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Methane Conversion Efficiency as a Simple Control Parameter for an Anaerobic Digester at High Loading Rates

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Abstract
The anaerobic digestion process is globally applied to the treatment of highly concentrated wastes such as industrial and rural effluents, and sewage sludge. However, it is known to be relatively unstable. When loaded with high concentrations of organic material, unwanted volatile fatty acids (VFA) are often produced rather than methane (CH_4) gas which can lead to digester acidification and failure. This study investigated digester behaviour under high loading rates, testing the usefulness of stoichiometric methane conversion efficiency as a digester control parameter at high loading rates.

Our results show that, in general, the CH_4 production rate was proportional to the feed rate (loading rate). However, at very high loading rates, the CH_4 production rate was not proportional to the increase in the feeding rate. Consequently, VFA accumulated and the H_2 partial pressure increased. The proportionality of the loading rate and gas production rate is stoichiometrically expressed as the conversion efficiency. We found that conversion efficiency was a useful indicator as an early warning of digester imbalance. The digester remained stable at conversion efficiencies above 75%. Dropping below 70% signified the onset of digester failure.

As loading rate and methane production data are readily available on-line in most anaerobic digestion plants, the conversion efficiency can be monitored on-line and used as an efficient control technique to maintain safe operation of anaerobic digesters at high loading rates.

Keywords
Anaerobic digestion, control technique, conversion efficiency, high load

INTRODUCTION
Anaerobic digestion is increasingly used as an effective method of treating agricultural, industrial and domestic wastes. During recent decades, much progress had been made on the use of anaerobic digestion, both to treat waste and to produce energy in the form of methane gas. Despite widely reported success and application of anaerobic digestion (Lettinga, 1995), some industries are reluctant to employ this process for waste treatment. The main reason for this is the reputation of the process for instability and the difficulty in failure control. Digester instability can result from any material (e.g. overloading, toxic compound) or effect (e.g. decrease in temperature) that interferes with methane formation.

Laboratory and pilot scale studies, as well as full-scale digester operations, indicate that the instabilities associated with the anaerobic process can lead to reduced digester performance and, in severe cases, to digester failure (Canovas-Diaz & Howell, 1988; Kennedy, 1985; Chynoweth, 1994). In order to successfully operate anaerobic digesters, constant monitoring of process parameters is necessary. Process indicators such as VFA, alkalinity, pH, gas production and composition, volatile solids and COD (chemical oxygen demand) reductions have been used (Switzenbaum *et al*., 1990). Most often, these parameters are monitored simultaneously, as there is no single process indicator which will reliably signal an imbalance between the two major bacterial populations (i.e. acid forming bacteria and methane forming bacteria).

In principle, digester failure due to overloading is caused by an imbalance of fermentation reactions that producing H_2 at a rate higher than H_2 consumption by the methanogenic bacteria. The increase in H_2 partial pressure and the formation and consumption of VFA has been extensively studied (Sterling *et al.*, 2001; Voolapalli & Stuckey, 2001; McInerny & Bryant, 1981), as has model development (Chen *et al.*, 2001; Hoh & Cord-Ruwisch, 1996; Hoh & Cord-Ruwisch, 1997) and process control strategies (Cord-Ruwisch *et al.*, 1997; Strong & Cord-Ruwisch, 1995). While on-line measurements of VFA and H_2 are useful in detecting digester overloading, they have not been widely used due to technical difficulties. pH monitoring is a simple method but not reliable because of the high buffer capacities of anaerobic digestion. In principle, as soon as the digester becomes imbalanced VFA and H_2 accumulate and CH_4 production reduces. This should be apparent from a lower CH_4 output per unit of organic loading. This study 1) investigates digester behaviour under high loading rates; and 2) tests the usefulness of stoichiometric methane conversion efficiency as a simple digester control parameter.

