0273-2289/91/2703—0217$4.20

Amelioration of Methane Yield in Cheese Whey Fermentation by Controlling the pH of the Methanogenic Stage

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Received February 19, 1990; Accepted April 11, 1990

ABSTRACT

A two-stage, no-mix anaerobic digester of 145 L capacity was used to investigate the effect of controlling the pH of the methanogenic stage on the biogas production and the pollution potential reduction of acid cheese whey. The digester was operated at a 15-d hydraulic retention time, and a temperature of 35°C. Controlling the pH of the methanogenic stage increased the biogas production rate and methane yield by 77.77 and 289.00%, respectively. Reductions of up to 32.19, 44.44, and 35.86% in the COD, solids and nitrogen were achieved.

Index Entries: Anaerobic fermentation; two-stage digester; cheese whey; methanogenic; pH control; sodium hydroxide.

INTRODUCTION

Cheese whey is the liquid byproduct of cheese-making process. It represents about 85–90% of the milk used in the cheese manufacturing process. Cheese whey contains a wide variety of constituents whose quality and composition depend on the type of cheese produced, and the manufacturing technique used. It contains about 52% of the nutrient present in whole milk processed into cheddar cheese, and 73% of the

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nutrients of the skim milk processed into cottage cheese (*1*). Generally, cheese whey contains approx 5% lactose, 1% nitrogenous compounds, 0.8% minerals, and small amounts of vitamins (*2*).

There are two different types of cheese whey: sweet and acid. Sweet wheys are produced by the production of rennet, coagulated cheeses, such as, cheddar and edan. These wheys generally contain very small amounts of lactic acid and have a pH in the range of 5.8 to 6.6. Acid wheys result from acid, coagulated cheeses, such as, cottage or baker's. These wheys contain a higher concentration of lactic acid or added mineral acids. The pH is in the range of 4.0 to 5.0.

It has been estimated that approx 1.5 billion kg of whey were produced in Canada in 1986, of which 49% was used for whey powder, 8% was fed to hogs, 17% was dumped into sewers, and 26% was disposed of on land (*3*). Dried whey powder is an industry that barely recovers its production cost because of poor markets and high energy expenditure. Also, because of high trucking costs, liquid whey can only be used for hog feeding within an economic radius of 30–40 km and, in many cases, the hog population is small in relation to the number of cheese plants (*4,5*). The disposal of the raw cheese whey into the sewer system is becoming a less reliable alternative. Because of its high BOD value (40,000 and 60,000 ppm), whey may disrupt the biological process of sewage disposal plants. Also, the cost of using the sewer has increased substantially, and many sewage treatment plants are now refusing to handle the whey because of its excessive volume, incompatability with other types of municipal wastes, and its low pH. Long-term land disposal of whey may also cause environmental pollution problems, as reported by Ghaly and Singh (*6*) and Ghaly et al. (*3*).

Anaerobic digestion is a biological process in which biodegradable organic materials are decomposed in the absence of oxygen to produce methane, carbon dioxide, and some other trace gases, such as hydrogen sulfide, water vapor, and nitrogen (*7*). The process is carried out in three stages, as shown in Fig. 1. These are:

1. A hydrolysis stage, in which extracellular enzymes are produced by microorganisms present in the system to hydrolyze the organic compounds into simple, soluble compounds;
2. An acid producing stage, in which acid forming bacteria convert simple organic compounds, such as, cellobiose and sugars to volatile acids, such as acetic acid and propionic acids; and
3. Methanogenic stage, in which methane-producing bacteria convert organic acids to methane and carbon dioxide.

The anaerobic treatment of cheese whey for biogas production and pollution potential reduction has been reported by several authors (*7–15*). Studies by Ghaly and Pyke (*16*) reported low biogas productivity and low methane yield because of the very low pH of the whey that affected the

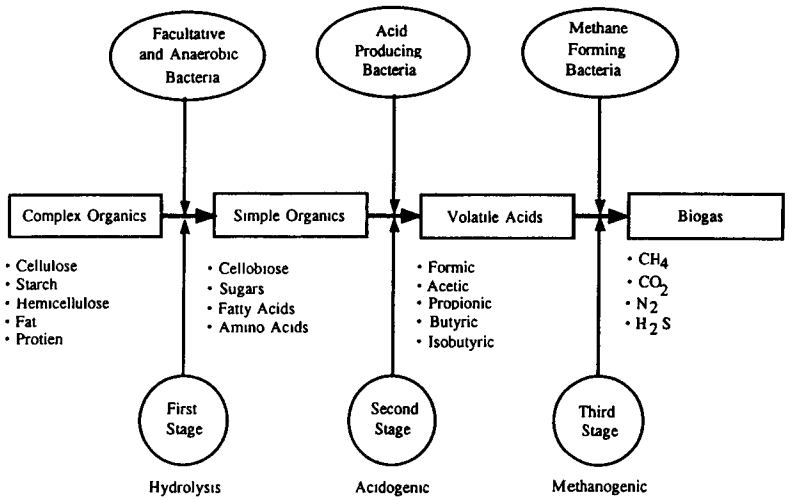

Fig. 1. Anaerobic digestion process.

third stage. In acidic environment, a massive growth of filamentous bacteria with low specific activity and poor stability may be produced, resulting in a lower treatment efficiency (*9,14*). The aim of this project was to study the effect of controlling the pH of the methanogenic stage on the biogas production from acid whey, using a pH-controlled two-stage digester.

OBJECTIVES

The main objectives of this investigation were to study the effect of controlling the pH of the methanogenic stage of the anaerobic digestion process of acid cheese whey on the biogas productivity and methane yield, using a two-stage, no-mix digester; and to evaluate the pollution potential reduction of the effluent as measured by the reductions in the chemical oxygen demand, solids, and nitrogen compounds.

EXPERIMENTAL APPARATUS

The experimental apparatus used in this research consisted of a two-stage, no-mix anaerobic digester and the associated whey feeding and effluent removal system, the gas collection, cleaning, measuring and storage system, and the temperature-controlled environmental chamber. The following are descriptions of the system components.

