Anaerobic Treatment of Cattle Manure for Biogas Production

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Abstract

Feedlot farming with abattoir integration in Malaysia is relatively new; therefore its waste management needs to be carefully administered. Although the cattle are only stored for 3 months cycle to be fatten up before being slaughtered, the manure and waste produced from abattoir can be as much as 200-300 tonnes per day. Batch anaerobic digestion of cattle manure was studied in a 10 L bioreactor at 53^{o}C and pH controlled at 6.95. Palm oil mill effluent activated sludge at ratio of 1 to 5 was used as seed sludge. The initial COD of the mixture was 42.5 g/L and it reduced by 51%. The biogas produced is 207 L/kg VS at hydraulic retention time of 17 days with ultimate methane yield of 184 L/kg VS. The biogas production dipped slightly on day 10 due to the availability of nutrient that has decreased tremendously. Increased N-NH_4^+ concentration above 1000 mg/L may also have inhibitory effect on the biogas production. Methane content obtained is between 58-83% throughout the culture. The H_2S concentration is well below than 0.26 ppm, therefore no further treatment is needed. Effluent on the final days was found to be high in COD (8.75 mg/L) and N-NH_4^+ (260 ppm) which are unsuitable for irrigation according to the Malaysian Water Standard. Further treatment such as post-digestion or chemical/physical treatment is needed.

Introduction

The application of anaerobic digestion (AD) technology to livestock treatment has received considerable attention because it can be used to produce valuable by-products such as biogas. The technology of biogas has been developed due to the advantage of producing energy as well as generating odor-free residues rich nutrients, which can be used as fertilizers (Karim et al., 2005). This would encourage sustainable agricultural practices in mitigating possible manure pollution problems, thereby sustaining development while maintaining environmental quality. Moreover, rural economic development would benefit from the implicit multiplier effect resulting from jobs created by implementing digester systems. Therefore, promising future waste-to-profit may add economic performance of an AD.

Although large scale production and advanced AD systems are well developed and in operation in countries like Europe, United States, Japan, China and Taiwan (Rodriguez et al., 1997), no known AD of cattle manure is found in Malaysia. Nonetheless, there are a few guidelines for cattle and poultry farming which suggest the integration of an anaerobic digester for waste management (Jabatan Perkhidmatan Haiwan, 2003). However, this system is not favored by small farmers due to high capital cost and lack of environmental consciousness. With a population of more than 300,000 pigs and cattle recorded in Penang alone, there is an urgent need to set up this technology (Jabatan Perkhidmatan Veterinar Pulau Pinang, 2001).

An estimation of the potential to produce methane of animal manures is essential. Parameters such as nutrients content, pH, temperature, organic loadings, solid content, mixture ratio and hydraulic retention time (HRT) are detrimental to biogas quality and quantity. These parameters would also determine the size of digester, auxiliary equipment needed, as well as the sizes and specifications of biogas treatment facilities. Maximum methane yield requires adequate and efficient nutrient supply for micro-organisms in the digester. Methane production from organic substrates mainly depends on their content of substances that can be degraded to CH_4 and CO_2. Composition and biodegradability are key factors for the methane yield from energy crops and animal manures (Balsari et al., 1983).

In well-established digesters, pH of the fermenting mass are buffered between 6.8 and 7.4. Bacteria have limited range of temperature, in which they are active. Methanogens, in particular, are very sensitive to temperature changes. In general, mesophilic anaerobic digestion of organic sludge is more widely used compared to thermophilic digestion, mainly because of the lower energy requirements and higher stability of the process. Thermophilic digestion, however, is more efficient in terms of organic matter removal and methane production (Buhr and Andrews, 1977) and (Ahring, 2001). Moreover, it enhances the destruction of pathogens, weed seeds and insect eggs; thus enabling effluent hygienization (Zábranská, 2000) which might be required in the short term for land application. During fermentation of organic wastes, acetic acid is usually the main product. The excess production of volatile fatty acids (VFA) may result in an inhibitory effect on the fermentation of organic wastes (Noike et al., 2000).