METHODS

Laboratory Scale Anaerobic Digester

A 1.3-L Braun Biolab anaerobic digester was filled with 1.0 L of active anaerobic sludge (13 g/L of dry suspended solids) leaving a 0.3 L gas volume. The reactor temperature was maintained at 35 ^{o}C by immersing the reactor in a water-bath thermostatically controlled by a Thermo Mix MM Braun heater. The sludge liquid was kept well mixed by a flat blade impeller stirring at 300 rpm. The feed to the reactor was supplied by a two-channel peristaltic pump (EYELA Micro Tube Pump MP-3) calibrated at the commencement of the experiments. The loading rate was regulated by a digital timer. The on-time setting of the timer was varied according to the changes in the loading rate while the off-time setting was maintained constant. The amount of feed entering the reactor was measured by a Sartorius electronic balance (BA 4 100 Goettingen, Germany). All the liquid connections were made using Tygon tubings. To keep the sludge volume constant, the reactor effluent was pumped out at the same rate of feed addition through a second channel in the pump. In the automatic set-up, the effluent was drawn out from the reactor by an anti-foam pump coupled with a liquid sensing device. This device turned on the pump whenever the liquid level exceeded the 1-L volume.

Synthetic substrate

The feed was composed of a C source (D-glucose 24.5 g/L, yeast extract 1 g/L and trytone 1 g/L), basal nutrients (NH_4CI 1.07 g/L, $MgCl_2.6H_20$ 1.02 g/L, $CaC1_2.2H_2O$ 0.01 g/L, KCl 0.52 g/L, Na_2SO_4 0.14 g/L, KH_2PO4 0.30 g/L, $NaHCO_3$ 2.10 g/L) and trace metals ($FeCl_2.4H_2O$ 0.2 mM, $CoCl_2.6H_2O$ 0.006 mM, $MnCl_2.4H_2O$ 0.0033 mM, $ZnCl_2$ 0.006 mM, H_3BO_3 0.0016 mM, $Na_2MoO4.2H_2O$ 0.0049 mM, $NiCl.6H_2O$ 0.0025 mM, $CuCl_2.2H_2O$ 0.006 mM) One-litre stock solutions were prepared and autoclaved for one hour to maintain sterile conditions. After cooling the feed medium, the trace elements (5 ml) and the $NaHCO_3$ buffer (25 ml) were added into the feed bottle through a 0.21µm sterile filter. The pH of the feed was adjusted to 7 - 7.5 by adding NaOH.

Source of Biomass

The biomass used was obtained from a hybrid anaerobic digester at Swan Brewery, Perth, Western Australia. The sludge was allowed to acclimatise to the feed medium for two weeks before it was used in the experiments.

Analysis

CH_4 production was measured by passing the biogas over NaOH pellets and through concentrated solutions of NaOH to remove the CO_2 gas. The volume of the gas produced was measured continuously by weighing the equivalent mass of water displaced by the CH_4 gas from the digester. A Sartorius balance was interfaced to a computer for continuous monitoring of the volume of gas produced. The workbench software was supplied by Stawberry Tree Incorporated and the LABVIEW Instruments.

Hydrogen gas concentration in biogas and VFA analysis were performed as described by Charles *et al.*, (2009).

RESULTS AND DISCUSSIONS

Computer simulation of the digester's response to a step change in the loading rate

Before carrying out experiments employing step changes in the loading rate, a computer simulation was tested to determine the theoretical effect of these changes on the gas production rate. The simulation was used to provide a theoretical basis for the design of future laboratory experiments in this study. The response of an anaerobic digester to step changes in the loading rate was simulated based on first order kinetics and a one-step biological model as:

$$- dS/dt = dP/dt = k S$$

where: dS/dt = rate of substrate degradation; dP/dt = rate of product formation; k = constant rate of reaction (Levenspiel, 1974).

A biologically catalysed reaction showing saturation behaviour is modelled by the Michaelis Menten equation (Becker & Deamer, 1991):

$$S + E \Leftrightarrow S\ E \Leftrightarrow P + E$$

where: S = substrate; P = product; E = enzyme; S E = enzyme-substrate complex

Under substrate limitation, the first order equation could sufficiently represent the anaerobic digestion of a readily soluble organic compound such as glucose. To evaluate the response of the digester to step changes in the loading rate, the rate of formation of product (dP/dt) was estimated at three different magnitudes of step change in the loading rate. Under steady state condition (i.e. dP/dt = constant), the rate of product formation increased in proportion with the loading rate (Figure1). For example, a 20 % increase in the loading rate resulted in a 20% increase in the production rate (from 0.20 to 0.24 mmoles P/ hr).

