic digestion process

Despite these advantages, anaerobic digestion has not enjoyed widespread acceptance among many farmers due to the relative instability of the system resulting from the sensitivity of anaerobic bacteria to adverse environmental conditions (Ghaly *et al.*, 2000). In particular, temperature is considered to be one of the most important environmental parameters affecting the growth and survival of anaerobic microorganisms (Chen and Day, 1986; Parkin and Owen, 1986; Angelidaki and Ahring, 1994; Burke, 2001; El-Mashad, 2004; Kim *et al.*, 2006; Chae *et al.*, 2008; Appels *et al.*, 2010; Lianhu *et al.*, 2010; Gustin and Marinsek-Logar, 2011). However, the effect of gradual variation in temperature in a diurnal cycle is yet to be investigated.

The aim of this study was to investigate the performance of a continuous mix anaerobic reactor operating under diurnally cyclic temperatures by evaluating reductions in the effluent solids and nitrogenous compounds and the profile of VFA.

## MATERIALS AND METHODS

**Experimental apparatus:** The experimental apparatus (Fig. 2) consisted of four bioreactors, a feeding system, a temperature control system, a gas collection system, a data acquisition and control system and computer.

Each bioreactor (Fig. 3) was constructed of a cylindrical PVC vessel, (458 mm length, 300 mm diameter and a 10 mm wall thickness) it provided a liquid volume of 25 L and a gas head space of 7.4 L. The cover of the bioreactor was made of a transparent Plexiglas plate (370 mm diameter and 10 mm thickness). It was secured to the bioreactor, through PVC lugs glued onto the top outer periphery of the vessel, by means of six bolts. A Vaseline-coated rubber gasket was fitted between the cover and the vessel to provide a gas-tight seal. The temperature and pH

sensors were mounted on special holders threaded through the reactor cover and immersed to a depth of 100 mm below the liquid surface. The contents of the bioreactor were stirred by means of a flat-bladed impeller driven by a 1/12 HP electric motor (Model No. 6105061401, Franklin, Bluffton, Indiana, USA) at a speed of 125 rpm. The manure feed inlet consisted of a 25 mm diameter PVC tube inserted through the bioreactor cover to a depth of 246 mm below the liquid surface. The effluent port was located opposite to the feed inlet port at a distance of 300 mm above the bottom of the bioreactor.

The manure feeding system consisted of a manure storage tank, a feed pump, a set of tubing, a distribution manifold and a set of solenoid valves. A 60 L plastic container was used to store the manure. It was fitted with a stirring paddle driven by a 1/12 HP electric motor (Model 55CP10FG17AX, General Electric, Mississauga, Ontario, Canada) mounted on the tank cover. A feeding port sealed with a rubber bung

as well as a ventilation port were provided on the tank cover. The outlet port of the tank was located at the lower portion of the tank side. A manual valve was provided to control the flow of manure from the tank. A peristaltic pump (Model 110-030, TAT Engineering Co., Logan, Ohio, USA) was used to feed the manure. At a rotational speed of 2 rpm and an output of 0.138 L of manure per revolution, the pump delivered the manure at a capacity of 16.56 L h<sup>-1</sup> from the storage tank through the valve, tygon tubing, the distribution manifold and a set of automatically controlled solenoid valves to the individual reactors. A digital timer controlled and synchronized the operation of the feed tank stirrer (Model 5935932, Type NSI-10R93, Bodine Electric Co, North York, Ontario, Canada), the feed pump and the solenoid valves to ensure the delivery of a well mixed manure to the bioreactors at a predetermined sequence and loading rate. Eight feeding cycles were carried out daily at an interval of 3 h.