Digester

A two-stage, no-mix anaerobic digester was designed and constructed from stainless steel and acrylic glass (Plexiglas™) materials. The digester

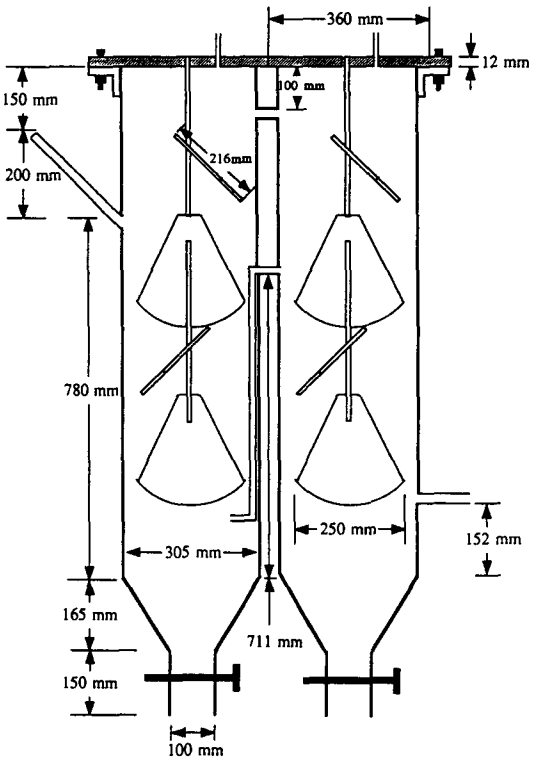

Fig. 2. A two-stage, no-mix anaerobic digester.

consisted of two separate chambers: the inlet chamber and the outlet chamber. The details of the digester are shown in Fig. 2. Each chamber was constructed from gage (2 mm) stainless steel cylinder. The inside diameter and the height of the cylinder were 305 and 1445 mm, respectively. Each chamber had a conical (funnel) shaped bottom with a height of 165 mm. A 100-mm diameter tube was connected to the lower end of the funnel of each chamber. A slide valve was connected to each tube and used for sludge removal from the bottom of each chamber. The total working liquid capacity of the digester was 145 L. This provided a head space above the liquid surface of approx 150 mm (11 L).

The lid of each chamber was fabricated from Plexiglas™ circular plate which allowed for visual inspection of the digester contents. The diameter and thickness of the plate were 360 and 12 mm, respectively. The lid is held in place by eight stainless steel bolts secured into eight stainless steel lugs welded around the upper outside wall of each chamber. A gas tight seal was insured by using a 5 mm thick neoprene ring gasket coated with vaseline. A hole was drilled and tapped through the lid to take a 5 mm hose adaptor to vent the gas. Another hole was drilled and used to accommodate a thermocouple sensor for temperature measurement.

The cheese whey inlet and the effluent outlet were placed below the level of the liquid surface in the digester in order to prevent air from enter-

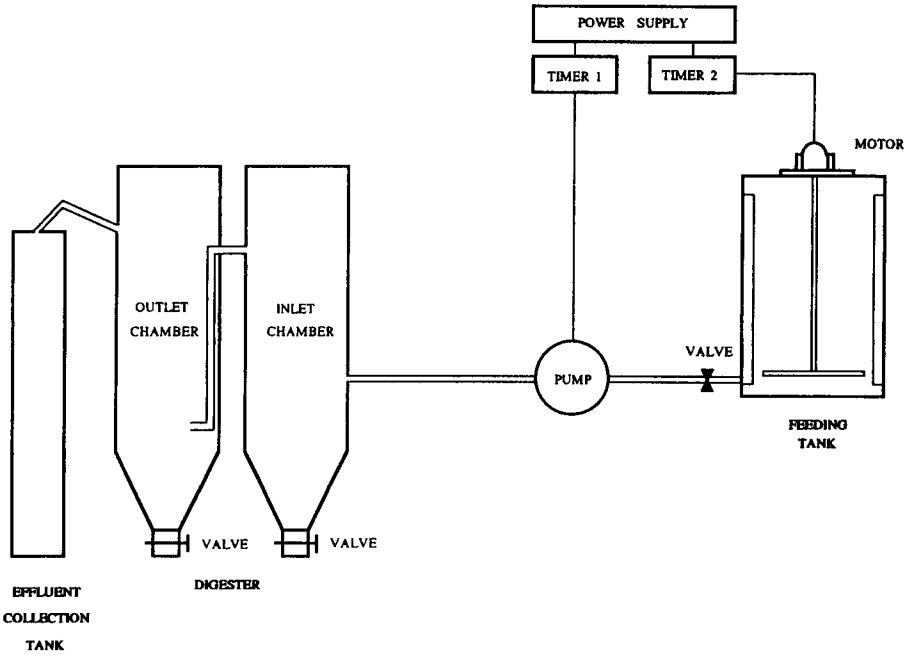

Fig. 3. A schematic representation of the whey feeding and effluent removal system.

ing into the digester. A 20-mm diameter stainless steel inlet tube was mounted on the wall of the inlet chamber at a height of 467 mm from the bottom of the digester, whereas a 20-mm diameter outlet tube was mounted on the wall of the outlet chamber at a height of 1095 mm from the bottom of the digester. A 20-mm diameter stainless steel tube mounted at a height of 1026 mm was used to connect the two chambers.

A system for trapping solid particles was designed and mounted at the center of each chamber. It consisted of a shaft carrying four stainless steel baffles, each measuring 250 mm in width and 216 mm in length. The baffles were welded into the shaft and positioned every 90 degrees. These baffles were used to minimize scum formation resulting from the upward movement of solid particles attached to gas bubbles.

Cheese Whey Feeding and Effluent Removal System

The cheese whey feeding system was fully automated, reliable, and easy to operate. The system consists of a feeding tank for the temporary storage of the cheese whey, a pump to transfer the whey from the feeding tank to the digester, and two mechanical timers for controlling the duration of the feeding periods and the intervals between feedings. Figure 3 shows a schematic diagram of the cheese whey feeding and effluent removal system.