The most potential biochemical methane production yield from animal waste and water can be as 0.2 m^3/kg of VS added (Chynoweth et al., 1993). Furthermore, the contents of nitrogen and phosphorus in the animal waste are sufficient to satisfy the cell growth requirements during the biogas production. The others elements, such as sodium, potassium, calcium, magnesium and iron are present in low concentrations. However, they may exhibit inhibitory effects at higher concentrations (Shyam and Sharma, 1994). On the contrary, there was insignificant effect of the retention time on biogas production. Van Der Vlugt and Rulkens (1985) performed the biogas production in 20 liter laboratory digesters and found that the biogas produced was not affected when reducing the hydraulic retention time (HRT) from 40 to 20 days. In contrast, in a 200 L farm scale digester, Kiely (1985) found that cattle slurry of higher VS produced higher amount of biogas over the total digestion period of 66 days.

Bioconversion of animal waste is a non-polluting and environmentally feasible process. The main aim of this present study is to evaluate the potential biogas production from cattle manure. The influence of anaerobic digestion parameters on the manure treatment and methane yield from cattle manure was investigated.

Materials and Method

Feedstock

Cattle manure was collected from the Alifah's farm situated at Kluang, Johore, Malaysia. The samples were kept in tightly closed polycarbonate bottle and stored at 4^{o}C until further use. Seed sludge was obtained from the palm oil mill effluent (POME) aerobic sludge and used without further purification.

Apparatus and Operation

A 5 liter volume of dilute cow manure (1:1) was mixed with 1 L of POME sludge and digested in a 10 L jacketed fermenter. The bioreactor system (Biostat B, Germany) is equipped with pH, mixer and temperature controller. The sample in the bioreactor was flushed with N_2 gas for 10 minutes at the beginning of experiment ensure anaerobic condition. The temperature was controlled at 53^{o}C and homogenous mixing was aided by a 150 rpm stirrer. The pH was controlled at 6.95 via the addition of 1 N HCl and NaOH. Hydraulic retention time (HRT) of 17 days was used in this study. The produced biogas was collected using gas sampling bag.

Analytical methods

Total solid, volatile solid, biological oxygen demand (BOD) and chemical oxygen demand (COD) were measured by following the procedures listed in Standard Methods (APHA, 1998). Total nitrogen content was determined via Kjeldal method while ammonia nitrogen was determined via Autoanalyzer (Lachat QC 800, USA). The metal content was analyzed via ICP-AES using the EPA3050B extraction method. While elemental content was measured using elemental analyzer (LECO CHNS932). Methane and carbon dioxide concentrations in the biogas were determined with a gas chromatograph (Shimadzu, Japan) equipped with a thermal conductivity detector (TCD) and Carboxen-1010 plot column 30m x 0:53mm ID (Supelco, USA). The injector, detector and oven temperatures were 150, 200 and 120^{o}C, respectively. Argon served as the carrier gas.

Results and Discussion

Characteristics of feedstock

The fresh cow manure were analyzed with respect to total solids and volatile solid content, total nitrogen and ammonia nitrogen content, metal content such as phosphorus, potassium, calcium, magnesium, iron, sodium and aluminium, elemental content and pH. The results are tabulated in Table 1. The total solid content was not very high therefore minor dilution is needed as most existing on-farm digesters are operating at total solid between 8 and 12% (Lo et al., 1983). Furthermore, the addition of seed sludge increases the solid content at the start of fermentation. Theoretically, high volatile solid will produce high yield of biogas, given that optimum condition applies in the digester. High content of 9.3 g/L of the total nitrogen could be attributed by organic nitrogen with only 800 mg/L exist as ammonia nitrogen form. Caution must be taken when digesting high nitrogen containing biomass because its conversion to free ammonia might cause toxicity to the bacteria. Free ammonia is known to be able to pass through the microbes' cell membrane, causing proton imbalance and potassium deficiency (Chen et al., 2008).