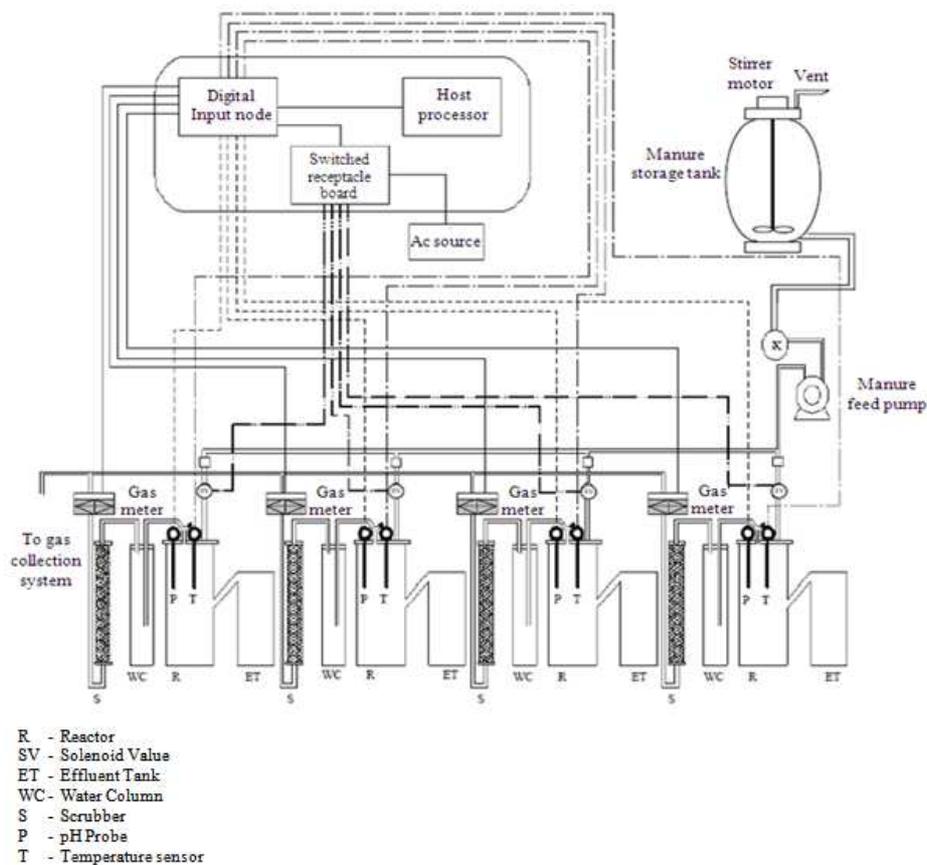


Fig. 2: Schematic of the experimental apparatus

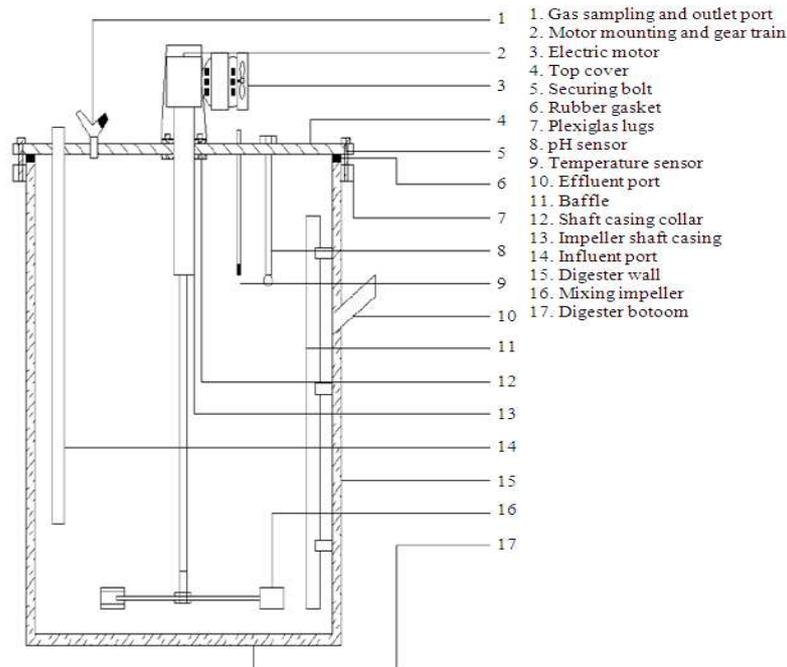


Fig. 3: The continuous mix anaerobic bioreactor

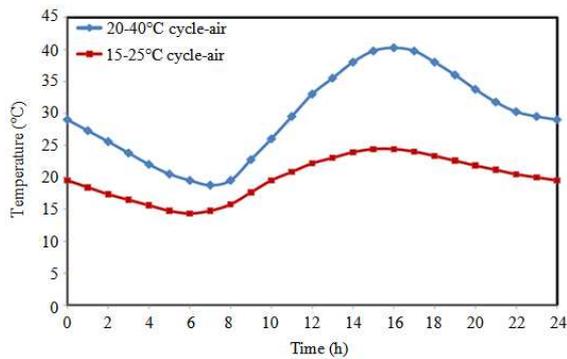


Fig. 4: Diurnal temperature profiles

The objective of the temperature control system was to maintain the profiles of the two temperature cycles (Fig. 4) in the enclosed chamber in which the digesters were located. It consisted of an insulated chamber, a chiller, two heaters, two cross flow heat exchangers, two fans, temperature transducers and ducts for directing the circulation of air (Fig. 5). The chamber was made of a 20 mm thick wooden box (2440 mm long, 710 mm wide and 525 mm deep) and divided into two compartments each was padded with 40 mm of Styrofoam insulation (R-value of 0.88 m<sup>2</sup> K/W). Each compartment was maintained at one of the two temperature profiles and contained two bioreactors.

On the floor of each compartment was a U-shaped galvanized steel duct of 100 mm inside diameter. A fan, a heat exchanger and a heater were located (in that order) inside one arm of each duct which circulated air in a closed loop. The fan drew air from the chamber into the duct and the air circulated over the heat exchanger and the heater and then left the duct through perforations on the other two sections of the U-shaped duct to bathe the bioreactor. The air was circulated using a thermally protected electric fan (Model 4C02A, Dayton Electric Manufacturing Co., Niles, Illinois, USA). The capacities of the heaters were 750 and 500 W for the compartments operated at the higher and lower cyclic temperature ranges, respectively. A digital rapid cool refrigerated bath (Series 900, Polyscience, Niles, Illinois, USA) with an operating temperature range of -35-150°C and an accuracy of ±0.02°C was used. The chiller had a maximum cooling capacity of 425 W at 20°C (or 225 W at -10°C), a bath capacity of 13 L and can deliver a maximum flow of 15 L min<sup>-1</sup> at zero head. Two submersible pumps (Model 1-MA, Little Giant, Bluffton, Indiana, USA), each delivered chilled water to one of the two heat exchangers, were immersed inside the chiller bath. With a power consumption of 3.73 W, each pump had a rated capacity of 10.72 L min<sup>-1</sup> at 0.3 m and a maximum pumping height of 1.85 m.

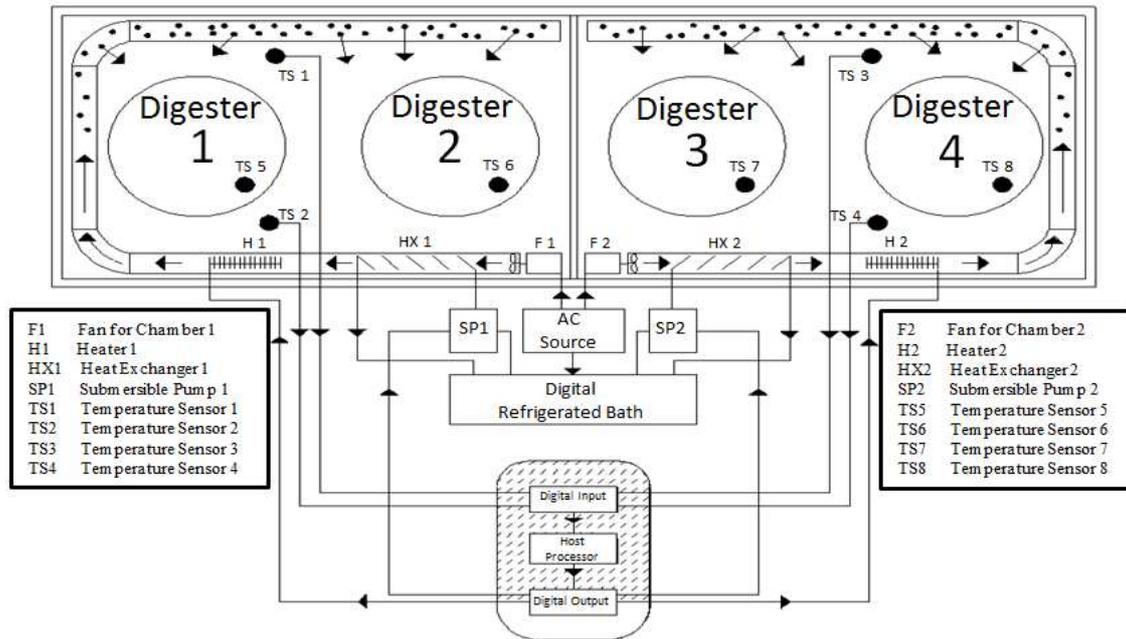


Fig. 5: The temperature control system

A Styrofoam cover of the same thickness as the wall insulation was provided for each of the chamber compartments in such a way that visual examination of the content of the reactors was possible without removing the covers. Four Temperature Sensors (TS1 and TS2 and TS3 and TS4) were mounted on the chamber covers (two for each compartment). During operation, the temperature transducers continuously sampled the air temperature in each of the chamber compartments and transmitted the signals through the digital input node of the data acquisition system to the host processor. Every 30 sec, the host processor computed the average temperature of each compartment and compared these with set point values. Depending on the error signal, the host processor generated a correction signal which either turned the heaters and the chilled water submersible pumps on and off (or vice versa), respectively.

Gas collection was effected through a Y-shaped nipple fitted on the cover. One end of the nipple carried a rubber septum through which gas samples were drawn with a syringe. The other arm of the nipples was fitted with flexible tubing which conveyed the evolved gases through a water column, gas scrubber and gas meter to the gas collection and storage system. The water column was used to provide back pressure in the reactor to maintain a constant liquid level. The scrubber was made of a gas-tight Plexiglas column (80 mm diameter and 450 mm long) filled with steel wool to strip the

biogas of hydrogen sulphide. The gas meter was a tipping balance meter which indicated when  $50 \pm 2$  mL of gas had been collected. The collected gas was subsequently pumped into a gas cylinder by means of a compressor.

**Manure collection, preparation and storage:** Dairy manure was collected from a commercial dairy farm located in Stewiacke, Nova Scotia, Canada. The manure was scrapped off the floor of the dairy barn and screened using a modified fish de-boner (Model SDX16, Bibun, Japan). During the sieving process, tap water was added to dilute the manure to 6.5% solid content. The manure was placed in buckets of 30 L and the buckets were sealed and transported to a commercial freezing plant (Associated Freezers, Dartmouth, Nova Scotia, Canada) where they were stored at  $-25^{\circ}\text{C}$  until needed. When needed, buckets of manure were removed from the freezer and kept at room temperature in the Waste Management Laboratory to thaw for 48 h and the manure was then loaded into the feeding tank. Some characteristics of raw manure are shown in Table 1.