The feeding tank was constructed of a Plexiglas™ cylinder of 450-mm diameter and 650-mm height. It has a capacity of approx 100 L. A mixing system, consisting of a motor (Bodine Electric Model NSI-10R93) and mixing shaft, was used to mix the tank contents. The motor was mounted on the cover of the feeding tank, and connected to the mixing shaft through chuck assembly. It was operated at a rotational speed of 50 rpm. A two bladed impeller was mounted on the shaft at the bottom end. A 25-mm diameter valve was fixed to the side of each tank at 20 mm from the bottom. It was connected to a whey feeding pump (TAT Pump Model 110–030 with oil-filled ball bearing and steel geared transmission). The speed and capacity of the pump were 2 rpm and 138 cm^3/revolution, respectively. Tygon tubing of 20-mm id was used to connect the pump to the digester inlet tube on one side, and the valve on the feeding tank on the other side.

A 24-h cycle timer (Dayton Model 6X758) was used to control the duration of feeding times and the intervals between feeding. The timer was designed to provide 1 to 12 operations daily with a minimum of 2 h between operations. Operation time can be adjusted to be from 30 s to 30 min. During a typical feeding process, the timer (T_1) was used to turn on the mixing apparatus in the feeding tank to mix the cheese whey. The mixing apparatus was turned on 5 min before the start of the feeding period, and continued on until the end of the feeding operation of the digester. The timer (T_2) was used to operate the feeding pump. The durations of the feeding process and the feeding intervals were maintained constant during the course of the experiment.

The effluent was collected in a polyvinyl chloride (PVC) cylinder of 220-mm diameter and 1200-mm height. A PVC disc of 20-mm thickness, machined to fit the bottom of the cylinder, was glued and screwed into place. The cover was made of a PVC disc of 240 mm diameter, and was machined to fit firmly into the top of the cylinder. Effluent removal was accomplished by a 20-mm diameter tygon tube. One end of the tube was connected to the digester outlet, below the liquid surface in the digester, whereas the other end of the tube was kept above the liquid surface of the digester to provide a constant back pressure in the head space of the digester that in turn maintained a constant liquid depth in the digester. This also kept the overflow tube filled with the supernatant, thereby sealing the digester from the atmosphere air.

Gas Collection, Cleaning, Measuring, and Storage System

Figure 4 shows a schematic representation of the gas collection, cleaning, measuring and storage system. The biogas was collected through a "Y" shaped plastic tube fixed onto the cover of the outlet chamber. One branch of the tube was fitted with a rubber septum so that gas samples could be taken with a syringe for analysis. The other branch was connected

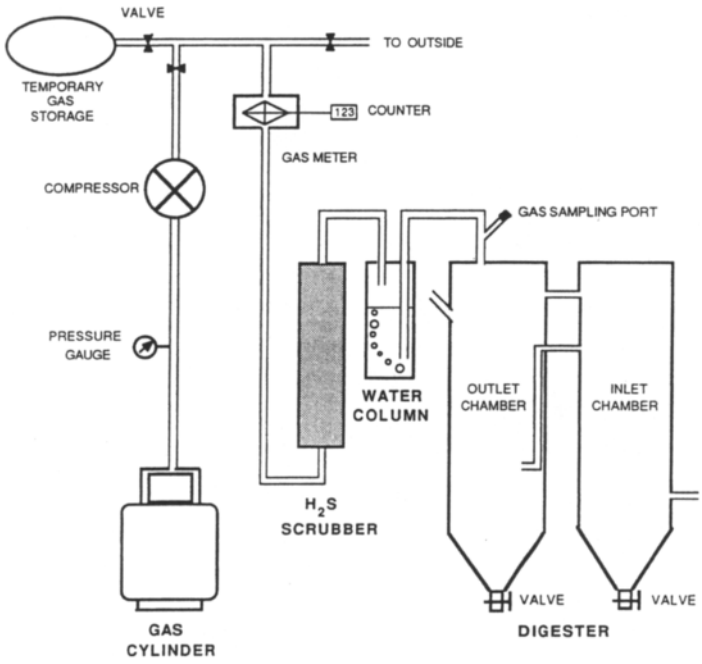

Fig. 4. A schematic representation of the gas collection, cleaning, measuring, and storage system.

to a water column. The gas was bubbled through 40-mm head of water that was sufficient to provide adequate back pressure to the head space of the digester in order to keep the working volume of the digester at 145 L.

The gas was subsequently fed into a gas scrubber for the removal of the hydrogen sulfide. Each scrubber was made of a Plexiglas™ cylinder. The gas inlet was placed at the top of the scrubber, whereas the outlet was placed at the bottom. The cylinder was filled with a mixture of fine and coarse steel wool. When the gas passed through the scrubber, the iron oxide reacted with the hydrogen sulfide to form iron sulfide, thereby stripping off the hydrogen sulfide from the biogas.

A cumulative volume gas meter designed for small gas flow was used to measure the gas production. The design of the meter was based on the tipping balance concept. The meter was calibrated to tip after 50 ± 0.2 mL of the gas had been collected in the meter chamber. The meter consisted of an inverted plexiglass trap with two adjacent chambers. The gas trap was immersed in water and pivoted on supports placed directly over the inlet gas tube. Initially, both chambers of the trap were filled with water. As gas bubbled from the inlet tube it was collected in one of the chambers. Once the chamber was filled with gas, it shifted the center of gravity to the other chamber, and the trap tipped. All gas collected in the first chamber was released and the incoming gas started to accumulate in the second chamber. An electric counter was used to keep a record of the number of

the gas meter tips. The tipping chamber in the meter was fitted, at the center point, with small disc-shaped magnets. A normally-opened read switch was attached to the outer wall of the meter so that the magnet would pass by it each tip and momentarily close the countercircuit, thereby increasing the count by one. The cumulative gas production for any period was measured, taking the counter readings at the start and at the end of the period and multiplying the number of tips by 50 mL.

The gas released from the meters was collected in a temporary storage bag made from a light plastic material. It was, then, pumped into a gas cylinder using a high pressure pump (Cole-Palmer Model Neuberger Model-No35 TTP).

Temperature-Controlled Environmental Chamber

The temperature controlled environmental chamber was constructed of 20 mm thick plywood sheets. The complete unit measured 800 mm in length, 600 mm in depth, and 1800 mm in height. The chamber was constructed in two sections to facilitate ease of operation. The lower section enclosed the digesters up to the digester covers, whereas the upper section was used as a cap to cover the tubing and thermocouple connections.