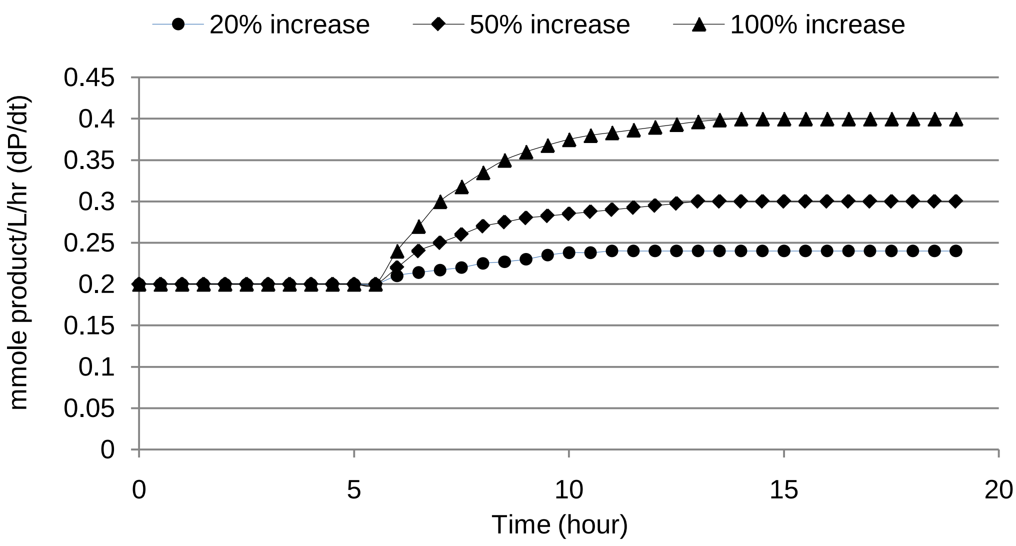

Figure 1: Simulation response in the methane production rate to a step change in the loading rate (assumption one step model; first order kinetics)

The use of conversion efficiency as a process indicator
According to the stoichiometry of the reaction:

$$C_6H_{12}O_6 \Rightarrow 3\ CH_4 + 3\ CO_2$$

three moles of CH_4 are produced per mole of glucose. According to this ratio, an increase of 30% in the feed flow rate is expected to result in a 30% increase in the methane production rate. The ratio of the actual methane production rate over the theoretical (or expected) methane production rate is called the **conversion efficiency** of the digester. As long as the CH_4 production rate stays proportional to the glucose loading rate, the conversion efficiency is expected to remain constant. A drop in the conversion efficiency after an increase in the feed rate would indicate that a fraction of the substrate is not converted to CH_4 or organic intermediates (e.g. VFA) had accumulated.

The relationship between the methane production rate (dCH_4/dt) and the loading rate in a laboratory scale digester
A 1-L constantly stirred laboratory scale digester was continuously fed with the synthetic substrate containing 24.5 g glucose /L. The base loading rate of 5.4 moles glucose/L/d was increased by 10 to 50 % (Figure 2a), to determine the effect of a step change in the loading rate on the gas production rate. Each step change in the loading rate was applied after the methane production rate has become constant for a period of 15 to 20 hours.

Generally, the change in the CH_4 production rate reflected the magnitude of the step change in the loading rate (Figure 2b). A 10 to 30 % increase in the loading rate resulted in a proportional increase in the gas production rate. A 40 to 50 % increase on the other hand, did not result in a proportional increase indicating that a fraction of the organic compounds in the feed was not degraded to methane.

During the step changes of 10 to 40 % in the loading rate, the conversion efficiencies fluctuated between 76 - 79% (Figure 2a). The efficiency decreased to 68 % only when the loading rate was increased to 11 mmoles glucose/L d, but readily returned above 70% when the loading rate was decreased to 7.1 mmoles glucose/L d. Throughout the experimental run, the digester showed no sign of volatile fatty acid (VFA) accumulation (data not shown). The pH remained within the reported safe pH range of 6.5 to 7.5 (Grady & Lim, 1986). Generally, the digester remained stable at conversion efficiencies over 70%. It appeared that at conversion efficiencies below 70%, unmeasured organic metabolites or intermediate compounds (probably alcohols or lactic acid) accumulate.