**Start-up procedure:** The bioreactors were started by adding 18.0 L (to each reactor) of actively digesting sewage sludge obtained from Mill Cove Municipal Wastewater Treatment Plant (Bedford, Nova Scotia, Canada). This was followed by the addition of 7.0 L of

screened dairy manure. The temperature control and the data acquisition systems were activated and the digesters were operated in batch mode for 48 h. The feeding system was used to feed the reactors. Reactors R1 and R2, were operated at the diurnal temperature cycle of 20-40°C and received feed at rates of 0.33 and 0.42 L d<sup>-1</sup>, respectively. Reactors R3 and R4 were operated at the diurnal temperature cycle of 15-25°C and received feed at rates of 0.33 and 0.42 L d<sup>-1</sup>, respectively. Feeding rates were equivalent to hydraulic retention times (HRTs) of 75 days for the feeding rate of 0.33 L d<sup>-1</sup> and 60 days for the feeding rate of 0.42 L d<sup>-1</sup>. The feeding rates were then adjusted to 0.5 L d<sup>-1</sup> for reactors R1 and R3 and 0.63 L d<sup>-1</sup> for R2 and R4 and were held constant for 72 h. These rates corresponded to HRTs of 50 and 40 days, respectively. These rates were maintained for another 48 h.

**Operating procedure:** After 7 days from start-up, R1 and R3 were operated at an HRT of 25 days while R2 and R4 were operated at an HRT of 20 days. The start-up period was concluded after a period of 32 days. Following the initial start-up period, monitoring of the biogas production was started on day 33 (from the start). Steady state was construed to have been achieved when a uniform gas production and/or uniform effluent quality were achieved. Once the steady-state was achieved at a given retention time, the system parameters were measured/monitored for a period of at least five days. The feeding rates of the reactors were adjusted for the next set of retention times (15 days for reactors R1 and R3 and 10 days for reactors R2 and R4). When the steady state was attained, sampling/monitoring was continued for five days.

Table 1: Characteristics of raw manure

Parameter	Mean value*
Total solids (g/L)	64.25
Total volatiles solids (g/L)	50.26
(% of total solids)	78.23
Total fixed solids (g/L)	13.99
Total suspended solids (g/L)	42.25
Volatile suspended solids (g/L)	31.00
Fixed suspended solids (g/L)	11.25
Total COD (g/L)	98.80
Soluble COD (g/L)	27.90
Total kjeldahl nitrogen (g/L)	3.80
Ammonium nitrogen (g/L)	2.45
NH <sub>4</sub> -N/TKN ratio	0.64
Volatile FATTY ACID (VFA)	
Acetic (g/L)	1.55
Propionic (g/L)	0.28
i-Butyric (g/L)	0.04
Butyric (g/L)	0.06
i-Valeric (g/L)	0.04
Valeric (g/L)	0.02
i-Caprioc (g/L)	0.01
Caprioc (g/L)	0.01
Heptanoic (g/L)	0.04
Total VFA as Acetic acid (g/L)	1.91

\* Each value represents the average of 5 samples

**Analyses:** The liquid samples were analyzed for Total Solids (TS), Total Volatile Solids (TVS), Total Fixed Solids (TFS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Fixed Suspended Solids (FSS), Total Kjeldahl Nitrogen (TKN), ammonium nitrogen (NH<sub>4</sub>-N) and Volatile Fatty Acids (VFA). The biogas samples were analyzed for gas composition.

The total solids and suspended solids analyses were performed according to procedures described in the Standard Method for the Examination of Water and Wastewater (APHA, 1985). The total Kjeldahl and ammonium nitrogen were determined using a Tecator Kjeltec Auto Analyzer (Model 1030 and Se catalyst, Tecator, Paris, France).

The individual volatile acids (C<sub>2</sub>-C<sub>7</sub>) contained in a sample were determined using a Hewlett-Packard gas chromatograph (Model 5890 series II, Mississauga, Ontario, Canada) equipped with an HP 76734A automatic injector. Extraction of the VFA was carried out by acidifying 3.0 mL of each of the manure samples using 0.1 mL 30% sulphuric acid. The acidified samples were well mixed and centrifuged at 7000 rpm for 20 min. 2.0 mL of the supernatants were decanted and an equal amount of diethyl ether was added. The mixtures were well shaken and then centrifuged at 5000 rpm for 5 min to break down the emulsion layer. The upper layer which consisted of di-ethyl ether was removed for analysis. Volatile acids were, also, extracted from a volatile acid standard mixture (No4-6975, SupelCo, Oakville, Ontario, Canada) using di-ethyl ether. The chromatograph was calibrated by injecting 1.0 mL of the extracted standard VFA mixture into the 25×0.2 mm capillary column of the liquid chromatograph whose film thickness is 0.33 mm. 1.0 mL of the extracted samples were injected into the column. A split ratio of 1:5 was applied. The column temperature was first maintained at 60°C for 3 min and then increased at a rate of 10°C min<sup>-1</sup> until a temperature of 150°C was attained. The column temperature was maintained at 150°C for 2 min. The injector was set to 180°C while the flame ionization detector was set at 250°C. The carrier gas was helium at a flow rate of 1.2 mL min<sup>-1</sup>.

The composition of biogas was determined using a gas chromatograph (Model HP 5980A, Hewlett Packard, Mississauga, Ontario, Canada). Samples of 0.1 mL were taken from the gas collected in the sampling tube using a gas tight locked syringe. The samples were injected into 152.4 mm ×3.2 mm (6 in×1/8 in) OD porapak Q stainless steel column of the gas chromatograph which is connected in a series bypass arrangement with a 152.4 mm ×3.2 mm (6 in ×1/8 in) OD molecular sieve 5 A 60180 stainless steel column. The switch valve of the gas chromatograph was adjusted to permit the molecular sieve column to store

nitrogen, methane and carbon monoxide until the elution of the CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> through the porapak Q stainless steel column. The column was maintained at 45°C with helium as the carrier gas at 30 mL min<sup>-1</sup>. The injector was set at 150°C while the thermal conductivity detector was set at 250°C.

### RESULTS

**Temperature:** Typical variations of reactor temperatures with those of the chambers for the 20-40 and 15-25°C diurnal temperature cycles are shown in Fig. 6. A summary of the reactor temperature profiles at the various operating conditions is presented in Table 2.

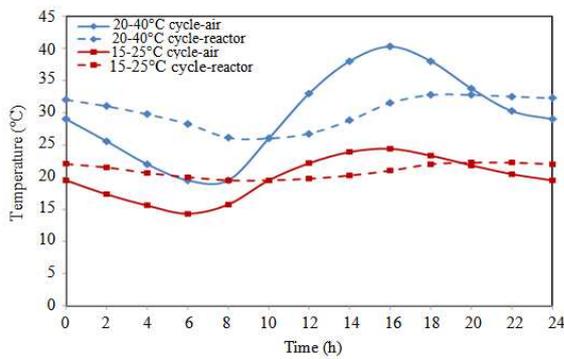


Fig. 6: Diurnal variations in bioreactor and ambient temperatures

**Total solids:** The average values of total, fixed and volatile solids concentrations of the effluent samples collected during the steady state and their reductions are shown in Table 3. The diurnal variations in the total solids of the effluent collected over a 24 h period during the steady state are shown in Fig. 7.

**Suspended solids:** The total suspended, fixed and volatile solids of the effluent samples collected at steady state and their reduction are shown in Table 4. The diurnal variations in suspended solids are shown in Fig. 8.

**Nitrogen:** The Total Kjeldahl Nitrogen (TKN) and the ammonium nitrogen (NH<sub>4</sub>-N) concentrations of the effluent samples collected at steady state and their reductions are shown in Table 5. Diurnally cyclic variations in the TKN were observed at all HRTs under both temperature cycles (Fig. 9).