A fan forced space heater (Philips Model HL2366G120VAC) measuring 270 mm in length, 140 mm in depth, and 210 mm in height was placed on the floor of the chamber. It has heat settings of 500, 1000, and 1500 W with a thermostat control unit. Two fans (Radio Shack Model 273-242 32CFM), measuring 80 mm in length, 40 mm in depth, and 90 mm in height, were mounted inside the upper section of the environmental chamber at a height of 1700 mm to circulate the air in order to maintain a homogeneous temperature distribution inside the chamber.

MEASURING AND CONTROL EQUIPMENT

pH Measuring and Control System

Figure 5 shows a schematic representation of the pH measuring control system. The system consisted of a feeding tank for the temporary storage of the alkali (1*N* NaOH), a pump to transfer the alkali from the storage tank to the outlet chamber of digester, a pH meter-controller to measure the pH in the outlet chamber and control the alkali feeding pump, and a pH meter to measure the pH in the inlet chamber.

The alkali storage tank was a low density polyethylene cylindrical tank (Nalgene Carboy Model 2318-0065). It has a diameter of 300 mm, a height of 540 mm, and a capacity of approx 30 L. A spigot was attached at the bottom of the tank. A feeding pump (Cole Palmer Masterflex-N-07568-00 with pump head series 7015-52 and masterflex tubing 6404-15) was used to supply the alkali to the digester. Masterflex Neoprene tubing of 48-mm

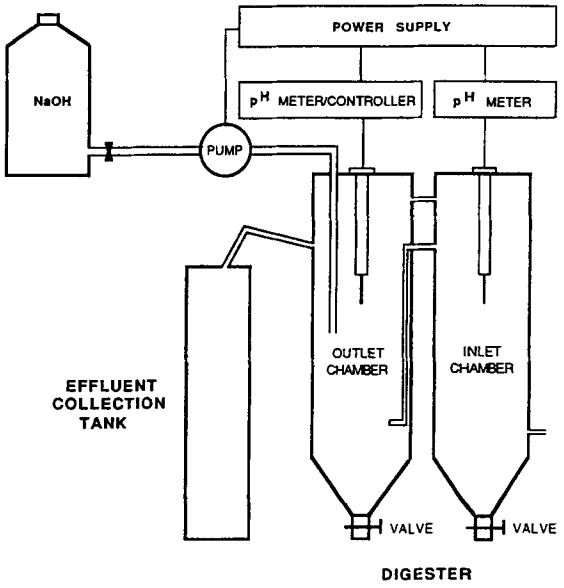

Fig. 5. A schematic representation of the pH measuring and control system.

id was used to connect the pump to the alkali addition tube in the outlet chamber of the digester on one side, and the storage tank spigot valve on the other side. The alkali addition tube was constructed of stainless steel tubing of 3 mm diameter and 150 mm length. The alkali addition tube was mounted in a gas tight plastic hose adaptor fitting that was threaded into the Plexiglas™ cover of the outlet chamber of the digester.

The pH of the inlet chamber was monitored using a single electrode pH probe (Fisher Scientific Model 16-639-3) connected to pH meter (Fisher Scientific Model 230 pH/ion meter). The pH of the outlet chamber was monitored and controlled, using a single electrode (Fisher Scientific ACCUphast No. 13-620-279) connected to a pH meter/controller (Fisher Scientific Model ACCUMET 805 MP). The pH electrodes were each mounted in PVC tubing of 13 mm diameter and 480 mm in length to form a pH electrode extension sleeve. Two O-rings were used in each sleeve to maintain a gas tight seal. The pH electrode wires were passed through a small hole in the environmental chamber, and were connected to the appropriate pH meter. Prior to insertion of the pH electrodes into the digester, a two point calibration standardization was performed, using the corresponding pH meter and Fisher Scientific certified pH solutions (BUFFER-PAC Cat. No. SB105).

The pH meter/controller determines the pH of the cheese whey in the outlet chamber and activates the alkali feeding pump, if the value of pH had fallen out of the specified pH limits. The sodium hydroxide pump will subsequently feed the outlet chamber of the digester with alkali until the pH of the cheese whey in this chamber is restored to within the specified limits on the pH meter/controller. Once the pH is within the specified limit, the pump will automatically be turned off.

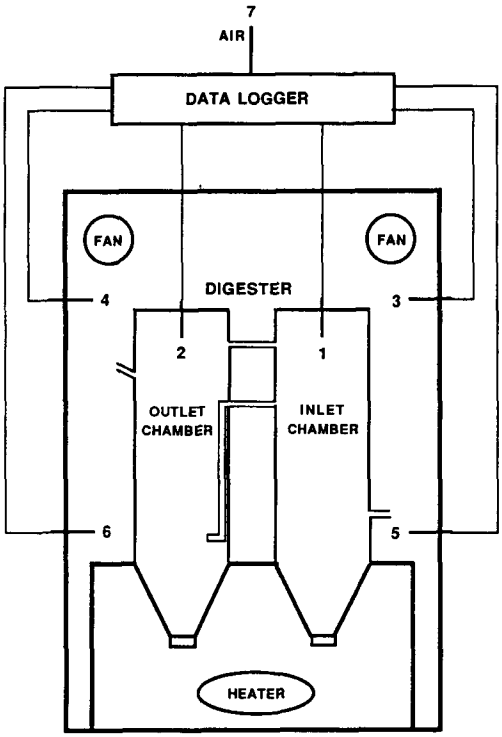

Fig. 6. A schematic representation showing the location of the seven thermocouples used for temperature measurement.