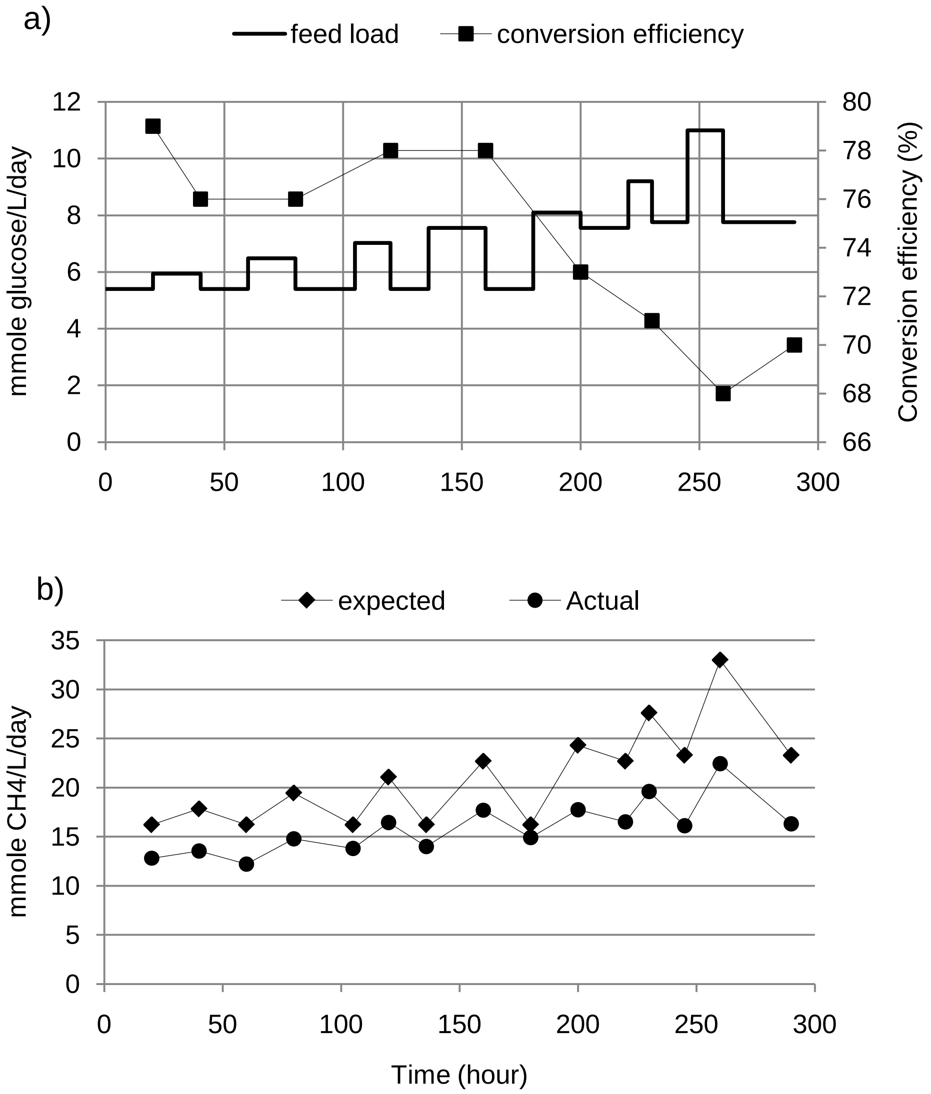

Figure 2: The response of the laboratory digester to small step increases in the loading rate of range 10 - 50 %. Data indicate average values over an interval of 15-20 hr step change. Expected methane production rate assumes 100% conversion efficiency. Feed concentration was 24.5 g glucose/L day. Biomass concentration = 5.99 g VSS/L

Determination of digester behaviour and conversion efficiency above the sustainable loading rate

The sustainable loading capacity of the digester is the limit to which a digester can be loaded with the organic substrate without causing an adverse accumulation of the intermediate products (eg. VFAs). This experiment investigated operating the digester at step increases at and beyond the maximum loading rate. In this case, the maximum loading rate is defined as the loading rate that can be applied to the digester without allowing the VFA concentrations to rise above 300 to 500 mg/L (about 5- 8 mM acetate). Kennedy (1985) and Chynoweth (1994) reported these values as the safe VFA range for normal digester operation.