**Volatile fatty acids:** The concentrations of Volatile Fatty acids (VFAs) in the effluent samples taken during the steady state conditions are shown in Table 6. The VFAs included: acetic, propionic, isobutyric, iso-valeric, valeric, iso-caprioc and heptanoic acids.

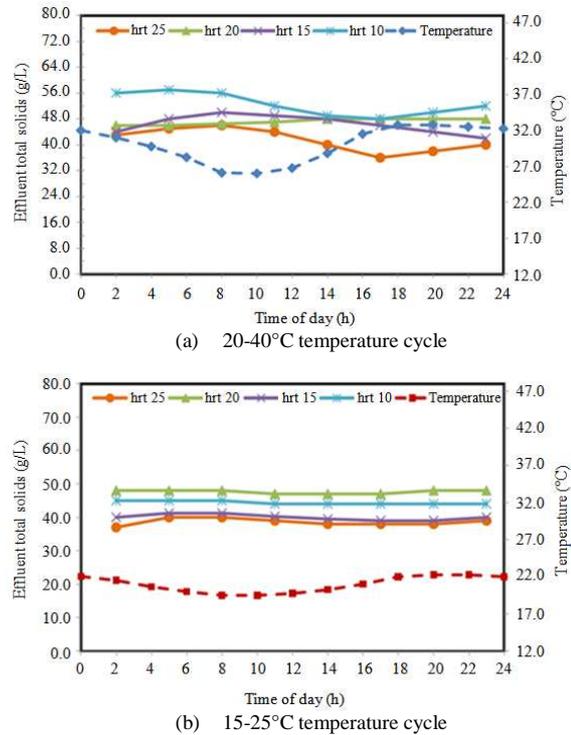


Fig. 7: Diurnal variations in total solids

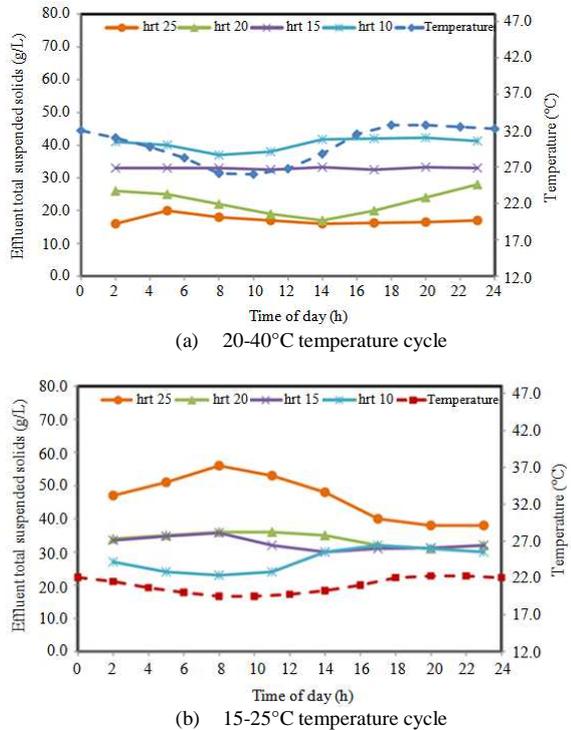


Fig. 8: Diurnal variations in total suspended solids

Table 2: Summary of reactor temperature profiles

Temperature Cycle (°C)	HRT (d)	Reactor Temperature (°C)			Lag at (h)	
		T <sub>min</sub>	T <sub>max</sub>	A	L <sub>min</sub>	L <sub>max</sub>
20-40	25	25.50	33.70	8.20	3.38	4.35
	20	25.10	33.60	8.40	3.30	4.69
	15	26.00	33.90	7.90	3.37	3.19
	10	25.20	33.80	8.60	3.27	3.49
	Mean	25.50	33.80	8.30	3.33	3.93
	SD	0.40	0.13	0.31	0.05	0.71
15-25	25	18.60	22.90	4.30	3.51	4.37
	20	18.30	22.40	4.10	3.47	4.47
	15	18.50	22.90	4.40	3.30	3.37
	10	18.80	22.80	4.00	3.19	3.60
	Mean	18.60	22.80	4.20	3.37	3.95
	SD	0.21	0.24	0.18	0.15	0.55
	CV	0.01	0.01	0.04	0.04	0.14

SD = Standard Deviation; CV = Coefficient of Variation; T<sub>max</sub> = Maximum temperature; T<sub>min</sub> = Minimum temperature; A = Amplitude; L<sub>min</sub> = Lag at minimum temperature; L<sub>max</sub> = Lag at maximum temperature

Table 3: Total solids

Temperature Cycle (°C)	HRT (d)	TS		TFS			TVS			
		Mean (g/L)	Reduction		Mean (g/L)	Reduction		Mean (g/L)	Reduction	
			(g/L)	(%)		(g/L)	(%)		(g/L)	(g/L)
20-40	25	40.60	23.65	36.8	10.60	3.39	24.2	30.0	20.26	40.3
	20	41.30	22.95	35.7	10.90	3.09	26.4	30.4	19.86	39.5
	15	44.10	20.45	31.4	11.80	2.19	15.7	32.3	17.96	35.7
	10	44.80	19.45	30.3	12.10	1.89	13.5	32.7	17.56	34.9
15-25	25	39.70	24.55	38.2	9.40	4.59	32.8	30.3	19.96	39.7
	20	44.90	19.35	30.1	10.20	3.79	27.1	34.7	15.56	30.9
	15	47.30	16.95	26.4	10.60	3.39	25.7	36.7	13.56	26.9
	10	48.60	15.65	24.4	11.00	2.99	21.4	37.4	12.66	25.2

TS = Total Solids; TFS = Total Fixed Solids; TVS = Total Volatile Solids; Initial TS = 64.25 g L<sup>-1</sup>; Initial VS = 50.26 g L<sup>-1</sup>; Initial FS = 13.99 g L<sup>-1</sup>

Table 4: Suspended solids

Temperature Cycle (°C)	HRT (d)	TSS		FSS			VSS			
		Mean (g/L)	Reduction		Mean (g/L)	Reduction		Mean (g/L)	Reduction	
			(g/L)	(%)		(g/L)	(%)		(g/L)	(g/L)
20-40	25	35.40	6.85	16.21	9.40	1.85	16.44	26.00	5.00	16.13
	20	37.20	5.05	11.95	4.40	6.85	60.89	32.80	-1.80	-5.80
	15	39.80	2.45	5.80	5.00	6.25	55.56	34.80	-3.80	-12.26
	10	42.30	-0.05	-0.11	7.00	4.25	37.78	35.30	-4.30	-13.87
15-25	25	35.40	6.85	16.21	9.40	1.85	16.44	26.00	5.00	16.13
	20	39.50	2.75	6.51	10.60	0.65	5.78	28.90	2.10	6.77
	15	42.30	-0.05	-0.11	10.70	0.55	4.89	31.60	-0.70	-1.94
	10	46.00	-3.75	-8.88	10.90	0.35	3.11	35.10	-4.10	-13.23

TSS = Total Suspended Solids; FSS = Fixed Suspended Solids; VSS = Volatile Suspended Solids; Initial TSS = 42.25 g L<sup>-1</sup>; Initial VSS = 31.00 g L<sup>-1</sup>; Initial FSS = 11.25 g L<sup>-1</sup>