Temperature Measuring and Control System

All measurements of temperature were recorded daily using a Data-Logger (Cole-Palmer Model N-08360-14). There were 7 type-T thermocouples incorporated in the experimental set up as shown in Fig. 6. Thermocouples 1 and 2 were used to record the liquid temperature in the two chambers. Thermocouples 3, 4, 5, and 6 were used to record the temperature of the environmental chamber. Thermocouple 7 was used to monitor the room temperature. Thermocouples 1 and 2 were each mounted inside a stainless steel tubing of 3-mm diameter and 460-mm length to form a thermocouple sensor. The thermocouple sensor was subsequently mounted in a gas-tight plastic fitting that was threaded into the plexiglass cover of each chamber. Thermocouples 3 through 6 were mounted on the inside of the environmental chamber, two in each side at heights of 550 mm and 1500 mm. Thermocouple 7 was mounted outside of the temperature controlled chamber to monitor the laboratory room temperature. All thermocouple wires were passed through a small hole in the environmental chamber and were attached to the rear panel strip of the data-logger. The 7 channels were internally linearized and cold-junction compensation was included. The temperatures were recorded in degrees celsius.

Table 1
Some Characteristics of the Cheese Whey

Item	Measured Value	Units
Total solids (TS)	65930	mg/L
Volatile solids (VS)	47280	mg/L
VS as percent of TS	71.71	%
Ash	18650	mg/L
Ash as percent of TS	18.29	%
Total chemical oxygen demand (TCOD)	72220	mg/L
Soluble chemical oxygen demand (SCOD)	69640	mg/L
SCOD as percent of TCOD	96.43	%
Total Kjeldahl nitrogen (TKN)	1450	mg/L
Ammonium nitrogen (AN)	260	mg/L
AM as percent of TKN	17.93	%
pH	4.5	

CHEESE WHEY COLLECTION, STORAGE, AND PREPARATION

The cheese whey was obtained from the Farmer's Cooperative Dairy plant in Truro, Nova Scotia. The plant is located approx 100 km from Halifax. The cheese whey was pumped from the plant cheese whey storage tank into 60-L plastic containers. The containers were subsequently sealed and transported to the cold storage facilities of the Associated Freezers of Canada in Dartmouth, Nova Scotia. They were stored in a large freezer at −25°C until required.

Prior to placing the cheese whey into the feeding tank, it was removed from the freezer and transferred to the Waste Management Laboratory at the Technical University of Nova Scotia. The whey was then allowed to completely thaw at room temperature for 48 h. Some characteristics of the cheese whey used in the study are presented in Table 1.

EXPERIMENTAL PROCEDURE

The digester was operated at a temperature of 35°C and a retention time of 15 d. For each experimental run, the digester was started by adding 25 L of the seed material and 50 L of cheese whey. The seed material was obtained from a similar no-mix anaerobic digester operating on dairy

manure. The remaining 70 L (to a full capacity digester) were made up with a continuous addition of whey for about 7 d at a loading rate of 9.7 L/d, that was equivalent to 15-d hydraulic retention time. After about 3 wk, the digester reached the steady state condition (constant pH value and consistent values of solids, COD, and gas production). Sampling was continued on a daily basis until 15 samples were collected during the steady state conditions. Samples were also taken from the sludges of the two chambers at the end of each experimental run.

The pH of the contents of the outlet and inlet chambers were also measured on daily basis. The room temperature, operating digester temperature, and the temperature of the controlled environmental chamber were continuously recorded. The daily gas production (in liters) was measured, and gas analyses were performed on the gas samples using a gas chromatograph (Perkin-Elmer Model Sigma I) to determine the CO_2 and CH_4 concentrations. The total and soluble chemical oxygen demand, total and suspended solids, and total Kjeldahl and ammonium nitrogen analyses were performed on the daily samples taken from the effluent and the sludge samples. These analyses were performed according to the procedures described in the Standard Method (*17*).

RESULTS AND DISCUSSIONS

pH and Temperature

The temperature and pH were measured on a daily basis during the steady state operation of the digester. The digester temperature remained at 35 ± 1.03°C. There was no fluctuation in the temperature of the digester as the system was kept in a temperature controlled chamber. The pH was very low in both chambers (about 3.3) that contributed to lower biogas production, lower methane percentage, and lower pollution potential reductions as measured by the COD, solids and nitrogen concentrations. Controlling the pH in the outlet chamber (about 5.7–6.0) resulted in a higher biogas production, a higher methane yield, and higher pollution potential reductions.

Biogas Production, Productivity and Composition

The daily rate of biogas production and the biogas productivity of the digester operating at steady state are shown in Table 2. The data are the average of 15 measurements each. Controlling the pH of the methanogenic stage in the outlet chamber increased the biogas production and biogas productivity from 0.054 to 0.096 L/L/d, and from 0.017 to 0.030 m^3/kg VS added, respectively.

Table 2
Comparing the Digester Productivity with Cheese Whey and Dairy Manure of the Same Solids Concentration

Type Waste	Biogas Production (L/L/d)	Biogas Productivity (m^3/kgVS added)
Whey with no pH control	0.054	0.017
Whey with pH control	0.096	0.030
Manure	1.040	0.290

Values are the average of 15 measurements each.
Percent of methane in the gas produced from manure = 60%.
Percent of methane in the gas produced from whey with no pH control = 20%.
Percent of methane in the gas produced from whey with pH control = 77%.

The biogas production rate of the system when operating on cheese whey was very low (0.054–0.096 L biogas/L digester/day), compared to that of the system (1.040 L biogas/L digester/day) when operating on a dairy manure of similar solid concentration, as shown in Table 2. The digester biogas productivity when operating on cheese whey was very low (0.017–0.030 m^3 biogas/kg VS added), compared to the biogas productivity of the system (0.215–0.290 m^3 biogas/Kg VS added) when operating on a dairy manure of similar solid concentrations. This could be attributed to the low pH. According to Schroder and De Haast (*15*), more biodegradable carbon source, such as, whey, would cause inhibition to occur owing to greater differences in the rates of acidogenesis and methanogenesis.

According to Ghaly and Ben-Hassan (*7*), Person Bartlett (*18*), and Hashimoto et al. (*19*), methane production proceeds quite well as long as the pH is maintained between 6.6 and 7.6, with an optimum range between 7.0 and 7.2. At pH values below 6.6, acute toxicity occurs, and base should be added to maintain the pH above 6.6. Wildenauer and Winter (*20*) reported that in conventional mixed reactor, washout of the bacteria would occur at a pH below 5.3. In the present study, the pH of the methanogenic stage was only maintained at 5.7. A pH above 7.0 may further improve both the biogas productivity and methane yield.