Table 1: Composition of fresh undiluted manure

Types of Analysis	Values
Total Solids (% wet)	16.7
Volatile Solids (mg/L)	1187.9
Total Nitrogen (mg/L)	9260
Nitrogen Ammonium (mg/L)	800 mg/L
Metals (ppm)	
Phosphorus	24.7
Potassium	44.2
Calcium	65.9
Magnesium	14.7
Ferum	10.3
Sodium	3.9
Aluminium	2.6
Elemental (wt %, dry basis)	
Carbon, C	43.5
Hydrogen, H	5.47
Nitrogen, N	1.84
Oxygen, O	49.2
pH	5.33

Cationic elements such as sodium, potassium and others are required for microbial growth in anaerobic digestion of waste, but can be inhibitory to microbial activity if present in high concentrations (Appels et al., 2008). The metal contents are however low in this case therefore, their presence effects the microbial growth positively. Elemental analysis of manure shows high content of oxygenated compound, probably due to the nature of the food given to the cattle. The food comprises of palm kernel cake (PKC), spent brewer grain (wheat and barley) and soy residue. PKC is a by-product of palm kernel oil milling containing 14-16% of crude protein (Chin, 2001) while soy residue contains around 16% protein (Hsieh and Yang, 2004) and spent brewer grain contains of 28% protein (Lim, 1967). PKC also contains oil between 5 and 12%. Though the oil content is not significant, this may give rise to the lipid content as in the manure. The carbohydrates in the feed may not be fully digested in the cow stomach therefore the remaining carbohydrates may have given substantial value of oxygen content.

Biogas and Methane Production

The cumulative biogas production and its respective methane content are shown in Figure 1. The first three days of the digestion indicates slow production of biogas concurring with the first phase of biomass decomposition via acetogenesis process. From observation, automatic addition of NaOH was intensive during this time. The production thereafter rises rapidly for 2 days and then less rapidly up to day 12. This rapid increment of biogas production is a result of acclimatized methane forming bacteria activities and high temperature used in the experiment. Only small increment was observed after day 12 until finishing run at day 17. The bacteria activities began to cease during this time possibly due to toxicity of high ammonia nitrogen content above 1 g/L especially for thermophilic digestion (Hansen et al., 1997). However, the methane content varied between 58 and 68% but exceptionally high on the final day at 83%. The average methane content is calculated to be 65% which is pretty decent when optimisation of the parameters is yet to be attempted. The composition of biogas was also analyzed to yield around 14 to 19% of CO_2 and maximum of 0.26 ppm H_2S. Low H_2S content in this case is very encouraging because post-treatment for the biogas is not needed.

Figure 2 represents the total solid and volatile solid concentration during the anaerobic digestion period. For this batch digestion, initial volatile solid was analyzed to be 290 mg/L giving rise to biogas production of 207 L/kg VS. The elemental composition of the raw manure was analyzed to calculate the theoretical methane yield, B_u using Bushwell's formula (Symons and Bushwell, 1933). The theoretical methane yield was calculated to be 393 L/kg VS as opposed to the ultimate methane yield of 184 L/kg VS, less than half methane was produced than expected. The cessation of biogas production on day 12 is obviously the reason. Volatile solid content on this day is still high at 265 mg/L proving food is still sufficient at this point. Toxicity of ammonia still stands as the main reason of the cessation and will be discussed in detail later. The total solid decreased insignificantly for the first seven days but increased quite significantly thereafter. This is most probably due to sampling difficulties. The same reasoning goes to the volatile solid.