Table 5: Total kjeldahl and ammonium nitrogen

Temperature Cycle (°C)	HRT (d)	TKN			NH <sub>4</sub> -N			NH <sub>4</sub> -N / TKN
		Mean (g/L)	Reduction		Mean (g/L)	Reduction		
			(g/L)	(%)		(g/L)	(g/L)	
20-40	25	1.87	1.93	51.32	3.06	-0.61	-40.00	1.63
	20	2.04	1.76	46.32	3.43	-0.98	-40.06	1.68
	15	2.24	1.56	41.05	3.61	-1.16	-47.35	1.61
	10	2.37	1.43	37.63	3.70	-1.25	-51.02	1.56
15-25	25	1.78	2.02	53.16	3.03	-0.68	-23.67	1.85
	20	2.02	1.78	46.84	3.21	-0.76	-31.02	1.59
	15	2.12	1.68	44.21	3.24	-0.79	-32.45	1.52
	10	2.30	1.50	39.47	3.45	-1.00	-40.82	1.50

TKN = Total Kjeldahl Nitrogen; NH<sub>4</sub>-N = Ammonium Nitrogen; Initial TKN = 3.80 g L<sup>-1</sup>; Initial NH<sub>4</sub>-N = 2.45 g L<sup>-1</sup>; Initial NH<sub>4</sub>-N/TKN = 0.64

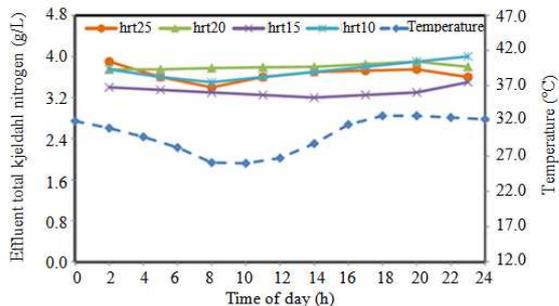
Table 6: Volatile fatty acids

Temp Cycle (°C)	HRT (d)	Concentration (mg/L)									
		Acetic acid	Propionic acid	i-Butyric acid	n-Butyric acid	i-Valeric acid	n-Valeric acid	i-Caproic acid	n-Caproic acid	Heptanoic acid	Total as acetic acid
20-40	25	5.5	26.60	15.60	8.40	9.80	<0.01	11.70	3.90	5.70	60.0
	20	44.0	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	44.7
	15	3.0	26.00	10.70	11.30	9.70	1.30	3.30	2.40	2.50	50.0
	10	53.8	56.90	35.70	8.20	11.50	5.00	9.00	4.70	16.90	154.8
15-25	25	54.1	73.60	13.70	18.30	3.90	<0.01	2.20	5.40	20.00	151.0
	20	70.8	102.10	19.10	26.00	19.80	4.70	6.10	6.10	58.40	231.8
	15	207.4	92.00	18.50	27.60	19.70	4.10	6.60	4.30	59.40	362.5
	10	645.0	431.40	139.70	38.60	36.00	25.00	22.70	17.80	30.10	1187.0
Raw manure		1548.4	283.50	44.50	60.50	40.20	21.00	7.00	11.30	37.10	1913.0

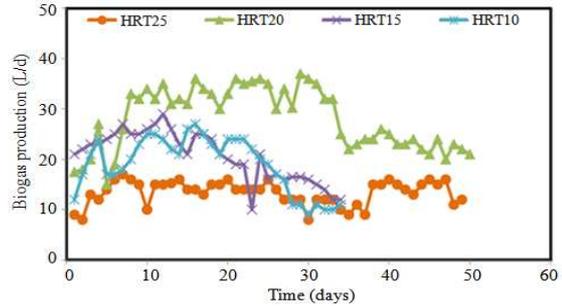
Table 7: Biogas composition\*

Temperature Cycle (°C)	HRT (d)	Gas composition				
		CH <sub>4</sub> (%)	SD (%)	CO <sub>2</sub> (%)	SD (%)	Others** (%)
20-40	25	69.0	1.73	25.8	1.490	5.2
	20	67.6	1.31	28.6	2.254	3.8
	15	62.6	0.98	37.3	0.980	0.1
	10	64.9	0.98	34.9	0.990	0.2
15-25	25	71.8	2.13	25.3	0.970	3.0
	20	69.6	1.79	27.3	0.900	3.1
	15	47.8	0.58	44.0	1.280	8.2
	10	44.6	0.53	43.6	1.840	11.8

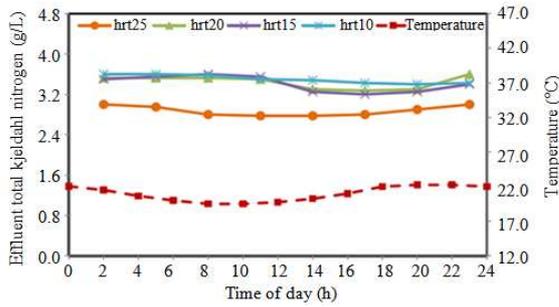
\* Each mean represents the average of 12 samples; \*\*: Nitrogen, hydrogen sulphide, carbon monoxide; SD = Standard Deviation



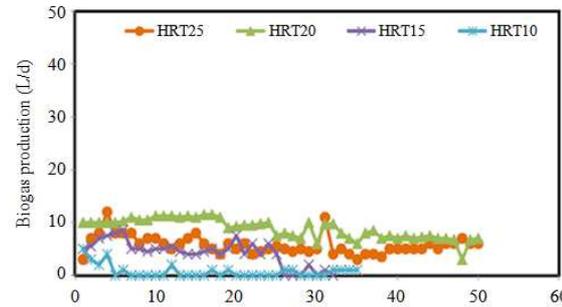
(a) 20-40°C temperature cycle



(a) 20-40°C temperature cycle



(b) 15-25°C temperature cycle



(b) 15-25°C temperature cycle

Fig. 9: Diurnal variations in total kjeldahl nitrogen

**Biogas production and composition:** Figure 10 shows the daily biogas production under various operating conditions. The diurnal variations in the mean rate of biogas production for the 25 h HRT are shown in Fig. 11.

Fig. 10: Daily biogas production

A summary of the average composition of the biogas collected under the various treatment combinations is shown in Table 7.

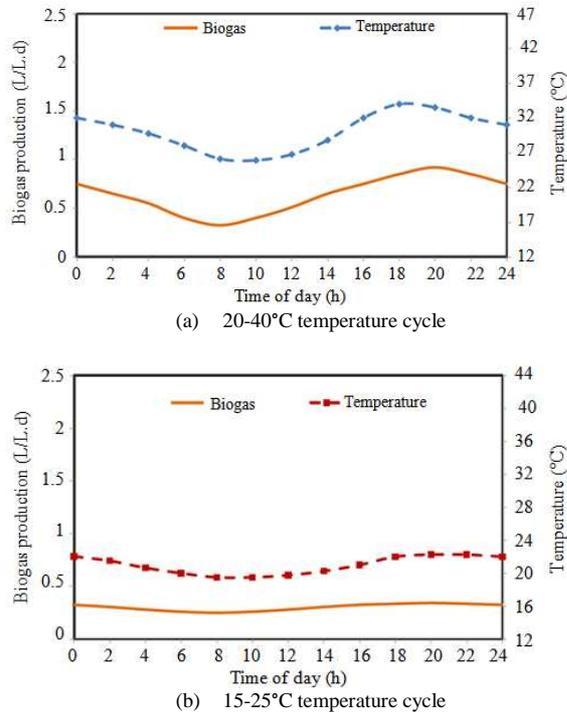


Fig. 11: Diurnal variations in biogas production at the 25 d HRT

## DISCUSSION

**Temperature:** The mean minimum and maximum temperatures for the reactors operating under the 20-40°C temperature cycle were 25.5 and 33.8°C, respectively giving a mean amplitude of  $\pm 8.3^\circ\text{C}$ . The mean minimum and maximum temperatures for the 15-25°C temperature cycle were 18.6 and 22.8°C, respectively giving a mean amplitude of  $\pm 4.2^\circ\text{C}$ . Relative to chamber temperature, there was a lag in the reactor temperature at both the maximum and minimum temperatures of both temperature cycles. The mean lag at the maximum and minimum temperatures for the 15-25°C temperature cycle and the 20-40°C temperature cycle were 3.37 h and 3.95 h and 3.38 h and 4.35 h, respectively. This was due to the significant differences between the density of air in the chamber and the liquid medium in the reactor and the thermal properties of the reactors' walls which affected the rate of heat transfer to and from the reactors.