The methane percentage was 20% when the system operated on cheese whey without pH control, which is considerably low compared to that of the gas produced from dairy manure (60%), using the same digester and operating at the same temperature (*7*). However, when the pH of the outlet chamber (methanogenic stage) was maintained at 5.70 ± 0.15, the methane percentage increased to 77. Clanton et al. (*21*), using a microprocessor to control the digester pH, obtained a biogas with a methane concentration of 27.8 to 82.1%. The high value (82.1%) was obtained with the addition of $Ca(OH)_2$ buffer that resulted in the precipitation of carbon

dioxide in a form of calcium carbonate, whereas the lower value (22.7%) was obtained with the addition of $NaHCO_3$ that resulted in higher CO_2 percentage as a result of the conversion of biocarbonate to CO_2 that escaped with the gas. Using sodium hydroxide to control the pH in an upflow anaerobic sludge blanket reactor treating low strength cheese whey, Yan et al. (*14*) reported a reduction of VFA from 600 to 50 mg/L and an increase in the methane percentage from 50 to 56% after approx 55 d startup period. Wildenauer and Winter (*20*) reported a methane content of 70% using a pH controlled upflow fixed film loop reactor. The authors explained that the high methane percentage resulted from the CO_2 being dissolved in the liquid of the gasmeter that they used in their study.

However, further research is needed to clarify whether the Ca^{2+} (divalent ion) concentration or the Ca^{2+}/Na^{+} (divalent/monovalent) ratio, or the Na^{+} (monovalent) concentration is the critical factor in the formation of a sludge with good settling ability that can be retained in the digester and, thus, increase biogas productivity and the removal efficiency. Ca^{2+} is believed to aid on the adhesion of microorganisms to the media, to stabilize the glucocalyx structure, to act as a linkage between negatively charged surfaces and microorganisms, and to enhance precipitation of bacterial extracellular polysaccharides and, thus, $CaCOH_2$ may be preferred over NaOH (*15*). However, the precipitation of calcium carbonate in a form of sludge is significant. Also, the addition of calcium hydroxide after the anaerobic culture had been exposed to acidic environment caused by long-chain fatty acid was found ineffective (*22*).

Chemical Oxygen Demand

Both the total chemical oxygen demand (TCOD) and the soluble chemical oxygen demand (SCOD) analyses were performed on the samples taken daily from the effluent of the digester during the steady state operation, as shown in Fig. 7. The total and soluble COD reductions of the effluent were also calculated as shown in Table 3. The total and soluble COD results obtained from the digester with and without pH control confirmed that the digester was operating at the steady state condition.

The reductions in the COD ranged from 355 to 23250 mg/L (0.49 to 32.19%) for the TCOD and from 830 to 23920 mg/L (1.19 to 16.24%) for the SCOD. Subsequently, higher reductions in both the TCOD and SCOD were obtained when the pH of the outlet chamber was maintained at 5.7 by the addition of sodium hydroxide. Also, the reductions in the SCOD were higher than those of the TCOD. The percent of the SCOD in the influent was 96.43. This was reduced to 95.76 and 93.36 in the effluents obtained from the system without and with pH control, respectively. These reductions resulted from the conversion of soluble material into insoluble microbial cells. No mixing resulted in settling of some solids to the bottom of the digester at the low temperature.

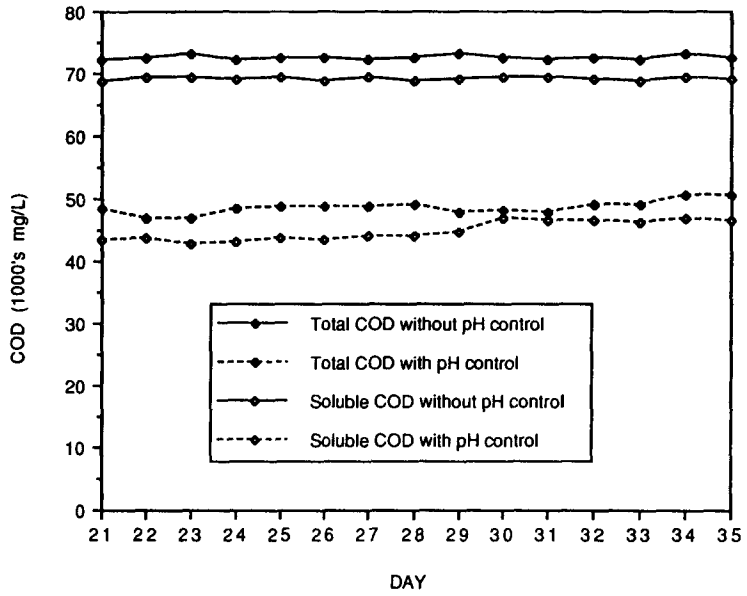

Fig. 7. The effluent chemical oxygen demand.

Table 3
The Chemical Oxygen Demand Reductions

pH Control	TCOD	TCOD Reduction		SCOD	SCOD Reduction	
	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)
No	71 860	355	0.49	68 810	830	1.19
Yes	48 970	23 250	32.19	45 720	23 920	34.35

Values are the average of 15 measurements each.
TCOD = total chemical oxygen demand.
SCOD = soluble chemical oxygen demand.
Raw whey TCOD = 72,220 mg/L.
Raw whey SCOD = 69,640 mg/L.

Solids

The influent whey was received in the inlet chamber where settlement of the solids and growth of microbial cell began. Slight mixing induced by the inflow of the influent was achieved in this chamber, thereby improving the conversion efficiency. The partially settled liquid whey was then received in the outlet chamber where further settlement of solids and growth of microbial cells took place. Because no mixing took place in the outlet chamber, loss of microbial cells with the effluent was minimized. The accumulated sludges at the base of the two chambers were periodically removed (at the end of the experiment), thereby ensuring that effective volume of the digester was maintained and hence, the hydraulic retention time was not significantly affected.