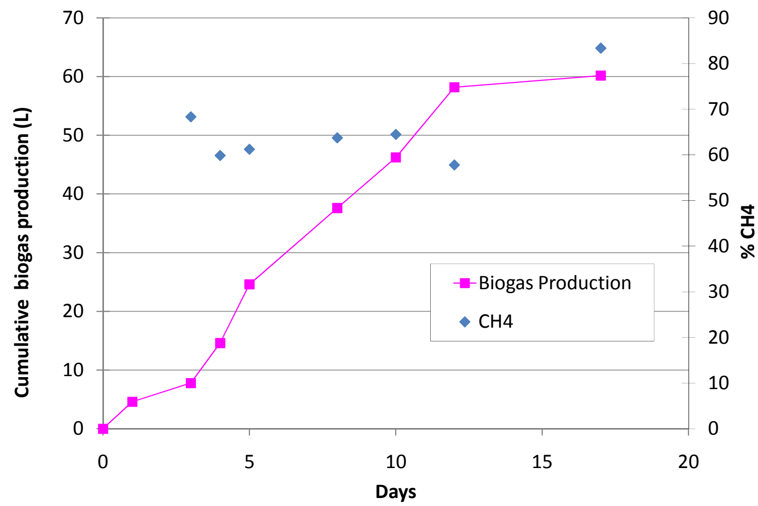

Figure 1: Cumulative biogas production and respective methane content for batch anaerobic digestion of cow manure.

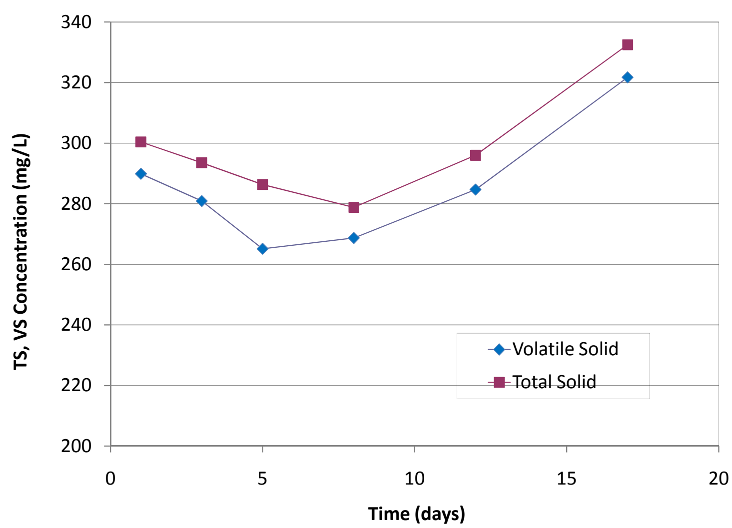

Figure 2: Total solid and volatile solid concentration with respect to the biogas methane yield during the digestion period.

COD removal and Ammonia

The initial COD of undiluted cattle manure is 17.4 g/L however, addition of seed material, the palm oil mill effluent (POME) digested sludge has increased the COD to 42.5 g/L. POME is well known for its high COD value due to its fat contents. Nonetheless, this high initial COD did not restrain the bacterial activity for at least the first 12 days of this batch culture. By the 12^{th} day, the COD value has decreased to 21.7 g/L, half of that initial value. Thereafter, the value started to stabilize around 21 g/L. It can be concluded that with little bacterial activity at this point, no further treatment of the waste took place.

Ammonia content was stable at the beginning of the culture at 400 mg/L until day 12 when the value shot up to 1.2 g/L. The organic nitrogen in the form of protein and lipids contained in the manure after degasification was converted to inorganic nitrogen in the form of ammonium during the mineralization process. It was found that inorganic nitrogen increased by 32% and organic nitrogen was reduced by 50% in the digested manure (Moller, 2006). Inhibition of ammonia has been found at concentrations as low as 0.7 g/L up to 1.1 g/L for adapted anaerobic digestion of manures (Hansen et al., 1998). The limit of which inhibition of methanogenesis is mainly depends on operating temperature and pH. At higher temperature, i.e. thermophilic conditions as in this study, although encompassing advantages such as high degradation rates and better sanitation effects, the production of ammonia was higher as compared to mesophilic conditions (Angelidaki and Ellegaard, 2003). Sung and Liu (2003) found that 50% inhibition of methanogenesis at pH 7.6 was under thermophilic condition even at 0.57 g/L of ammonia. Higher tolerance of the current study as compared to Sung and Liu's possibly attributed to differences in substrates, inocula, pH and acclimatization period. The pH in this study was controlled at 6.9 and from observation, as the digestion progressed, more acid was automatically added. This may have prevented the pH to increase further and prohibit growth. Nonetheless, the ammonia produced due to high temperature is adequate to cease the microbial growth. Figure 3 represents the amount of COD removed and ammonia-nitrogen being produced during the digestion period.