**Total solids:** Diurnally cyclic variations in the effluent total solids were observed under the 20-40°C temperature cycle. However, the diurnally cyclic variations in total solids were not distinct at the 15 and

10 d HRTs under the 15-25°C temperature cycle. Similar diurnally cyclic variations were observed for the effluent total volatile solids and total fixed solids.

For the 20-40°C temperature cycle, the TS reductions ranged from 30.3-36.8% (19.45-23.65 g L<sup>-1</sup>), the TVS reductions ranged from 34.9-40.3% (17.56-20.26 g L<sup>-1</sup>) while the TFS reductions ranged from 13.5-24.2% (1.89-3.39 g L<sup>-1</sup>), depending on the hydraulic retention time. For the 15-25°C temperature cycle, the TS reductions ranged from 24.4-38.3% (15.65-24.55 g L<sup>-1</sup>), the TVS reductions ranged from 25.2-39.7% (12.66-19.96 g L<sup>-1</sup>) while the TFS reductions ranged from 21.4-32.8% (2.99-4.59 g L<sup>-1</sup>), depending on the hydraulic retention time.

Higher TS reductions were achieved with the high diurnal temperature cycle (20-40°C) than those with the lower diurnal temperature cycle (15-25°C) at all HRTs. Walkie *et al.* (2004) obtained the highest TS reduction of 46.7% during the treatment of dairy manure at a low temperature range of 11.7-32.4°C. Elango *et al.* (2007) achieved a TS reduction of 87.6% during the treatment of solid wastes over the temperature range of 26-36°C. The TS reduction achieved in the present study (25.2-39.7%) are within the values reported in the literature.

The hydraulic retention time (HRT) had a significant effect on the TS reduction in the present study. Generally, the shorter the HRT, the lower the solids reductions. Ribas and Barana (2003) reported that a decrease in the HRT from 16.6-9.7 d increased the TS of anaerobically treated wastewater from 2.3-4.8%. Umana *et al.* (2008) reported an increase in the TS removal efficiency from 14.6-68.8% when the HRT was increased from 1-5.5 d during the treatment of dairy manure. Rico *et al.* (2011a) noted that the concentration of TS increased from 39.2-45.3 g L<sup>-1</sup> as the HRT was decreased from 20-10 d during the treatment of dairy manure.

The absolute values of TVS reductions (g/L) were generally lower than those of the TS. This may be explained by the fact that volatile solids are converted to microbial biomass, volatile fatty acids (VFAs) and biogas. While microbial biomass contributes to the total solids content of the effluent, the VFAs are evaporated at 105°C and therefore, are not detected in TS measurements (Ghaly and Echiegu, 1993).

The HRT had a significant effect on the effluent TVS. Generally, the shorter the HRT the lower the TVS reduction. De la Rubia *et al.* (2002) reported an increase in the TVS reduction (from 53-73%) as the HRT increased from 27-75 d. Ribas and Barana (2003) reported an increase in the TVS from 1.6-4.3% in a wastewater treatment system as the HRT was decreased from 16.6-9.7 d. Umana *et al.* (2008) reported an

increase in the TVS reduction (from 26.3-78.8%) during the treatment of dairy manure as the HRT was increased from 1-5.5 d. Rico *et al.* (2011b) noted that the concentration of TVS increased from 23.7-27.8 g L<sup>-1</sup> during anaerobic treatment of dairy manure as the HRT decreased from 20-10 d. The reduction in the TVS obtained in this study (25.2-39.7%) were within the range reported in the literature.

The diurnal cycling temperature also affected the TVS reductions, the higher the temperature the higher the TVS reduction. Walkie *et al.* (2004) achieved the highest TVS reduction of 60.4% at a temperature of 32.4°C during the treatment of dairy manure wastewaters. Elango *et al.* (2007) reported 88.1% reduction in TVS over the temperature range of 26-36°C. Trazcinski and Stuckey (2011) reported TVS reductions in the range of 40-75% at the temperatures of 21-35°C during anaerobic digestion of solid waste. The TVS reductions achieved in this study (25.2-39.7%) are within the range reported in the literature.

Fixed solids represent the inorganic components of the waste and it consists of potassium, sodium, calcium, magnesium, iron, copper and other minerals (Ghaly and Echiegu, 1993). Unlike carbon and nitrogen, little or no significant losses in these inorganic compounds are generally expected to occur since they do not play a very significant role in the anaerobic digestion process. In this system, a fixed solid recovery ranging from 64.3-112.0% was recorded. Converse *et al.* (1977) reported a fixed solid recovery ranging from 90-104%. In this study, the losses in fixed solids may have been due to inadequate mixing of the bioreactor contents which may have resulted in the settling out of the inorganic mineral resulting in the lower concentration of these compounds in the effluent. They may, also, have been due to the fact that changes in the nature of these inorganic compounds may have occurred at the higher temperature (550°C) used in the determination of total ash content.

**Suspended solids:** Diurnally cyclic variations in the TSS were observed at all hydraulic retention times for both operating temperature cycles. The variations were in phase with the measured bioreactor temperature at all HRTs under the 20-40°C diurnal temperature cycle. They were, also, in phase at the 25 d HRT under the 15-25°C diurnal temperature cycle but out of phase with the reactor temperature by 7-11 h for other HRTs (10-20 d). The variation in Volatile Suspended Solids (VSS) followed a pattern similar to that of TSS, but the fixed suspended solids did not exhibit any diurnally cyclic variation at all HRTs.

With the 20-40°C diurnal temperature cycle, the TSS reductions ranged from -0.11-16.21% (-0.05-6.85 g L<sup>-1</sup>), the FSS reductions ranged from 16.44-60.89% (1.85-6.85 g L<sup>-1</sup>) while the VSS reductions ranged from -13.87-16.13% (-4.30-5.00 g L<sup>-1</sup>), depending on the HRT. With the 15-25°C diurnal temperature cycle, the TSS reductions ranged from -8.88-16.21% (-3.75-6.85 g L<sup>-1</sup>), the FSS reductions ranged from 3.11-16.44% (0.35-1.85 g L<sup>-1</sup>) while the VSS ranged from -13.23-16.13% (-4.10-5.00 g L<sup>-1</sup>), depending on HRT.

The TSS reductions achieved in this study ranged from -8.88-16.21%, the longer the HRT the higher the TSS reductions. Kayranli and Ugurlu (2011) found that the TSS concentrations in the anaerobic treatment of wastewater is higher at shorter HRTs. Lew *et al.* (2004) noted an increase in TSS reduction during the treatment of domestic wastewater as the HRT was increased from 3-24 h. Alvarez *et al.* (2008) reported TSS reductions of 63 and 85% during the anaerobic digestion of wetland plants at HRTs of 5 and 16 h, respectively.

The results also showed that the diurnal cycling temperature had a significant effect on the TSS reductions. Higher TSS reductions were observed with the higher diurnal temperature cycle. Lew *et al.* (2004) reported increased TSS concentrations (from 17-120 mg L<sup>-1</sup>) as the temperature decreased from 28-10°C. Kayranli and Ugurlu (2011) found that as the temperature was decreased from 25-10°C during anaerobic treatment of wastewater the concentration of TSS increased from 6-10 mg L<sup>-1</sup>.

