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Carbon dioxide rich microbubble acceleration of biogas production in anaerobic digestion

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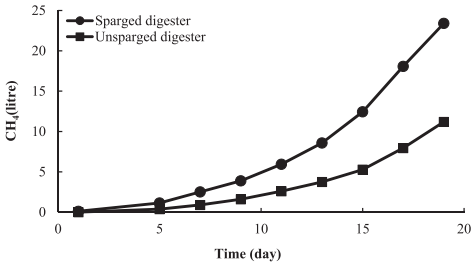
HIGHLIGHTS

- Sparging pure nitrogen has negative effect on the production of methane in AD.
- Recirculation of biogas in anaerobic digestion can enhance production of CH_4.
- The methane production rate increases with pure CO_2 in microbubble sparging.

GRAPHICAL ABSTRACT



Cumulative methane production from the gaslift digester and conventional digester when the pure carbon dioxide is sparged

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ABSTRACT

This paper addresses the use of anaerobic bacteria to convert carbon dioxide to biomethane as part of the biodegradation process of organic waste. The current study utilises gaslift bioreactors with microbubbles generated by fluidic oscillation to strip the methane produced in the gaslift bioreactor. Removal of methane makes its formation thermodynamically more favourable. In addition, intermittent sparging of microbubbles can prevent thermal stratification, maintain uniformity of the pH and increase the intimate contact between the feed and microbial culture with lower energy requirements than traditional mixing. A gaslift bioreactor with microbubble sparging has been implemented experimentally, using a range of carrier gas, culminating in pure carbon dioxide, in the anaerobic digestion process. The results obtained from the experiments show that the methane production rate is approximately doubled with pure carbon dioxide as the carrier gas for intermittent microbubble sparging.

1. Introduction

Renewable fuels have become the main focus for many researchers interested in the production of sustainable energy. Alternative clean sources of energy are available, for instance, solar, hydroelectric, wind and bio-fuels such as bio-diesel and bio-ethanol from agricultural crops, waste or microalgae. None of these sources, however, have so far been able to produce sufficient energy to provide a substitute for fossil fuels (Schenk et al., 2008; Singh, 2012; Chisti, 2007; Eriksen, 2008; Kadam, 1997).

Anaerobic digestion represents a renewable energy source (Budzianowski, 2012; Wang et al., 1999). It is commonly used for nutrient and energy recovery from biomass and also to stabilise the sludge produced in wastewater treatment (Tiehm et al., 2001). Organic matter is broken down through four biodegradation stages into methane (CH_4), carbon dioxide (CO_2), varying amounts

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of hydrogen sulphide (H_2S), and the digested sludge, which can be used as a soil fertiliser (Poeschl et al., 2010; Budzianowski, 2012). Bio-methane can be used for the generation of electricity or used as a biofuel for vehicles after upgrading processes. The production and upgrading costs of biogas are lower than the costs of production and upgrading of bio-fuel produced from agriculture crops or from microalgae (Appels et al. 2008; Sahlström, 2003; Ahring, 2003; Metcalf and Eddy, 2003). However the challenges facing anaerobic digestion implementation have become a major obstacle to this source becoming a leading renewable energy source. Among these challenges are the low volumetric yields of biogas and difficulties relating to the stability of large-scale continuous operation (Salomoni and Petazzoni, 2006; Metcalf and Eddy, 2003).

This paper introduces the premise of using a microbubble sparging system in anaerobic digestion (AD) primarily to extract methane from the bioreactor. Methane has a low solubility in water and therefore is likely to adhere to the organic phase – biomass and microbial membranes. The typical exit route for methane from an AD reactor is to build up a gas layer on the organic phase until sufficient volume is created that buoyant forces detach a large bubble, which is in equilibrium with the aqueous phase due to the long contact time. In this paper, we report on experiments that periodically sparge with a bubble size distribution that includes sub 100 μm size microbubbles. Such microbubbles have a terminal rise velocity 10^{-3} m/s or less, and as shown in Al-Mashhadani et al. (2015a), are readily entrained and therefore have a long residence time – minutes rather than seconds. These circulating microbubbles provide local gas-liquid interfaces which can interact with the methane-rich boundary layers of the organic phase to provide an exit route from the system. Hypothetically, the build-up of methane rich boundary layers surrounding microorganisms could serve as an inhibitor to their metabolism in accordance with Le Chatelier's principle. Such thermodynamic principles are important in anaerobic processes such as those considered in this work which operate close to chemical equilibrium (Hoh and Cord-Ruwisch, 1996). Reducing the chemical activity of the product gases in solution (or the fugacity in the gaseous phase) leads to a negative change in Gibbs free energy. Hence the reaction becomes thermodynamically favourable and provides impetus for the formation of more products. We will describe the chemical potential non-equilibrium thermodynamic drivers underpinning the hypothesis in Section 2; methods and materials in Section 3; and the results in Section 4. Our conclusions will be presented in Section 5.

2. Hypothesis of present study

Sparging of anaerobic digestors will affect the dissolved concentrations of gaseous species such as CH_4, CO_2, H_2, NH_3, H_2S. Since all of these gases are produced by anaerobic digestion of biomass, the most common effect will be for sparging to reduce levels of these species by a stripping effect. This would certainly be the case for sparging with an inert carrier gas such as N_2. On the other hand, if sparging is carried out with sufficiently high partial pressures of a gas that is produced during anaerobic digestion, there may be a driving force for this species to enter solution thereby increasing its dissolved concentration. If we restrict ourselves to the key species involved in anaerobic carbon catabolism, Note that we are neglecting any other gaseous products or intermediates, most notably NH_3 and H_2S.

The mathematical relationship between Gibbs free energy and species partial pressure is as follows:

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \quad (1)$$

$$\Delta G = \Delta G^o + RT \ ln\frac{[CH_3CH_2CH_2COOH][CO_2][H_2O]^3}{[CH_3COOH][H_2O]^2} \quad (2)$$

Where ΔG is the Gibbs free energy change, ΔG° is the standard Gibbs free energy, R is universal gas constant, T is temperature of reaction.

From the above equation, it is possible to note that decreasing the partial pressure of the products contributes negatively to the Gibbs free energy, hence the reaction becomes thermodynamically favourable towards the formation of more products, and vice versa (Gary, 2004). Biogases produced by AD can be either present in a gaseous film or dissolved in the bulk liquid as Eqs. (1) and (2) are completely general. For ideal gases, the partial pressure is equal to the fugacity from which the chemical potential and species activity can readily be computed.

In biological processes, some required reactions are not spontaneous – i.e. they are thermodynamically unfavourable ($+\Delta G$). Typically, these reactions are driven forward by one of two mechanisms as described below.

The first mechanism employed in metabolic networks is to provide enough energy to endergonic reactions to convert them to spontaneous reactions. Reducing the partial pressure (chemical potential) of products by their removal is another method that can be used to make reactions spontaneous in bioprocesses sharing intermediates. This principle underlies reactive separation that is a staple chemical engineering approach to intensify reactions. For example, fermentation of acetate in anaerobic digestion has a positive standard Gibbs free energy and this reaction shown in Eq. (3) is, therefore, thermodynamically not favoured unless the partial pressure of hydrogen can be reduced by methanogenic bacteria to sufficiently low levels such as 10^{-4} atm.