To allow the digester to approach its actual sustainable loading capacity, the loading rate of 10 mmoles glucose/L/d was increased stepwise over an interval of 12 hours (Figure 3a). The response of the digester towards these step increases was monitored in terms of gas production rate, VFA concentration, and H_2 pressure in order to assess digester performance and conversion efficiency prior to, and after, reaching its actual sustainable loading rate.

As expected, the increase in the loading rate was reflected by the increase in the methane production rate (0 to 36 h, Figure 3b). This trend was observed until at 19 mmoles glucose/L d (HRT = 8 days), a maximum gas production rate of 52 mmoles CH_4/L/d (or 1.42 L CH_4/L d) was obtained (Figure 3b, 36 h). During this period, acetic and propionic acid concentrations increased from 1 mM to about 2 mM (Figure 3c, 36 h), indicating that the balance between the acid production and methane formation reactions had been slightly disturbed. To determine whether the loading rate could be further increased without resulting in acid accumulation, the feed flow rate was raised to 22.9 mmoles of glucose/L d, (HRT=6 days). This time, the increase in the loading rate did not result in a further increase in the methane production rate (Figure 3b, 48 h). The conversion efficiency dropped from 76% to 69%, signifying an accumulation of organic intermediates. The acetic acid concentration increased by almost threefold to 3.5 mM in twelve hours (Figure 3c, 36 h) while no change in the propionic and butyric acids was observed. Although the acid concentrations were still within the range reported for stable digesters, the fact that the VFA concentrations were increasing was clear evidence that digester imbalance had occurred and that the risk of failure had increased.

Further increasing the loading rate to 27 mmoles glucose/L day (HRT= 5 days) resulted in a sharp increase of acetic and propionic acid while methane production remained unchanged. As a result conversion efficiency dropped to 59%. At critical loading rate of 32 mmoles glucose/L day (HRT = 4 days) methane production declined 36%. Within twelve hours after the increase in the loading rate, the propionic and acetic acid concentrations rose to 13 mM and 7 mM respectively, indicating that the balance between the activities of the acid forming bacteria and the methanogens had been severely disrupted. Due to the accumulation of the propionic, acetic and butyric acids in this experiment, the pH dropped from 6.5 to 5.1. The methane conversion efficiency correspondingly reduced to only 41%, indicating that more than half of the substrate failed to convert to end product biogas.

Another clear indicator of digester imbalance was the build up of H_2 from 40 ppm to 160 ppm during the 60 hours digester run (Figure 3b). This is a result of the relative increase of the H_2 producing bacteria compared to the H_2 consuming methanogens (Wolin, 1974). Towards the end of our experiment, the digester was allowed to recover by decreasing the loading rate to 7.32 mmoles glucose/L d and the pH was adjusted to 6.98 by addition of NaOH. In this experiment, with feed concentration of 24.5 g glucose/L, the hydraulic retention time (HRT) was relatively high (4-7 days) and this affected the biomass concentration in the reactor, particularly the methanogens. Recovery rarely occurred, possibly due to the washout of the methanogens. The propionic and acetic acids continued to increase and butyric acid started to accumulate. While acetic acid easily decreased when the loading rate was lowered to 2.5 mmoles glucose/L day, propionic and butyric acids showed some difficulty in degrading.