The volatile suspended solids are usually used as an indicator of the cell mass concentration of the system. Higher loading rates (shorter HRTs) promote the formation of larger populations of anaerobic bacteria. The formation of bacteria contributes to the volatile suspended solids content of the system as is reflected in the higher effluent suspended solids content (lower suspended solids reductions) recorded at shorter hydraulic retention times. If the mixing process is not completely perfect, longer hydraulic retention times allows the settling out of some of the settleable components of the suspended solids, the formation of scum at the liquid surface and the attachment of biomass to the walls of the bioreactor. These phenomena would prevent the suspended solids from being washed out with the effluent.

The results showed that higher VSS reductions were observed with longer HRTs. Maharaj and Elefsiniotis (2001) reported VSS reduction of 71.8, 72.9 and 74.6% during the anaerobic digestion of industrial and municipal wastewaters at HRT of 30, 48 and 60 h,

respectively. Chu *et al.* (2011) noted VSS concentrations of 21.50 and 13.25 g L<sup>-1</sup> during molasses fermentation at HRTs of 4 and 8 h, respectively. Al-Ghusain *et al.* (2002) reported VSS concentrations of 4725 and 4614 mg L<sup>-1</sup> during anaerobic sludge digestion at HRTs of 10-20 d, respectively.

The results also showed that the VSS reductions were significantly affected by the reaction temperature. Higher VSS reductions were obtained with the high diurnal temperature cycle. Maharaj and Elefsiniotis (2001) found that the VSS reduction increased from 50-74.6% during the anaerobic digestion of industrial and municipal wastewaters as the temperature was increased from 8-25°C. Al-Ghusain *et al.* (2002) reported VSS concentrations of 4725 and 4549 mg L<sup>-1</sup> during anaerobic sludge digestion at the temperatures of 30 and 40°C, respectively.

**Nitrogen:** Fresh undigested dairy manure contains a substantial amount of organic nitrogen. During the anaerobic digestion process, some of the organic nitrogen is converted by microbial action into ammonium nitrogen. The oxidized forms of Nitrogen (NO<sub>2</sub> and NO<sub>3</sub>) cannot exist in anaerobic environments, hence, the forms of nitrogen that can be present is limited to organic and ammonium nitrogen. These two forms are customarily combined and referred to as Total Kjeldahl Nitrogen (TKN).

The effluent NH<sub>4</sub>-N concentration showed diurnally cyclic variations at the 25 and 20 d HRTs under the 20-40°C diurnal temperature cycle and at all HRTs under the 15-25°C diurnal temperature cycle. The TKN and NH<sub>4</sub>-N concentrations increased with decreases in the HRT under both diurnal temperature cycles. TKN reductions ranged from 2.7-20.31% while NH<sub>4</sub>-N reductions ranged from 3.6-27.6%, depending on operating conditions.

The higher reductions in the nitrogen compounds achieved at the longer HRT were probably because the hydrolytic bacteria responsible for the conversion of organic nitrogen to NH<sub>4</sub>-N were offered greater opportunity to effect the hydrolytic process. Diurnal fluctuations were less with the 15-25°C diurnal temperature cycle compared to the 20-40°C diurnal temperature cycle. The effects of a diurnally cyclic temperature may, therefore, have been less felt at the 15-25°C temperature cycle by the hydrolytic bacteria. This may have led to a higher conversion rate of organic nitrogen to ammonium nitrogen and, hence, to higher losses. The ratio of ammonium to total kjeldahl nitrogen in the effluent sample ranged from 1.52-1.85. These values are comparable to those reported by other researchers (Converse *et al.*, 1977; Rico *et al.*, 2011a;

Sooknah *et al.*, 2004). The aim of anaerobic treatment is to promote the conversion of organic nitrogen into ammonium nitrogen.

**Volatile fatty acids:** The VFAs concentration in the effluent ranged from 45-1200 mg L<sup>-1</sup>, depending on the operating conditions. The effluent VFAs concentration generally increased with decreases in the HRT and higher VFAs concentrations were recorded at the lower temperature cycle. At the 20-40°C diurnal temperature cycle, the VFAs (measured as acetic acid) first decreased from 60-44.7 mg L<sup>-1</sup> as the HRT was reduced from 25-20 d. Further reductions in the HRT resulted in increasingly higher concentrations of VFAs, up to 154.8 mg L<sup>-1</sup> was recorded at the 10 day HRT. Among the individual volatile acids, propionic acid had the highest concentration at all but 20 d HRT. At the 20 d HRT, only acetic acid was detected in measurable levels. At the 15-25°C diurnal temperature cycle, the total volatile acids concentration increased from 151.0 mg L<sup>-1</sup> at the 25 d HRT to 1187.0 mg L<sup>-1</sup> at the 10 d HRT. Propionic acid concentration was higher than that of the rest at the 25 and 20 d HRTs while acetic acid concentration was the highest at the 15 and 10 d HRTs.

The HRT has a significant influence on the production of VFAs, the shorter the HRT the higher the VFAs concentration. Colmenarejo *et al.* (2004) reported that the highest VFAs production was achieved when the HRT was decreased from 5.2-1.7 h. Lew *et al.* (2004) reported that the VFA concentration increased when the HRT was decreased from 24-3 h during the treatment of domestic wastewater. Elefsiniotis and Oldham (1994) reported an increase in VFA production when the HRT was increased from 6-12 h which then decreased with further increase in the HRT to 15 h. Maharaj and Elefsiniotis (2001) noted highest VFA concentration at an HRT of 30 h as appose to 48 and 60 h while an aerobically treating wastewaters. De la Rubia *et al.* (2002) found that the VFA production increased from 5532-6432 mg L<sup>-1</sup> as the HRT decreased from 75-20 days.

The results also showed the importance of temperature on the production of VFAs. Higher VFA production was observed with lower diurnal cyclic temperature. Maharaj and Elefsiniotis (2001) noted increased VFA concentrations as the temperature was increased from 8-25°C, which then decreased upon further increase in temperature (from 25-35°C). Choorit and Wisarnwan (2007) noted that the VFA concentration slightly increased from 160.71-166.64 mg L<sup>-1</sup> as the temperature decreased from 43-37°C and from 245.07-338.71 mg L<sup>-1</sup> as the temperature decreased from 55-49°C. De la Rubia *et al.* (2002)

observed an increase in VFA production from 830-5688 mg L<sup>-1</sup> during digestion of anaerobic municipal sludge as the temperature increased from 35-55°C.

However, values of effluent VFAs concentrations reported in the literature vary depending on the type of waste. Converse *et al.* (1977) reported effluent VFAs concentrations of 423-1113 mg L<sup>-1</sup> (as acetic acid) using CSTR operated on dairy manure of 12.8-13.4% TS content and a temperature of 35°C. Jeyanayagam and Collins (1984) reported effluent VFAs concentrations of 754-1515 mg L<sup>-1</sup> using laboratory digesters operated on dairy manure of 4.0-6.5% TS content at hydraulic retention times of 15-20 d and a temperature of 35°C. Lo and Liao (1986) reported a VFAs concentration of 584 mg L<sup>-1</sup> using a fixed film reactor operated on a screened dairy manure of 3.7% TS content at an HRT of 20 d and a temperature of 12°C. Peck *et al.* (1986) reported effluent VFAs concentrations of 64-98 mg L<sup>-1</sup> using manure of 3458-4109 mg L<sup>-1</sup> TS at 10-25 d HRTs and a temperature of 35°C. The VFA concentrations observed in this study are within the range of values reported in the literature.