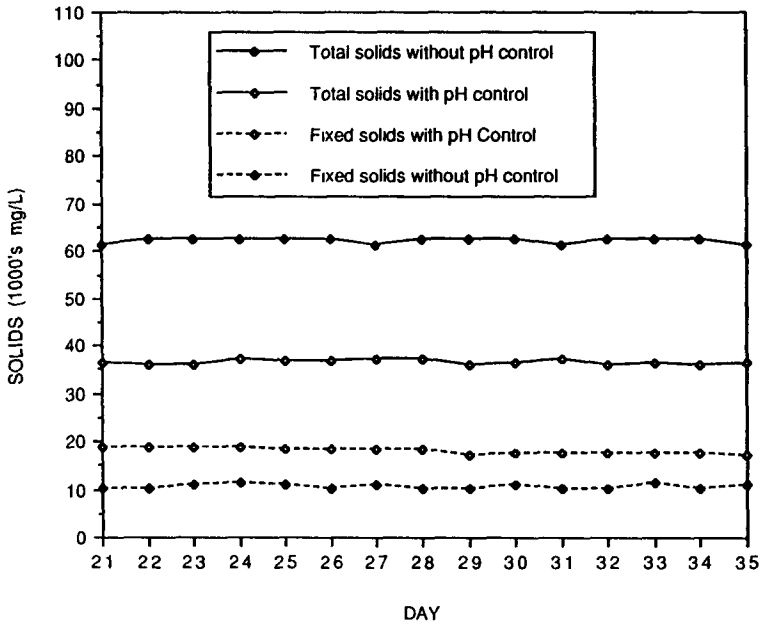

Fig. 8. The effluent solids.

The solids (total and fixed) analyses were performed on the samples taken from the digester effluent during the steady state condition. The results are presented in Fig. 8. The volatile solids portion of the total solids was calculated by subtracting the fixed solids from total solids as shown in Table 4. The reductions in the total, volatile, and fixed solids are presented in Table 5. Controlling the pH increased the reductions in the total and volatile solids. The reductions varied from 5.81 to 44.44% for the total solids and from 5.33 to 59.15% for the volatile solids. The reduction in the fixed solids was not significantly affected by the pH. The trend in the solids reductions is in agreement with that of the COD results.

The suspended solid results are presented in Table 6. The suspended solids to the total solids was only 5.15%, as the majority of the solids were in the soluble form. There were reductions in the suspended solids as shown in Table 7. Substantial reductions in the total, volatile, and fixed suspended solids were observed. Unlike the fixed solids portion of the total solids, the fixed solids portion of the suspended solids was affected by the pH. However, lower reductions were observed at higher pH.

Nitrogen

The total Kjeldahl and ammonium nitrogen analyses were performed on the samples obtained from the effluent during the steady state condition. The organic nitrogen was then calculated by subtracting the ammonium nitrogen from the total Kjeldahl nitrogen. The results are presented in Table 8. The reductions in the nitrogen compounds are presented in Table 9.

Table 4
The Effluent Total Solids

pH Control	Total Solids (mg/L)	Volatile Solids (mg/L)	Fixed Solids (mg/L)
No	62 100	44 730	17 370
Yes	36 630	19 300	17 330

Values are the average of 15 measurements each.
Raw whey total solids = 65,930 mg/L.
Raw whey volatile solids = 47,250 mg/L.
Raw whey fixed solids = 18,680 mg/L.

Table 5
Total Solids Reductions

pH	Total		Volatile		Fixed Solids	
Control	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
No	3 830	5.81	2 520	5.33	1 310	7.01
Yes	29 300	44.44	27 950	59.15	1 350	7.23

Table 6
The Effluent Suspended Solids

pH Control	Total (mg/L)	Volatile (mg/L)	Fixed (mg/L)
No	2 370	2 250	120
Yes	2 400	2 270	130

Values are the average of 15 measurements each.
Raw whey total suspended solids = 3400 mg/L.
Raw whey volatile suspended solids = 3230 mg/L.
Raw whey fixed suspended solids = 170 mg/L.

Table 7
Suspended Solids Reductions

pH Control	Total		Volatile		Fixed Solids	
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
No	1 030	30.29	980	30.34	50	29.41
Yes	1 000	29.41	960	29.72	40	23.53

Table 8
The Effluent Nitrogen Compounds

pH Control	Total Kjeldahl (mg/L)	Organic (mg/L)	Ammonium (mg/L)
No	1 440	1 180	260
Yes	930	650	280

Values are the average of 15 measurements each.
Raw whey total kjedahl nitrogen = 1450 mg/L.
Raw whey organic nitrogen = 1190 mg/L.
Raw whey ammonium nitrogen = 260 mg/L.

Table 9
Nitrogen Reductions

pH Control	Total Kjeldahl		Organic		Ammonium	
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
No	10	0.07	10	0.08	0.00	0.00
Yes	520	35.86	540	45.38	(+)20.00	7.69

(+) gain.

The results showed that the concentration of the ammonium nitrogen remained unchanged. The observed reductions in the total Kjeldahl nitrogen were, in most part, resulted from the reduction in the organic nitrogen. The reduction was affected by the pH, the higher the pH the higher was the reduction. This could be attributed to the settling of some organic nitrogen to the bottom of the digester. The decrease in nitrogen concentration accompanied by an increase in COD removal indicates that acidogenic bacteria are largely responsible for cellular material in the reactor and, therefore, for nitrogen consumption (*15*).

Sludge Characteristics

The chemical oxygen demand, solids, and nitrogen analyses were performed on the samples of the sludges obtained from the input and output chambers. The results are shown in Table 10. The total chemical oxygen demand of the sludges obtained from both chambers was higher than that of the influent material. Higher values were, also, observed with the sludge obtained from the outlet chamber as compared to that of the inlet chamber. Controlling the pH of the outlet chamber (methanogenic stage) resulted in a significant increase in the total COD of the sludge in this chamber. Unlike the total COD, the soluble COD of the sludges obtained

Table 10
Sludge Characteristics

Chamber	pH Control	COD (mg/L) Total	COD (mg/L) Soluble	Total Solids (mg/L) Total	Total Solids (mg/L) Volatile	Total Solids (mg/L) Ash	Nitrogen (mg/L) TKN	Nitrogen (mg/L) AMN
Input	No	71430	67900	79130	60030	19100	3110	400
	Yes	71900	68190	80100	69000	19100	3179	410
Output	No	68870	65040	84180	61450	22730	4610	500
	Yes	174430	39500	143000	102500	40500	6000	605