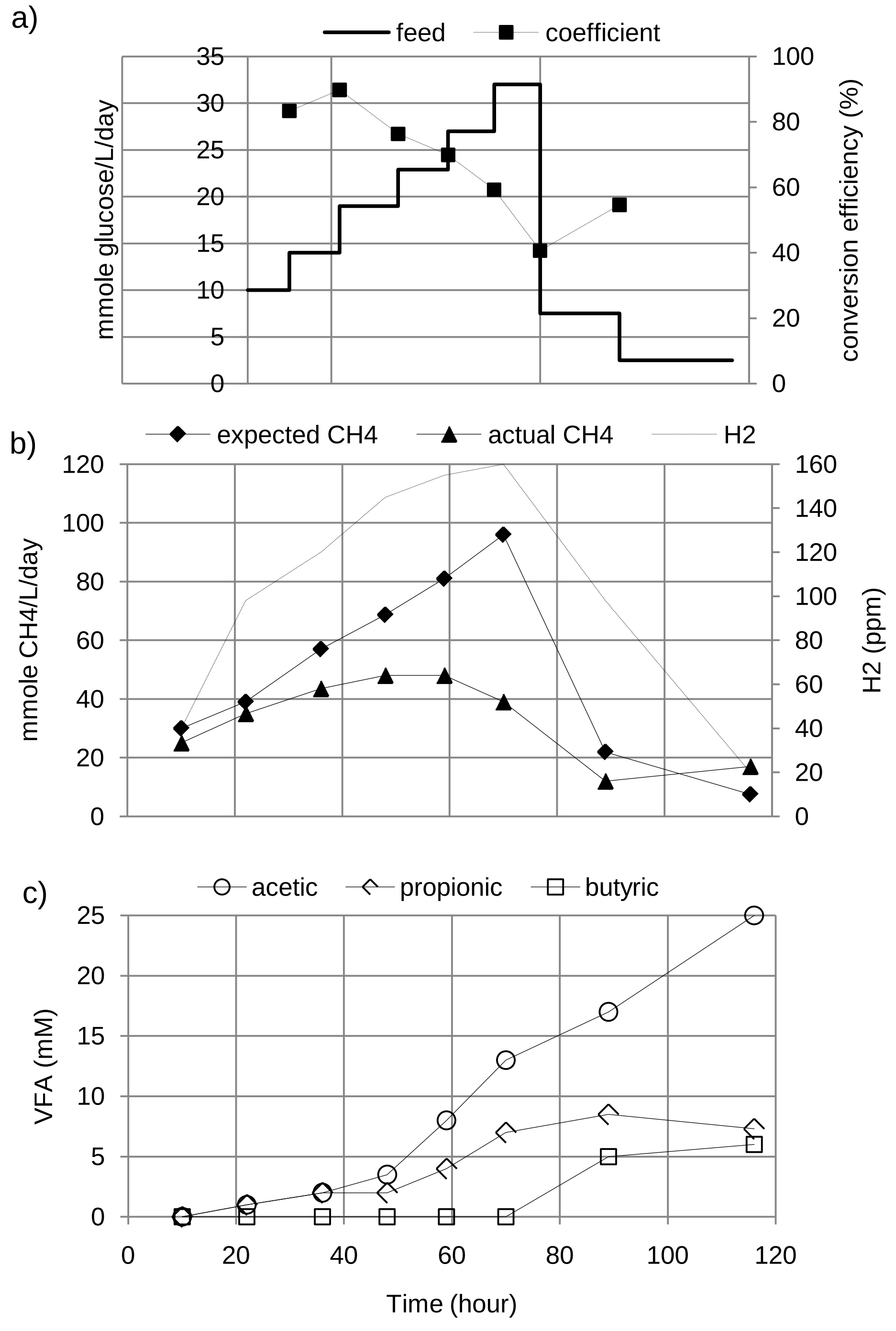

Figure 3: Response of the laboratory digester to continued increases in the loading rate using low feed concentration of 24.5 g/L d. The loading rate was increased over a12 hr interval. The pH dropped from 6.5 to 5.8 at t= 59 h, and dropped further to 5.51 at t = 72 h.

CONCLUSIONS

This study showed that the methane production rate reflects the increase in the loading rate at feed rates below the actual sustainable loading capacity of the digester. A loading rate applied beyond the actual sustainable loading rate could result in VFA accumulation, drop in pH, H_2 overproduction, a decline in the methane production rate, and eventually a decrease in methane conversion efficiency. The experiment also indicated that conversion efficiency could play an important role in the development of a simple on-line process control technique by giving an early warning of digester imbalance. The experiment has also shown that the digester could remain stable at conversion efficiencies above 75%. A reduction below 70% signifies concern for the digester performance.

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