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2 \ \ \Delta G^o = +48.1 \text{ kJ/mole} \quad (3)$$

There has been much investigation of the mathematical relationship between partial pressure and Gibbs free energy with widespread applications. But the major results have emerged from biological processes, particularly for bio-hydrogen production. This process has caused debate among researchers about how to control the partial pressure of hydrogen or carbon dioxide and its effects on the production of hydrogen. Many researchers have noted that an increase in hydrogen production could be achieved by reducing the partial pressure of hydrogen or carbon dioxide or both depending on the following equation:

$$C_6H_{12}O_6 + 2H_2O \xrightarrow{Bacteria} 2CH_3COOH + 2CO_2 + 4H_2 \quad (4)$$

Tanisho et al. (1998), Park et al., (2005) and Alshiyab et al., (2008) studied the effects of the reduction of the partial pressure of carbon dioxide on hydrogen production. Tanisho et al. (1998) found that hydrogen production increased when the partial pressure of carbon dioxide decreased. Park et al. (2005) demonstrated that reducing the concentration of carbon dioxide from 24.5% to 5.3% in the headspace caused an increase in the hydrogen yield of 43%. Alshiyab et al. (2008) indicated that there was an increase in the hydrogen yield when partial pressure of carbon dioxide was decreased. Moreover, Liang et al. (2002), Mizuno et al., (2000), Kim et al. (2006) and Kraemer and Bagley (2008) all reported that reducing the partial pressure of hydrogen caused an increase in hydrogen production rate. These investigations have shown the importance of the removal of gases from biological processes and the effect this has on increasing production of hydrogen.

Similarly, for anaerobic digestion, the removal of some gases

during the fermentation could therefore enhance the favorability of biological reactions and intensify the production of methane. However, the overall effect is complicated by the multiple intermediate reaction steps as shown in Fig. 3 and the relative populations of the bacteria facilitating each step. For example, a decrease in the number of bacteria that consume gaseous intermediates (CO_2 and H_2) in methane production can oppose the effect of physically removing these gases. It is clear to the authors of this work, therefore, that further theoretical and experimental study of systems to manipulate the concentrations gaseous species in anaerobic digestion is required.

This work was motivated by the idea that injection of microbubbles into the bioreactor can locally modify in the heterogeneous environment near the particulate organic phase and the microorganisms. In general, microorganisms show surfactant properties, hence are likely to interact with microbubble gas-liquid interfaces.

This paper proposes a simple hypothesis which can be summarised as follows. The use of a sparging system in anaerobic digestion should increase the methane production rate by locally reducing the partial pressure of methane, while enhancing mixing efficiency. See Al-Mashhadani et al. (2015a) for an explanation of how microbubbles increase liquid mixing. In addition, the present study also tests a new microbubble generation technology for the sparging of anaerobic digesters. Microbubbles generated by a fluidic oscillator were injected in an airlift bioreactor to intensify the performance of the digestion process.

Zimmerman et al. (2009, 2011) describe the use of fluidic oscillation to generate microbubbles.

3. Material and method

3.1. The Experimental Setup

Two lab-scale digesters of the same dimensions were used in the present study: a conventional digester and a gaslift digester provided with a ceramic diffuser to sparge microbubbles generated by fluidic oscillation as shown in Fig. 1. The gaslift digester was subjected to different patterns of aeration: pure nitrogen (N2-generated (Peak scientific Ltd) with 99.9%) in the first set of experiments; pure nitrogen followed up by pure carbon dioxide was sparged with the different sparging regimes in the set experiments; circulation of diluted and undiluted biogas was carried out in the third set of experiment, finally pure carbon dioxide was sparged in the final experiment. All gases were sparged through a micro porous ceramic diffuser (HP technical ceramics) with 20 μm size pores. Both digesters were operated under mesophilic conditions. The biogas was collected continuously before and after bubbling intervals, while the concentrations of methane, carbon dioxide, and hydrogen sulphide were measured using a biogas analyser. The gaslift digester was sparged periodically with different gases, however, carbon dioxide rich bubbles was sparged for only 5 min daily to prevent a drop in the pH value. The design of the digesters is described in our previous studies (Al-Mashhadani et al., 2012a, 2015a). The flow rate used in the current experiments was 300–400 ml/min.

Each digester contains digested sludge, which was collected from the outlet stream of a full-scale mesophilic digester at the Woodhouse wastewater treatment plant in the city of Sheffield in the UK. In each digester kitchen waste was used as a substrate for bacteria, 15 ml was fed daily to the digester to provide an appropriate organic loading as suggested previous studies. In order to maintain the volume of sludge in each anaerobic digester, 12–15 ml was discharged daily from each reactor. Additional losses due to evaporation explain why less than 15 ml was sometimes discharged to keep a constant level in the digester (Al-Mashhadani et al., 2015b). The chemical oxygen demand (COD) of the digested sludge and kitchen waste were about 33 and 127 g/L respectively.

In the present study, a proportional-integral-derivative (PID) controller was used to maintain the temperature in the digester at 35 ± 1 °C. A temperature control system was constructed using a 500 W heater and thermocouple sensor type K with a range of −128 °C to 539 °C.

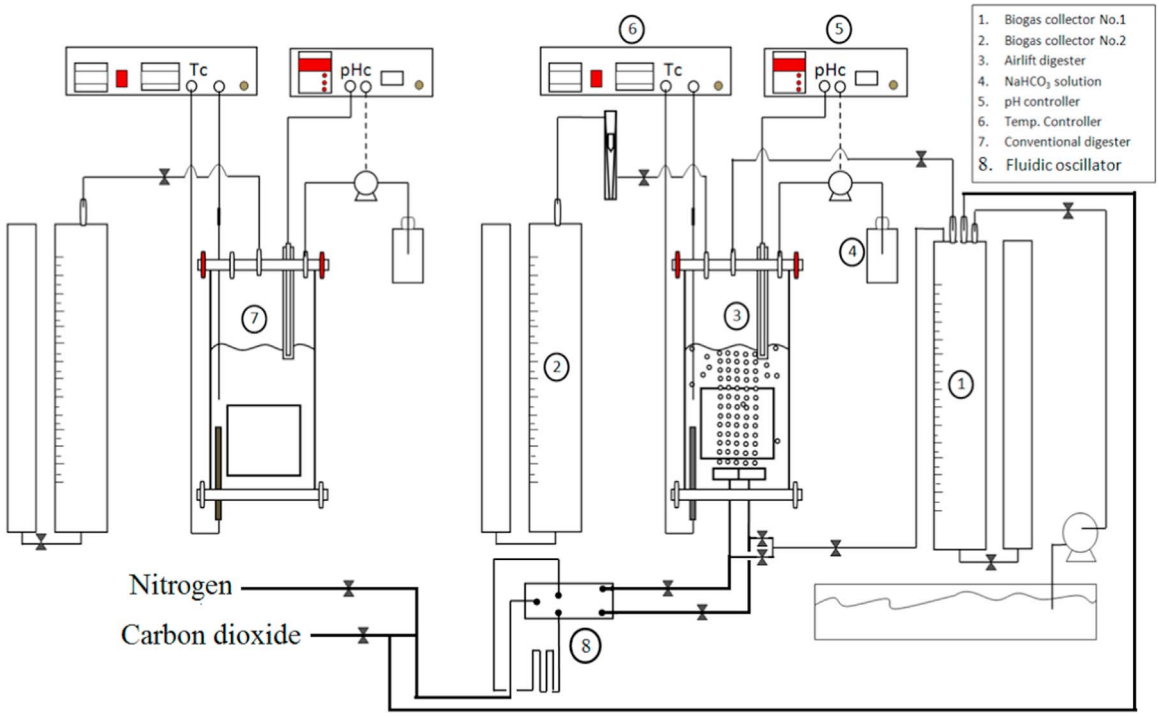

Fig. 1. Schematic of experimental work. Two digesters: a gaslift (or airlift) digestor and an unsparged digester as a control are compared in this work. Sparging is carried out using carbon dioxide rich microbubbles, with composition a controlled variable with five different levels from 0% to 100% CO_2.