Raw Whey Total Chemical Oxygen Demand = 72,220 mg/L.
Raw Whey Soluble Chemical Oxygen Demand = 69,640 mg/L.
Raw Whey Total Solids = 65,930 mg/L.
Raw Whey Total Volatile Solids = 47,280 mg/L.
Raw Whey Total Ash = 18,650 mg/L.
Raw Whey Total Kjeldahl Nitrogen = 1450 mg/L.
Raw Whey Ammonium Nitrogen = 260 mg/L.

from both chambers was lower than that of the influent material. Lower values were also observed with the sludge obtained from the outlet chamber as compared to that of the inlet chamber. Controlling the pH of the outlet chamber resulted in lower soluble COD of the sludge of that chamber. The lower values of the soluble COD indicate that sludges are partially stabilized.

The total, volatile and fixed solids of the sludges were higher than those of the influent material. Higher values of these solids were also observed with the sludge obtained from the outlet chamber as compared to those of the sludge obtained from the inlet chamber. Controlling the pH of the outlet chamber has significantly increased the values of these solids in the sludge obtained from this chamber.

Both the total Kjeldahl nitrogen and ammonium nitrogen of the sludges obtained from both chambers were significantly higher than those of the influent material. Higher values were also observed with the sludge obtained from the outlet chamber. Controlling the pH of the outlet chamber increased the concentration of the total Kjeldahl nitrogen and ammonium nitrogen in the sludge obtained from this chamber.

CONCLUSIONS

Anaerobic digestion of acid cheese whey without pH control is not feasible. The biogas production rate (L biogas/L digester/d) and the biogas productivity (m^3/kgVS added) were extremely low. The reductions in the pollution potential as measured by the concentrations of COD, solids, and nitrogen compounds were very low.

pH control of the digester contents is necessary for successful digester operation. Controlling the pH of the whey in the feeding tank did not sig-

nificantly affect the pH of the digester. Controlling the pH of the methanogenic stage in a two-stage digester significantly increased the biogas productivity, methane yield, and the pollution potential reduction as measured by COD, solids, and nitrogen compounds.

When operating the digester at a temperature of 35°C and a retention time of 15 d with pH control, reductions of up to 32.19, 44.44, and 35.86% in the total COD, total solids, and total nitrogen were achieved, respectively, when producing a biogas with 77% methane.

REFERENCES

1. Zall, R. H. (1979), Whey Treatment and Utilization, *Food Processing Waste Management*, Green, J. H. and Kramer, A. (eds.), AVI, Westport, CT.
2. Singh, R. K. and Ghaly, A. E. (1984), Single Cell Protein Production from Cheese Whey. ASAE Paper No. 84-6528, St. Joseph, MI.
3. Ghaly, A. E., Echiegu, E., and Pyke, J. (1988). Pollution Potential of Land Disposal of Cheese Whey. Proceedings of the 1988 Ford Processing Waste Conference, Atlanta, GA.
4. Muller, P. G. (1979), Economic Evaluation of Feeding Liquid Whey to Livestock. Technical Report, Food Research Institute, Research Branch, Agriculture Canada, Ottawa.
5. Singh, R. K. and Ghaly, A. E. (1985), Feasibility of Cheese Whey Processing for Production of Food and Feed Supplements. CSAE paper No. 85-504, Ottawa, Ontario.
6. Ghaly, A. E. and Singh, R. K. (1985), Land Application of Cheese Whey. Proceedings of the Fifth International Symposium on Agricultural Wastes. St. Joseph, MI.
7. Ghaly, A. E. and Ben-Hassan, R. M. (1988), *Appl. Biochem. and Biotechnol. J.* **20/21,** 541–559.
8. Switzenbaum, M. S. and Danskin, S. C. (1982), *Agricultural Waste,* **4,** 411–426.
9. Nordstedt, R. A. and Thomas, M. V. (1984), Inoculum requirements for start-up of anaerobic fixed bed reactors. ASAE paper No. 84-4090. St. Joseph, MI.
10. Samson, R., Van den Berg, B., Peters, R., and Hade, C. (1984), Dairy waste treatment using industrial scale fixed-film and up-flow sludge bed anaerobic digesters: Design and start up experience. Proceedings of the 39th Industrial Waste Conference, Purdue University, pp. 235–241.
11. Williams, D. W. (1984), Fixed-film anaerobic digestion of cheese whey. ASAE paper No. 84-4095. St. Joseph, MI.
12. Barford, J. P., Gail, R. G., Callander, I. J., and Floyd, E. J. (1985), *Biotechnol. Bioeng.* **28,** 1601–1607.
13. Lo, K. V. and Liao, P. H. (1986), *Biomass* **10,** 243–252.
14. Yan, J. Q., Lo, K. V., and Liao, P. J. (1989), *Biological Wastes* **27,** 289–305.
15. Schroder, E. W. and DeHaast, J. (1989), *J. Dairy Res.* **56,** 129–139.
16. Ghaly, A. E. and Pyke, J. A. (1988), Biogas production from cheese whey. ASAE paper No. 88-6604, St. Joseph, MI.

17. APHA, (1980), Standard methods for the examination of water and wastewater, 15th Ed., American Public Health Association, New York.
18. Person, S. and Bartlett, H. D. (1978), Converting manure into gas potential source of energy. The Pennsylvania State University Journal of Science in Agriculture **26(1),** 15–23.
19. Hashimoto, A. G., Chen, Y. R., and Prior, R. L. (1979), *J. Soil Water Conservation* **34(1),** 16–19.
20. Wildenauer, F. X. and Winter, J. (1985), *Appl. Microbiol. Biotechnol.* **22,** 367–372.
21. Clanton, C. J., Dackus, B. D., Goodrich, P. R., Fox, E. J., and Morris, H. A. (1987), Anaerobic digestion of cheese whey. Proceeding of the 1987 Ford Processing Waste Conference, Atlanta, GA.
22. Hanaki, K. Matsuo, T., and Nagase, M. (1981), *Biotechnol. Bioeng.* **23,** 1591–1610.