Organic wastes are first converted to long chain fatty acids in the acidogenic stage of anaerobic digestion processes. Volatile acids are further converted to acetic acid which together with hydrogen and formate serve as substrates for methane bacteria. Different species of anaerobic bacteria are involved in the conversion of specific long chain fatty acids to acetic acid. The increased proportion of propionic acid relative to acetic acid indicated that the different species of anaerobic bacteria did not respond in a similar manner to the effect of diurnally cyclic temperature. The fact that individual VFAs are removed at different rates under adverse conditions such as a drop in temperature has been observed by other researchers (Peck *et al.*, 1986). A lower methane yield was recorded under the conditions in which the propionic acid concentration was high indicating that propionic acid was not available for conversion to methane.

**Biogas production:** There appears to be a definite relationship between the bioreactor temperature and the rate of biogas production. Biogas production followed a diurnally cyclic pattern similar to that of the bioreactor temperature under most operating conditions. The highest reactor temperature and the maximum rate of biogas production occurred at the 18.00 h while the lowest reactor temperature and the minimum biogas production rate occurred at the 09.00 h. This trend was observed at all HRTs when operating under the 20-40°C diurnal temperature cycle and at the 20 d HRT when operated under the 15-25°C diurnal temperature

cycle. The daily amplitude of the gas production cycle was higher under the 20-40°C diurnal temperature cycle than that observed under 15-25°C diurnal temperature cycle. Smaller amplitude in the gas production cycle was recorded in the lower operating temperature cycle because of the smaller diurnal amplitude of the reactor temperature. With digesters operated under stressful conditions such as a combination of low temperature and high loading rate (short HRT), the recorded diurnal variations in the rate of biogas production were either less pronounced or non-existent. The direct relationship between the rate of biogas production and the reactor temperature is supported by the known fact that microbial activity increases with temperature.

Under the operating temperature cycle of 15-25°C, a steady gas production was achieved at the 25 d HRT only after a few days. At the 20 d HRT, a steady, but not rapid, decline in biogas production was observed after the 15<sup>th</sup> day, following the initial rise in biogas production. At the 15 d HRT, the gas production declined unsteadily after the first 8 days until it completely stopped at the 28<sup>th</sup> day. At the 10 d HRT, the gas production declined rapidly from the start, ceasing completely after the 5<sup>th</sup> day. These results indicated that, the bioreactors did not operate satisfactorily at HRTs shorter than 25 d under the 15-25°C diurnal temperature cycle. The failure of the digesters at 15 and 10 d HRTs is due to the combined effects of the low cyclic diurnal temperature and high loading rate.

The biogas production observed at the 20-40°C diurnal temperature cycle was characterized by rapid rise in production followed by a rapid decline, the shorter the retention time, the more pronounced was the decline. This rapid rise in biogas production experienced at the beginning of each retention time can be attributed to the response of anaerobic bacteria to increased food supply as a result of the higher loading rate. Apparently, the acid forming bacteria responded faster to the increased loading rate. The accumulation of VFAs resulted in bacterial inhibition and, hence, reduction in biogas production. The higher rate of biogas production attained at a 20 d retention time indicated that at HRT longer than 20 d, the reactors may have been underfed whereas at shorter retention times, the reactors may have been overloaded.

In this study, higher biogas production was obtained with the 20 h HRT. However, literature reports on effect of HRT on biogas production vary depending on the type of waste and system used. Hossain *et al.* (2009) noted that the biogas production increased in wastewaters as the HRT increased from 2-8 h, but a

further increase in the HRT from 8-14 h lead to a decrease in biogas production. Huang *et al.* (2011) reported that the higher biogas yields were achieved at lower HRTs (8-12 h) during wastewater treatment. Rico *et al.* (2011b) noted that as the HRT decreased from 20-12.5 d, the biogas production increased from 0.66-1.21 m<sup>3</sup> during the anaerobic digestion of dairy manure.

In this study, higher biogas production was observed with higher temperatures (within the temperature range studied). However the reports on the effect of temperature on biogas production vary. Hossain *et al.* (2009) reported that biogas production increased as the temperature increased from 30-40°C during wastewater treatment, but further increase in temperature from 40-45°C resulted in a decrease in biogas production. Wu *et al.* (2006) noted that the biogas production increased as the temperature increased from 20-40°C during anaerobic digestion of solid wastes and decreased with further increase in temperature to 45°C while a further increase to 55°C lead to a rapid increase in biogas production. Yu *et al.* (2002) reported that more biogas production was achieved at temperatures of 55°C during anaerobic digestion of wastewaters than those obtained at 37°C. Banerjee and Biswas (2004) illustrated that during anaerobic digestion of wastes over the temperature range of 35-55°C maximum biogas production was achieved at 50°C.

**Biogas composition:** Diurnal variations in gas composition were observed at the all HRTs under the 20-40°C diurnal temperature cycle. Similar variations were observed at the 20 d HRT under the 15-25°C diurnal temperature cycle. A better gas quality (higher methane content) was obtained at all HRTs under the 20-40°C diurnal temperature cycle. Higher methane content was also obtained at the 25 and 20 HRTs under 15-25°C diurnal temperature cycle. Rises in the methane content of biogas as a result of a decrease in the bioreactor temperature have been reported by other researchers (Peck *et al.*, 1986). The increase in the quality of biogas is attributed to the raised solubility of carbon dioxide at the lower temperature cycle. Exceptions were observed with failed digesters. In stressed methanogenic systems, hydrogen production and volatile fatty acids (more reduced than acetic acid such as propionate, butyrate) have been reported to be produced in greater proportions (McInerney and Bryant, 1981).

The mean percentage of methane in the biogas ranged from 44.6-71.8%, the carbon dioxide content ranged from 25.3-44.0% while the composition of the

other gases (nitrogen, hydrogen sulphide) ranged from 0.1-11.8%. Methane values reported in the literature ranged from 40-75% (Converse *et al.*, 1977; Hills and Stephens, 1980; Jeyanayagam and Collins, 1984; Lo and Liao, 1986; Peck *et al.*, 1986). The observed values are, thus, within the range reported in the literature.

## CONCLUSION

An experimental apparatus, including data acquisition and control system, was developed and used to investigate the effects of two diurnally cyclic temperature ranges (20-40 and 15-25°C) and four levels of hydraulic retention times (25, 20, 15 and 10 d) on the performance of anaerobic reactors operated on screened dairy manure. The reactor temperature exhibited a lag relative to the chamber temperature. For the 20-40°C temperature cycle, the average lag at the maximum and minimum chamber temperatures and 4.37 h, respectively. For the 15-25°C temperature cycle, the average lag at maximum and minimum chamber temperatures was 3.61 and 4.34 h, respectively. The effluent solids content, total kjeldahl nitrogen and ammonium nitrogen concentrations were not adversely affected by the reactor diurnally cyclic temperature. The observed values of these parameters compared fairly well with the values obtained by other researchers. The effluent total solids, volatile suspended solids, TKN, NH<sub>4</sub>-N and methane content of the biogas diurnally cyclic patterns were out of phase with the diurnally cyclic pattern of the reactor temperature by about 12 h under most of the investigated operating conditions. The pH and the carbon dioxide content of the biogas all exhibited a diurnally cyclic pattern which was in phase with the reactor diurnally cyclic temperature. The reductions in total solids, total suspended solids, fixed suspended solids, total kjeldahl nitrogen and ammonium nitrogen and methane yield were all significantly affected by the diurnal temperature range and hydraulic retention time. The measured reactor pH followed a diurnally cyclic pattern which was in phase with the reactor temperature. At the 20-40°C temperature cycle the reactor pH ranged from 6.81-7.51 while VFA concentration ranged from 44.7-154.8 mg L<sup>-1</sup>. At the 15-25°C operating temperature cycle, the pH ranged from 6.30-6.60 while the VFA concentration ranged from 151.0-1187.0 mg L<sup>-1</sup>.

## ACKNOWLEDGEMENT

This research was supported by the National Science and Engineering Research Council of Canada.

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