Continuous measurement of biogas yield was accomplished by means of the downward displacement of acidic aqueous solution (0.2 M HCL, pH < 4). Methane, carbon dioxide and hydrogen sulphide concentration in the biogas captured using the collection system were measured daily using a biogas analyser (Data Gas UK analyser, Model 0518). Each digester was provided with a pH controller. The pH control system used in this study is an ON/OFF relay controller, which consists of three main parts (Controller, peristaltic pump and pH probe sensor). The type of pH controller system used in the experiment was a BL931700 pH minicontroller.

3.2. Microbubbles size analysis

Since the use of microbubbles was a key aspect of this work, we report an analysis of bubble sizes from the same ceramic diffuser and fluidic oscillator (Zimmerman et al., 2009) for the water/air system with same gas flow rate (300 ml/min) as used for the sparged digestor. The study was done using a high speed camera. The reactors used in the experiments were cylindrical in shape but this made it difficult to directly measure bubble size in the cylinder due to curvature distortion. Therefore, a rectangular tank with the same diffuser materials was constructed for bubble sizing. Estimation of the bubble size distribution was carried out by image analysis software, which gives the area of the bubbles' cross section in two dimensions.

Fig. 2 shows the micro-bubbles' diameter distribution. An image containing more than 130 bubbles was analysed. The average diameter of these bubbles was 550 μm with the 400–500 μm and 500–600 μm diameter range being the most abundant, respectively having relative frequencies of 37% and 27% of the total number of bubbles. The relative frequency of larger bubbles decreases with increasing diameter and no bubbles are found with diameters greater than 1100 μm. Only about 5% of bubble diameters are smaller than 400 μm, spread over the range 0–400 μm. The presence of very small bubbles with diameters of less than 100 μm is interesting and, although they only occupy a very small fraction of the total, these may have a disproportionately large effect in promoting biogas production as discussed later.

The bubble size distribution at various points throughout the tank would be much more representative than that in the plume above the diffuser. However, the isolating a plane of bubbles for measuring purpose is necessary to get the accurate average of bubble's diameter by optical approaches. Of course, taking the many lines of pores hence planes bubbles at different areas of diffuser was considered in the present study. There are two manuscripts (Brittle et al. (2015) and Rehman et al. (2015)) in production that compare optical, laser diffraction and acoustic resonance spectroscopy as methodologies for bubble sizing.

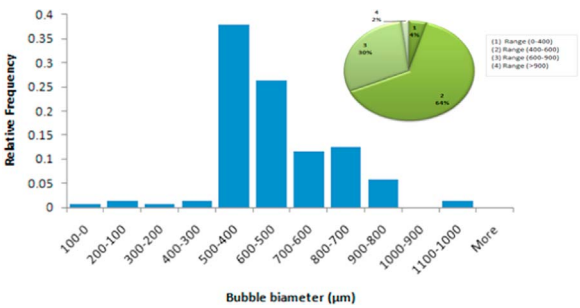

Fig. 2. Bubble size distribution using the ceramic diffuser for the air/water system at 300 ml/min.

4. Results and discussion

As can be seen in Fig. 3, some of these reactions have a negative standard Gibbs free energy signifying that the reactions are spontaneous and favourable thermodynamically, while others have a positive sign, which means these reactions are unfavourable energetically and oppose spontaneous production of methane causing the failure of the digestion process as a whole (Metcalf and Eddy, 2003; Schmidt and Ahring, 1993). However, there is a relationship between the methanogenic and acidogenic bacteria that is termed "mutually beneficial". This relationship helps to convert unfavourable reactions into favourable reactions by maintaining a very low partial pressure of hydrogen. The partial pressure should be lower than 10^{-4} atm (Ahring and Westermann, 1988), to allow the necessary equilibrium shift in the right direction and formation of more formate and acetate. Thus, the actual Gibbs free energy change will be negative under these conditions.

In fact, the methanogenic bacteria play an important role in the process. Therefore, the failure to provide a suitable environment for these bacteria opposes hydrogen from being consumed in sufficient quantity and thus will inevitably lead to accumulation of VFAs and occurrence of low pH, and ultimately the failure of this process (Metcalf and Eddy, 2003; McCarty and Smith, 1986; Schmidt, 1993).

4.1. Sparging with pure nitrogen

The effects of sparging with nitrogen (Table 1) on the performance of anaerobic digestion were investigated in our previous study (Al-Mashhadani et al., 2012b). The results showed that using nitrogen leads to stripping of carbon dioxide and hydrogen produced from degradation of the organic matter. These gases are necessary for the generation methane by hydrogen reduction bacteria, as is illustrated in the following equations.

$$3C_6H_{12}O_6 \rightarrow 4CH_3CH_2COOH + 2CH_3COOH + 2CO_2 + 2H_2O \quad (5)$$

$$CH_3CH_2COOH + 2H_2O CH_3COOH + CO_2 + 3H_2 \quad (6)$$

$$C_6H_{12}O_6 CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (7)$$

$$CH_3CH_2CH_2COOH + 2H_2O 2CH_3COOH + 2H_2 \quad (8)$$

$$C_6H_{12}O_6 + 2H_2O 2CH_3COOH + 2CO_2 + 4H_2 \quad (9)$$

$$CO_2 + 4H_2 \xleftrightarrow{\text{Hydrogen reduction bacteria}} CH_4 + 2H_2O \quad (10)$$

Therefore, methane production was reduced in comparison to conventional digestion as can be seen in Fig. 4.

Fig. 5 shows the cumulative methane production from two anaerobic digesters: a gaslift digester operating with microbubble (GDM) and a control of a conventional digester. The figure indicates that during the first eight working days, the accumulated methane production from the GDM was more than that produced from the control digester. But this does not mean that methane production increased throughout the entire period. The figure illustrates that the rate of methane produced from the GDM decreased from daily, while the rate of methane produced by the traditional digester remained more or less stable throughout the test period. Therefore, there was slightly more total methane production in the control digester than in the GDM digester. On the other hand, the GDM produced more carbon dioxide than the control digester throughout the test period although production decreased daily, as is shown in the Fig. 6. It seems that the stripping process removed all the biogas found in the digester: either

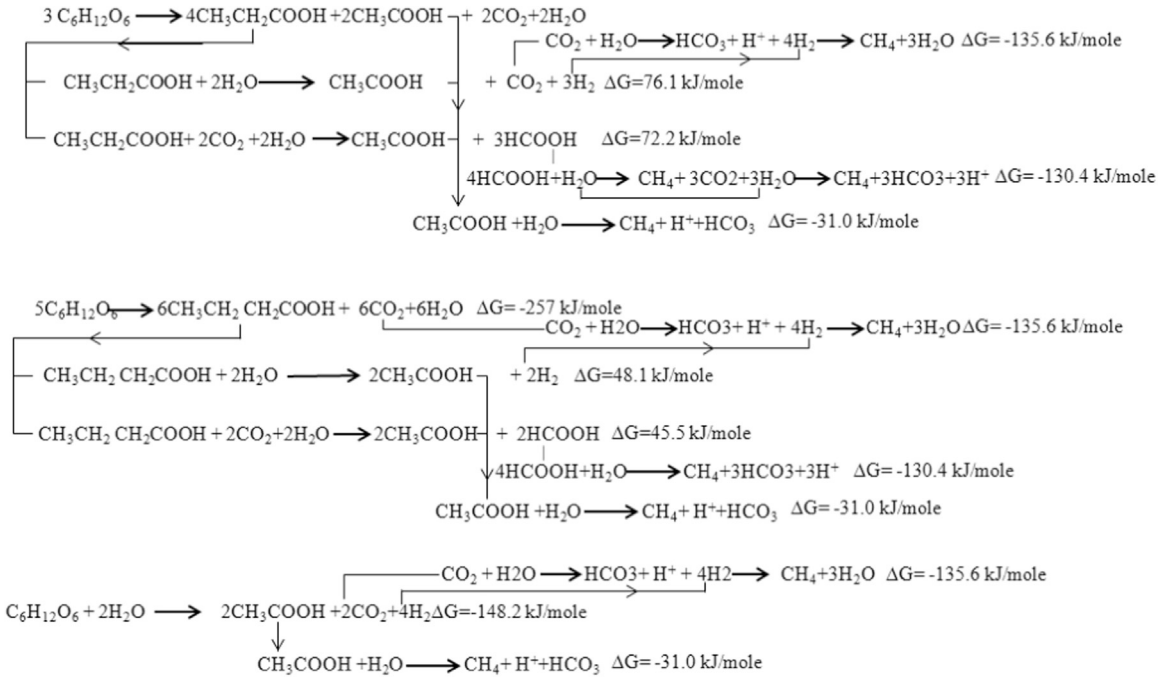

Fig. 3. Biological reactions in anaerobic digestion.

Table 1
Operational conditions applied in the first set of experiments.

Number of stage	Flow rate of nitrogen (ml/min)	Time of sparging (min)	Working days
First stage	300	100	12
Second stage	300	60	4
Third stage	300	30	4
Fourth stage	300	15	3
Fifth stage	300	5	4
Sixth stage	300	0	11

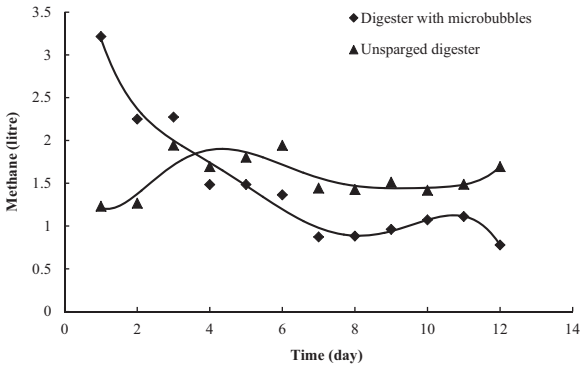

Fig. 4. Effect of sparging with nitrogen on biomethane production.

as dissolved gas, bubbles, or in the headspace and, in addition the growth of anaerobic bacteria was slow.

The results obtained from the experiments show that the sparging process, using pure nitrogen in anaerobic fermentation to breakdown organic matter, has a negative effect on biogas production generally and on methane production especially. Less methane was produced in the airlift digester than produced from the unsparged digester. Even when the sparging time was changed, this situation remained the same, although the decline in methane production was less when the sparging period decreased and cessation of sparging led to a return of the production of methane to expected levels as illustrated in Fig. 7. If the responses

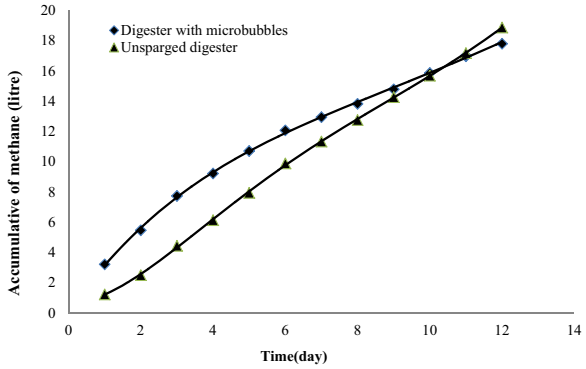

Fig. 5. Cumulative methane production from the GDM and conventional digester in the first stage.

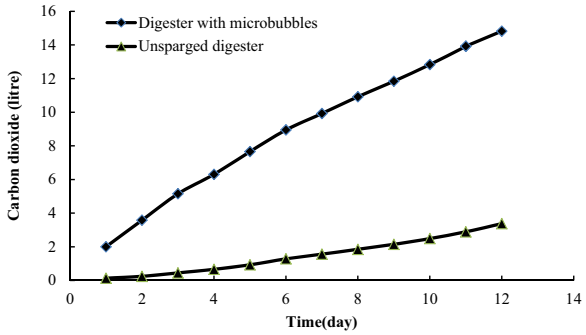

Fig. 6. Cumulative carbon dioxide production produced from the GDM and conventional digester in the first stage.

are collated within the same figure, a clear picture can be obtained about the role of sparging with nitrogen on methane production. Fig. 8 shows the production of methane in the two digesters during different sparging periods across 38 days. It can be clearly seen that the decline in methane production occurred in the early stages of the experiment, especially when the sparging time was 100 or 60 min. This decline then started to slow down when the

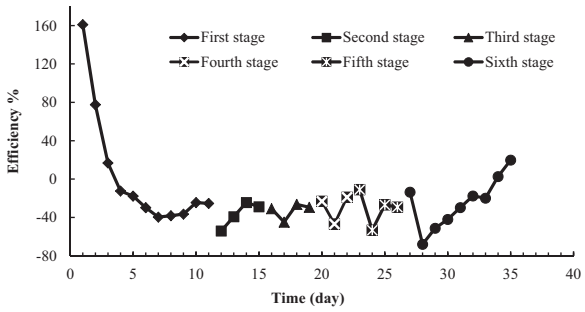

Fig. 7. Percentage ratio of cumulative methane production from the sparged digesters compared to the unsparged digester during the six stages of sparging.

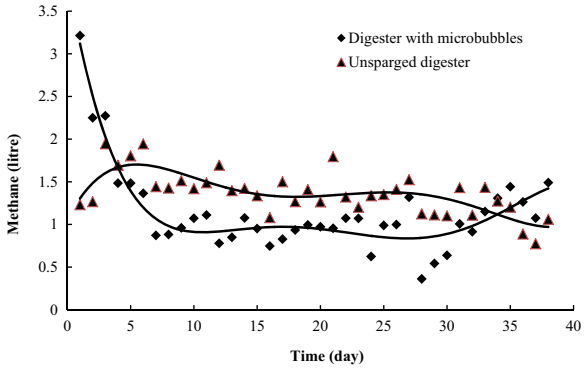

Fig. 8. Methane produced from the sparged digesters and unsparged digester.

sparging period was reduced to 30, 15 and 5 min. A big increase in methane production ensued when sparging with nitrogen ceased completely.

It can be concluded that the use of sparging has an effect across the different stages of methane production, since the process does not just strip methane gas produced in the final stage, but also strips the carbon dioxide and hydrogen that are necessary for other bacteria involved methane production.

The daily methane production before and after the sparging process in the gaslift digester is illustrated in Fig. 9. The results were compared with those for methane production in the control digester. The data indicate that the use of nitrogen for sparging in the gaslift digester leads to a decrease in methane production, with a subsequent return to normal methane production when the sparging process is stopped. The sparging system was stopped at day 28, so the methane production returned to expected value. Hence the conclusion is that N_2 sparging is always poorer than upsparged for the rate of methane production.

The use of inert gases such as nitrogen or argon has been shown previously to increase the efficiency of hydrogen production in the biodegradation of glucose in biohydrogen processes

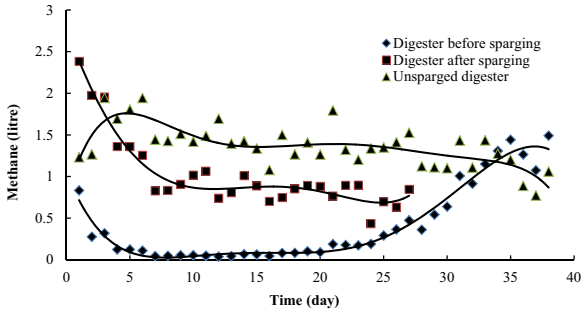

Fig. 9. Methane produced in the sparged digester (before and after sparging the process) and in the unsparged digester.

(Tanisho, et al. 1998, Park et al. 2005, Alshiyab, et al. 2008). These experiments demonstrated that the increase in efficiency is due to the sparging with nitrogen stripping the hydrogen and carbon dioxide. This stripping process causes a reduction in the partial pressure of hydrogen and carbon dioxide, thereby making the Gibbs free energy change more negative and encouraging hydrogen reduction bacteria to degrade organic material more quickly and produce more hydrogen. However, and according to our results, this behaviour does not apply to all biological processes, in particular, not to processes that consist of more than one stage and have mutually beneficial relationships across these stages, as is case in anaerobic digestion which consists of four stages, with mutually beneficial relationships between the second and fourth phases. The gases produced at a certain stage are used in another stage. Therefore, the use of inert gases (such as nitrogen) in anaerobic digestion adversely affects the production of biogas. Indeed, these gases can remove all the other gases necessary for the intermediate bio-transformations in the same process, as was the case in our tests with pure nitrogen. The results showed that much less methane was produced when nitrogen was used by reducing the activity (concentration or partial pressure depending on phase) of methane and carbon dioxide.

4.2. *Staging sparging with nitrogen followed by CO_2 replenishment*

To investigate the path of bioreactions in anaerobic digestion, *carbon dioxide was sparged after nitrogen* to replenish any carbon dioxide stripped out during the nitrogen sparging (see Table 2). The first regime of sparging every day lasted for 7 working days. Fig. 10 shows that the cumulative methane production from the gaslift digester was more than that from the control digester. Fig. 11 shows that large amount of methane was obtained during sparging with pure nitrogen and carbon dioxide. However, the yield of methane fell from day to day as shown in the Fig. 12.

In second stage the sparging regime was carried out every 48 h. In second stage the sparging regime was carried out every 48 h. Fig. 13 indicates that the production of methane from both digesters is almost the same during these periods of operation.

The efficiency of methane production in both digesters (i.e. gaslift reactor and unsparged digester) was estimated for the first stage and second stage and the results are collated in the same Fig. 14. Although the efficiency of methane production in the gaslift digester in the first stage was greater than that of the unsparged digester, the efficiency decreased continuously. However in the second stage, the decline in the efficiency of methane production was reduced.

As discussed above, the production of methane in anaerobic digestion requires the presence of carbon dioxide and hydrogen, as reactants, at the same time. The period of bubbling was therefore

Table 2
Operational conditions applied in the second set of experiments.

Number of stage	Flow rate N_2	Time (min)	Flow rate CO_2	Time (min)	Duration days	Periodicity
First stage	300	12	300	3	7	1
Second stage	300	12	300	3	10	2
Third stage	300	12	300	3	12	3
Fourth stage	300	12	300	3	15	5
Fifth stage	300	12	300	3	8	8
Seven stage	300	12	300	3	13	13
				Total	65	

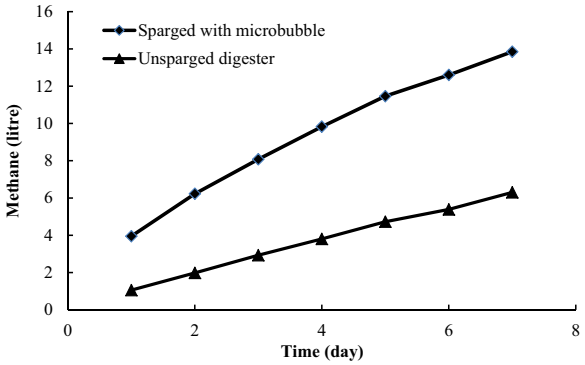

Fig. 10. Cumulative biomethane produced from the sparged digester and unsparged digester in the first stage.

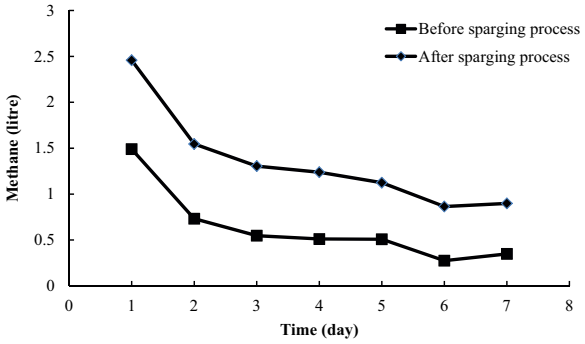

Fig. 11. Biomethane produced from the sparged digester (before and after the sparging process).

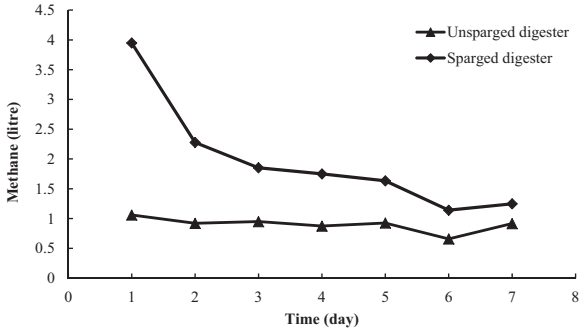

Fig. 12. Biomethane produced from sparged digester and unsparged digester in the first stage.

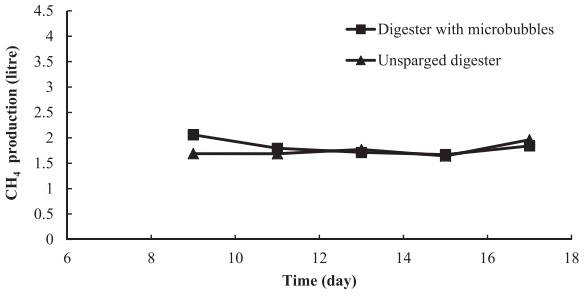

Fig. 13. Biomethane produced from the sparged digester and the unsparged digester in the second stage.

increased to allow the bacteria to produce more hydrogen to react with the carbon dioxide. However, stopping the sparging process in the gaslift anaerobic digester for 48 h did not achieve the effect of increasing methane production within this digester. According to the results, the production of methane was stable at 1.7 L per

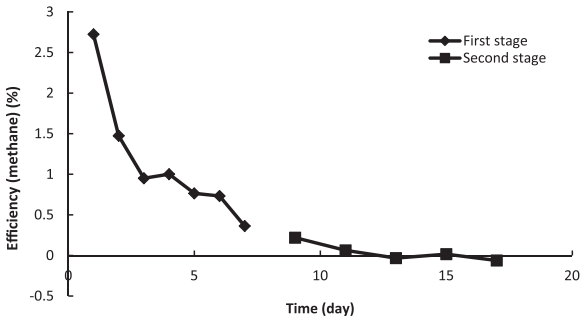

Fig. 14. Efficiency of cumulative methane production from sparged digester and unsparged digester in second stage.

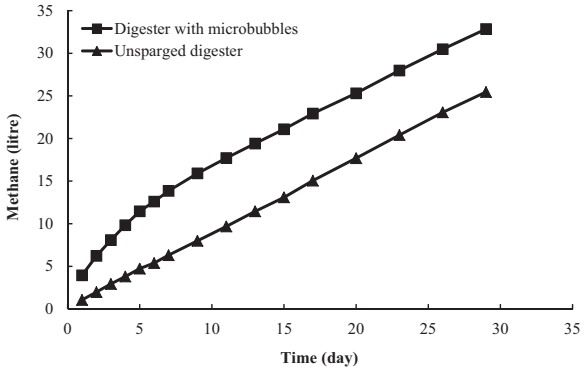

Fig. 15. Cumulative biomethane production from the sparged digester and unsparged digester up to the third stage.

day. This equalled the amount of biogas produced in the conventional digester; thus, the net efficiency of microbubble sparging was about zero during this period.

In the third stage, the gaslift digester was sparged every 72 h (3 days). The period of operation was 12 days. Again, the target of this stage was to provide enough time to generate hydrogen to react with carbon dioxide via methanogenic bacteria to produce methane. Fig. 15 displays methane production from the gaslift and conventional digesters, while Fig. 16 shows the efficiency of methane production in the gaslift digester compared with the unsparged digester for days 21–29 of the period of operation.

It can be seen that the effect of sparging once every three days is to give stable daily methane production at a very similar rate to the unsparged reactor. Indeed, when the frequency of sparging was reduced still further to once every five days and lower, the same results was observed. In other words, the daily production rates of the sparged and unsparged digester are very similar and quite constant over time.

The gaslift digester produced less methane than the conventional digester. The efficiency remained at around −6%. Although

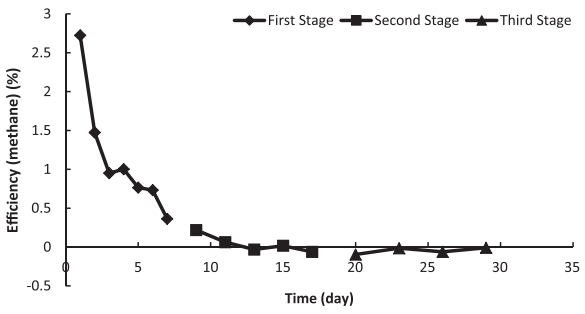

Fig. 16. Efficiency of cumulative biomethane production from the sparged digester and unsparged digester up to the third stage.

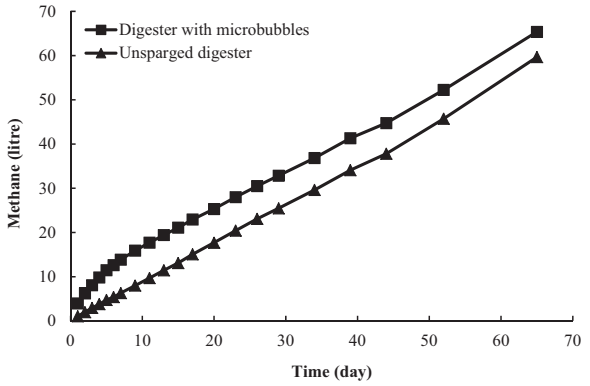

Fig. 17. Cumulative biomethane production from the sparged digester and unsparged digester up to fourth stage.

the unsparged digester produced more methane than the gaslift digester, cumulative methane production from the gaslift digester still exceeded that of the conventional digester because methane production in the unsparged digester was less than the cumulative methane production in the gaslift digester in the first days, as shown in the Fig. 17. It seems that stopping the sparging for a longer period increases the amount of methane stripped from the sludge; however, it is difficult to strip more methane than the amount found originally in the digester, either as bubbles, dissolved, or in the headspace of the digester. This is evident from the results obtained from the subsequent tests whereby the sparging process was stopped for 8 and 13 days as illustrated in Fig. 17.

For example, in first the bubbling process (i.e. at the beginning of the experiment), the amount of methane stripped was approximately 2.5 L, whilst daily continuing of the sparging led to a decrease in the methane stripped from the digester as shown in the Fig. 18. However, stopping the bubbling process gave the bacteria time to compensate the stripped biogas. Therefore, it can be seen that the amount of methane increases when the non-sparging time increases.

As is well-known, the solubility of methane in distilled water is about 0.017 mg/L, this means that the amount of methane that can dissolve in each digester is no more than 0.24 L. However, the volume of methane stripped from the sludge was about 2.5 L (i.e. 25% of the gaslift digester's volume). This means that methane held in the unsparged digester, either in dissolved form or as small trapped bubbles was the equivalent of up to 12 times its solubility in distilled water. In fact, density, viscosity, and bubbles size are important parameters in determining the terminal velocity of the bubbles in the fluid, according to Stoke's equation. In addition, the suspended solids in the sludge present obstacles that significantly hamper even large bubbles from rising to the top. The sparging process contributes to moving the suspended solids away from the large bubbles, thus the effect of suspended solids on the rising biogas bubbles is reduced, whilst, the small bubbles become

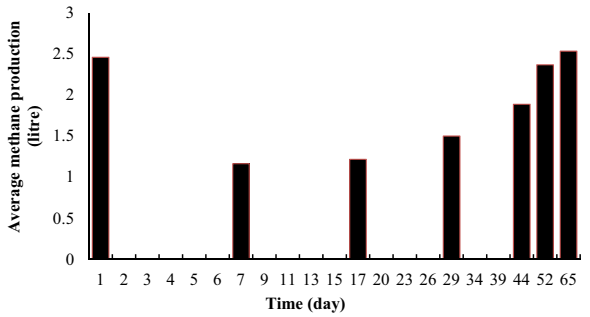

Fig. 18. Average biomethane production from sparged digester.

attached (by coalescence) to nitrogen bubbles to form big bubbles that are able to overcome the effects of the physical properties of the sludge.

Thus, when bacteria produce biogas, that biogas dissolves in the sludge until a state of equilibrium is achieved, and then the remaining bubbles either stay as bubbles or rise upward and leave the sludge.

In the conventional digester, because the sludge is already oversaturated, the methane produced from the anaerobic bacteria will leave the digester directly in bubbles, and go into the collector. Therefore, the sparging process will help to remove all methane (dissolved or remaining bubbles) from the sludge. Meanwhile, the anaerobic bacteria will continue to produce methane until the sludge reaches a state of saturation. Then, the sparging process can be repeated. The time required to reach a state of saturation with methane depends on the activity of the anaerobic bacteria.

The headspace also contains some biogas, since the pressure in this area of the reactor is 1 atm; therefore, the biogas exiting from the sludge in the gaslift digester remains in the headspace until the pressure increases to more than 1 atm. In addition, biogas can be stripped if the digester is sparged with pure nitrogen or any other gas, whilst increasing the sparging time does not lead to the stripping of any more methane than that originally found in the sludge or in the headspace.

The lower methane production of the first stage was particularly apparent in the first six days (about 12%), while in the fifth stage, the percentage of methane in the biogas rose to about 40%. This increase in the concentration of methane in the produced biogas reduces the difference in the amount of methane produced in the gaslift and conventional digesters.

The above results illustrated that the sparged digester produced less methane than the unsparged digester, even when the non-sparging periods were increased. The results indicated that compensation of carbon dioxide in the sparged digester does not lead to increased production of methane, even for very infrequent patterns of sparging. The data showed again the negative role of nitrogen in the sparging system depletes hydrogen in digester. It was found in this part of the study that the application of microbubbles generated by a fluidic oscillator in a sparging system does not give a sustainable increase in methane production in comparison to methane production in a conventional anaerobic digester.

The above results point to the negative role of nitrogen in the process through bio-hydrogen removal from anaerobic digestion, which is considered one of the important materials in the formation of methane. Therefore, the carbon dioxide compensation encourages other bio-reactions in digestion.

The methane production by methanogenic bacteria is carried out via two routes: the fermentation of acetate and the combination of carbon dioxide and hydrogen according to Eqs. (11) and (12):

ΔG^o= + 48. 1kJ/mole ΔG= − 31. 0

$$CH_3COOH+H_2O \xleftrightarrow{\text{Acetate reduction bacteria}} CH_4 + CO_2\Delta \quad G^o = -31.0\text{kJ/mole} \tag{11}$$

$$CO_2 + 4H_2 \xleftrightarrow{\text{Hydrogen reduction bacteria}} CH_4 + 2H_2O\Delta G^o = -135.6\text{kJ/mole} \tag{12}$$

In spite of the relative Gibbs free energy of acetate reduction being less than that of hydrogen reduction, the first reaction produces more methane than the second reaction (Metcalf and Eddy, 1991). In addition, carbon dioxide is used for the formation of acetate, which represents an essential material in the production of methane from propionate and butyrate, as is shown in Eqs.

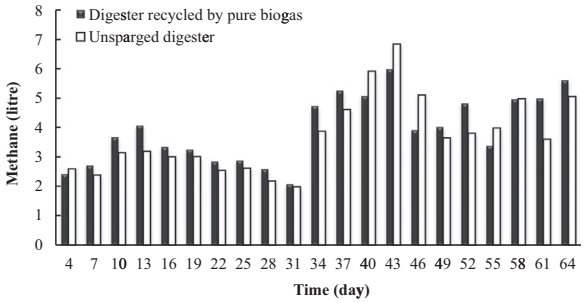

Fig. 19. Methane produced from sparged and unsparged digester.

(13) and (14).

$$CH_3CH_2COOH + 2CO_2 + 2H_2O \rightarrow 2CH_3COOH + 3HCOOH \quad (13)$$

$$CH_3CH_2CH_2COOH + CO_2 + 2H_2O \rightarrow 2CH_3COOH + 2HCOOH \quad (14)$$

Sparging with carbon dioxide, therefore, will tend to increase the production of methane from carbon dioxide and hydrogen (Eq. (12)), but will also tend to increase acetate production via the fermentation of butyrate and propionate in reactions (13) and (14). The resulting increased supply of acetate could counteract the direct negative effect of higher levels of CO_2 in reaction (11), increasing methane production through this more important route as well as reaction (12).

4.3. Recycling the biogas

4.3.1. Recycling the undiluted biogas

The third set of experiments was aimed at maintaining the concentration of biogas in the sludge by recirculation of biogas produced in the same digester. Fig. 19 represents methane production from sparged and unsparged digestion. It can be clearly seen that more methane was produced from the sparged digester than from the unsparged digester. This behaviour was not evident in previous experiments when either nitrogen or nitrogen followed up by carbon dioxide were used.

In addition, the conventional digester produced less methane than the sparged digester for the first 37 days. Then, the pattern of behaviour changed, since the unsparged digester began to produce more methane than the other digesters, especially between 40 and 46 days. The reason for this reduction is that sedimentation of suspended solids occurred in the conventional digester, which made the sludge lighter than the sludge in the other digesters. This process contributed to a reduction in thermal resistance, thus the heat transfer flux to all areas of the reactor increased. As a result, during days 40–46 then unsparged (conventional) digester was operating closer towards thermophilic operation (i.e. temperature = 42 °C) and this gave temporarily increased methane production until this issue was rectified. The problem was addressed by changing the setting on the controller to ensure that all the digesters were operating at 35 °C as shown in Table 3. After fixing the problem, methane production in the unsparged digester returned to normal.

Table 3
The temperature of the sludge before and after adjusting the setting of the controller.

	Temperature of sludge		
	Conventional digester	Sparged digester with pure biogas	Sparged digester with biogas and CO_2
Before setting	42±1	35±1	35±1
After setting	35±1	35±1	35±1

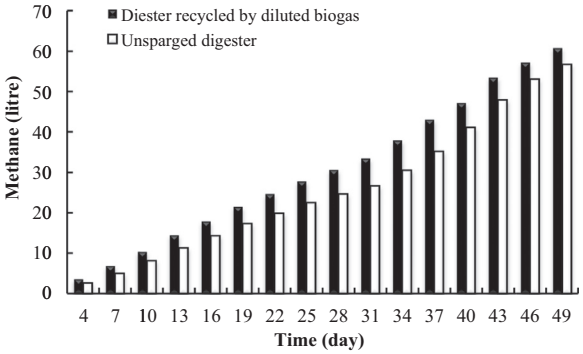

Fig. 20. Cumulative methane production from sparged digester and unsparged digester.

4.3.2. Recycling the CO_2 diluted biogas

In the third set of experiments, methane concentration in biogas produced from sparged digestion was diluted by carbon dioxide. The aim of the dilution was to strip more methane from the sludge, since the transfer of methane from the liquid phase to the gas phase increases when the concentration of methane in the bubbles is less than that in the sludge. Fig. 20 shows the cumulative methane production from the conventional digester and sparged digester after dilution of the biogas.

Whilst similar problems occurred to those experienced in the previous part, the cumulative methane production was higher than with conventional unsparged operation.

Recycling the biogas to the anaerobic digester in both cases led to an increase in methane production, maintaining the concentration of gases in the digestion, improving the efficiency of mixing and preventing the formation of thermal layers in the reactor.

The data obtained from the experiment illustrated that recirculation of biogas (either pure gas or biogas diluted with carbon dioxide) in anaerobic digestion did not, contrary to previous studies, reduce the performance of the digestion, although the proportion of methane in the gas phase reached as much as 60%.

In fact, we observed an increase in the total methane produced by using sparging with both undiluted recycled biogas as well as recycled biogas that had been diluted by carbon dioxide. Thus the bio-degradation steps continued without any negative effect on the production of methane. Low solubility of methane in the liquid and high carbon dioxide concentration in the biogas contributed to controlling the solubility of methane in the liquid phase.

On the other hand, the presence of methane gas and carbon dioxide together helped in controlling the environment of the whole process. Indeed, the methane acted as a determinant of the amount of carbon dioxide dissolved in the liquid phase. Therefore,

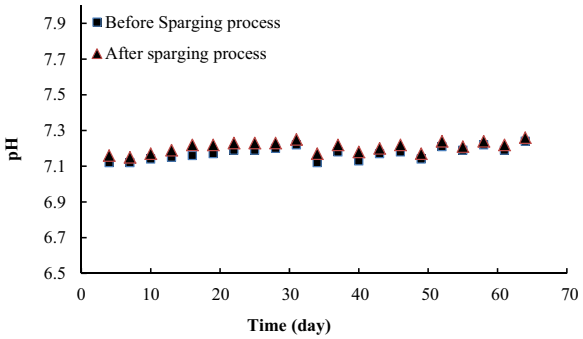

Fig. 21. pH values in the sparged digester (before and after bubbling process).

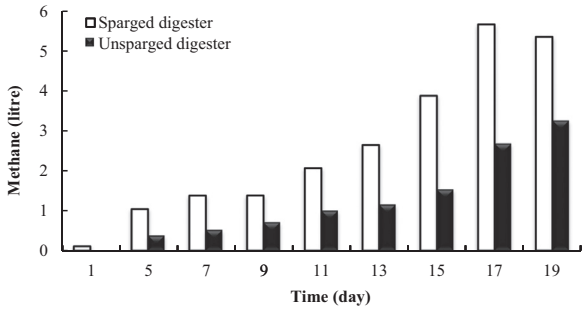

Fig. 22. Methane produced from the gaslift digester and the conventional digester over 19 days of operation.

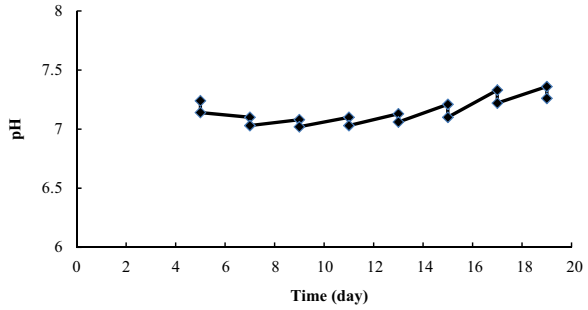

Fig. 24. pH value in the gaslift digester sparged by pure carbon dioxide for a 5 min period daily.

it can be noted that the pH value remained within the required level as shown as in the Fig. 21.

In addition, the recycling process causes stripping of hydrogen sulphide, the presence of which has a negative effect on the efficiency of methanogenic bacteria in the digester.

The results obtained from these experiments (recycling the diluted and undiluted biogas) demonstrated that recycling the biogas does not reduce the efficiency of the process; in fact, the data show that the gaslift anaerobic digester produced more methane than the unsparged digester.

4.4. *Sparging with pure CO_2 microbubbles*

Fig. 22 shows that the digester sparged by CO_2 produces methane faster than the conventional digester. Sparging with carbon dioxide (without a nitrogen sparge as in Figs. 5–13) also helps in the removal of methane found in the headspace of the digester.

After the daily sparging process is complete, the equilibrium partial pressure of the methane in the headspace is significantly reduced. The methane level then increases as the methane produced by the bacteria is transferred to the headspace until the next sparging event. The results show that production of methane in the digester with carbon dioxide exceeded the quantity produced by the unsparged digester by 109% as shown in Fig. 23.

The high interfacial areas, resulting from the small microbubble size, and the low solubility of methane are parameters that play an important role in this process. These factors enable the sparging system to remove a large amount of methane in a short time while the small effect on the value of the pH is quickly compensated and controlled at the required level as can be seen in Fig. 24.

Fig. 24 shows quite clearly that CO_2 rich microbubbles have a dramatic effect on the production rate of methane. Although periodic, daily sparging does extract the methane content of the liquid medium during its operation, and has a residual effect of lowering the partial pressure of the methane in the headspace for some time, we find that all the biogas produced has a nearly

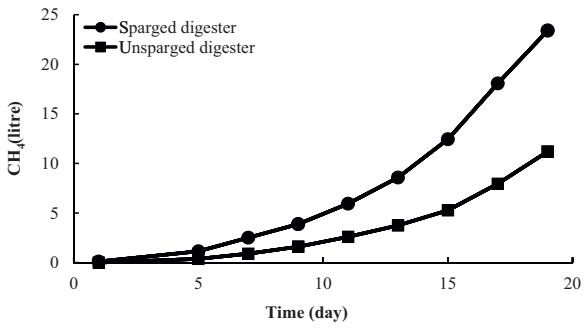

Fig. 23. Cumulative methane production from the gaslift digester and conventional digester when the pure carbon dioxide is sparged.

constant composition. An argument has been made surrounding Eqs. (12) and (13) that chemical thermodynamic non-equilibrium drivers with high CO_2 activity should spur greater methane production speed. But an overall mass balance would show that these arguments are insufficient to warrant a 109% increase in biogas production rate. The chemical species mass balance requires more H_2 to reduce CO_2 to CH_4. What is the source of this extra H_2 flux?

Ultimately, there is only one source of H_2 in an anaerobic digester – the organic material used as a substrate by the bacteria consortium. Hence an additional concept is needed to describe why CO_2 rich microbubbles accelerate the H_2 flux from the organic substrate. If methanogens are fixing H_2 on CO_2, from where is it sourced, as H_2 is the limiting reactant and present at zero dissolved concentration, as the methanogens are hydrogen starved? In our opinion, the only source for additional hydrogen is the sugary biomass which is hydrolysed more rapidly if methane is produced more rapidly. Based on some of our novel and, as yet, unpublished results on low energy microbubble induced cell lysis in Pseudomonas putida, we can speculate on one possible mechanism for the additional flux of hydrogen.

Fig. 2 shows that there is a small fraction of CO_2 microbubbles, about one percent, that are sufficiently small, to have high enough interfacial energies to support free radicals (less than 100 μm diameter). When such a microbubble collides with a cell wall / membrane, the free radical disrupts it, and the CO_2 is then released into the cytoplasm, creating a pH shock locally, potentially lysing the cell. This concept has been coined the “hammer and wedge” mechanism. The free radical is the wedge that prises open the cell membrane before being hit with the pH shock hammer. Alternatively, microbubbles that dissolve away are also known to create free radicals like a sonochemistry ultrasound cavitation created bubble collapse (Takahashi et al. 2007). Pure CO_2 microbubbles could dissolve away completely if the liquid is subsaturated. Microbubbles with lower CO_2 composition (higher N_2 content) showed less increase in methane production rate, consistent with both lower pH shock, but also less propensity for total dissolution. The issue of low energy cell lysis via sub 100 μm bubble population fractions with high CO_2 content is being explored with an ongoing experimental programme.

According to results obtained from the above five sets of experiments, the effect of sparging system on the methane production at different gases can be summarised in the Table 4.

5. Conclusions

This study discusses how a sparging system was applied in anaerobic digestion using an airlift bioreactor and different gas types (nitrogen, nitrogen and carbon dioxide, biogas (methane and carbon dioxide)) and pure nitrogen under mesophilic conditions.

The results show that the application of the bubbling system

Table 4
Effect the sparging system on methane produced from anaerobic digester.

CO_2 fraction	Gas used in sparging system	Efficiency
0	Pure Nitrogen	Negative effect (see Fig. 5)
	Pure Nitrogen + pure carbon dioxide	Zero effect
40%	Recycling the undiluted biogas	Positive effect (12–14%)
80%	Recycling the diluted biogas by carbon dioxide	Positive effect (10–12%)
100%	Pure carbon dioxide	Positive effect (100–110%)

with pure nitrogen in anaerobic digestion had a negative effect on the production of methane. This was because the sparging system stripped the carbon dioxide and hydrogen that are consumed by hydrogen utilising methanogenic bacteria in a route which normally accounts for 30% of total methane production. The results obtained from the experiments also showed that compensation with carbon dioxide after nitrogen bubbling does not lead to a sustained increase in daily methane production, regardless of the length of the period of sparging. This is despite the fact that sparging does initially increase methane production, but this is not sustained as was found for sparging with pure nitrogen. The results indicate that the daily sparging regime actually leads to a decrease in methane production, but this can be corrected by less frequent sparging to give the same production as can be achieved in a conventional digester. However, the results indicated that recirculation of biogas in anaerobic digestion process can enhance production of methane (10–14%).

The present study has also investigated the effect of periodic, daily sparging with carbon dioxide in a batch anaerobic fermenter. The type of gas in sparging system in biological processes plays an important role in determining the path of bio-reactions, in particular, processes that consist of more than one stage and have mutually beneficial relationships across these stages, as is case in anaerobic digestion. The results also showed that the digester sparged with carbon dioxide and using microbubbles generated by a fluidic oscillator produced more methane than the unsparged digester. The data obtained from the current experiments indicate that the sparging system helps in stripping the methane produced by anaerobic bacteria. Removal of biogas from the headspace contributes to the transfer of biogas dissolved in the sludge to the headspace due to the difference in concentration between the two phases. Ultimately, the increased biogas production rate must be due to greater release of H_2 from the organic substrate, but the mechanism whereby CO_2-rich microbubbles achieve this is still unknown.

The general trend is clear that increasing the CO_2 fraction within the microbubble increases the production rate of methane, and taken to its extreme, pure CO_2 has a surprisingly large effect – more than doubling the methane production rate. This is completely unexpected on the grounds of the stripping mechanism alone, as both pure nitrogen and pure CO_2 strip out all the available methane. Recycling with biogas, since it left the bioreactor in equilibrium with the liquid medium, has the effect of permitting stripping methane without stripping CO_2. Diluting the biogas with CO_2 increases the stripping effect, but stripping with microbubbles, due to the high surface area per unit volume, should strip all the methane. Hence on the basis of stripping alone, pure CO_2 microbubbles should not increase the methane production over diluted biogas. Alternatively, we can invoke thermodynamic principles to explain this effect. Considering the metabolic routes to methane, there are two in which CO_2 is utilised. Firstly, it is consumed by hydrogenotrophic methanogens and secondly it can be reduced to acetate via the Wood–Ljungdahl pathway of acetogenesis. This latter route has been proposed as the means by which injection of CO_2 has enhanced methane production form anaerobic digestion in previous research work (Fernández et al., 2014; Salomoni et al., 2011). Neither of these studies, however, have addressed the issue that greater production of H_2 must also occur since it is a co-substrate in both these routes. This requires us to consider additional mechanisms to explain our striking results, such as the release of more sugary materials from the feedstock by additional cell lysis, must be in play, as greater methane production rate can only occur with greater H_2 metabolic flux, as it is the limiting reagent in methanogenesis.

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