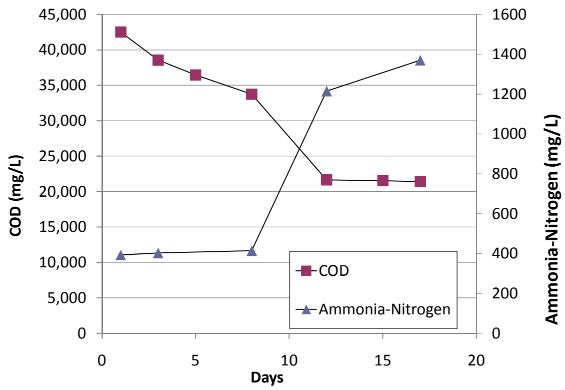

Figure 3: COD removal and ammonia production during the anaerobic digestion of cow manure

Conclusions

There is no doubt that methane and power produced in anaerobic digestion facilities are becoming favorably utilized to replace energy derived from fossil fuels, and hence reduce emissions of greenhouse gases. In this study, biogas methane was produced via anaerobic digestion of cow manure in a 10 L stirred bioreactor. The digestion was carried out at thermophilic temperature of 53ºC and a controlled pH at 6.9. Findings suggested that the ammonia produced led to the prohibition of microbial growth. The COD was removed by 51% from 42.5 g/L to 21 g/L, indicating no further treatment of the waste took place due to minimal bacterial activity. It was found that the inhibitory effect caused by the increasing ammonia concentration led to reduction of the biogas methane content during the digestion period. However, the average biogas methane produced is about 65% with only traces of H_2S concentration. This would give a promising evidence of the anaerobic digestion as a viable and feasible treatment technology of organic waste, in particular, the animal manure, simultaneously, generating biogas as the renewable energy. Further investigation is yet to be carried out to finalize the optimization of the parameters involved in this study.

References

Ahring, B.K., Mladenovska, Z., Iranpour, R. and Westerman, P. (2001). State of the art and future perspectives of thermophilic anaerobic digestion, *Proceedings* *of the 9th World Congress on Anaerobic Digestion, vol. 1* Antwerpen, Belgium, pp. 455–460.

Angelidaki, I. and Ellegaard, L. (2003). Codigestion of manure and organic wastes in centralized biogas plants, *Applied Biochemistry and Biotechnology*, 109: 95-105.

American Public Health Association (1998). Standard Methods for the Examination of Water and Wastewater 15th Ed. Washington, APHA.

Appels, L., Baeyens, J., Degreve, J. and Dewil, R. (2008). Principles and potential of the anaerobic digestion of waste-activated sludge, *Progress in Energy and Combustion Science*, *In press*.

Balsari, P., Bonfanti, P., Bozza, E. and Sangiorgi, F. (2008). Evaluation of the influence of animal feeding on the performances of a biogas installation (mathematical model), In: Third International Symposium on Anaerobic Digestion. Boston, MA, USA, 14–20 August 1983, A 20, pg. 7.

Buhr, H.O. and Andrews, J.F. (1977). The thermophilic anaerobic digestion process, *Water Resources,* 11**:**129–143.

Chen, Y., Cheng, J. J., Creamer, K. S. (2008). Inhibition of anaerobic digestion process: a review, *Bioresource Technology*, 99: 4044-4064.

Chin, F. Y. (2001). Palm kernel cake (PKC) as a supplement for fattening and dairy cattle in Malaysia, *Report of the 26th Session of the Animal Production and Health Commission for Asia and the Pacific (APHCA),* 24-26 August 2002. Subang Jaya, Malaysia.

Chynoweth, J.N. Owen (1993). Biochemical methane potential of municipal solid waste components, Water Sci. Technol. 27, 1–14.

Hansen, H. H, Angelidaki, I. and Ahring, B. K (1998). Anaerobic digestion of swine manure: Inhibition by ammonia, Water Resource. 33 (8), 1805-1810.

Hsieh, C. and Yang, F. C. (2004). Reusing soy residue for the solid-state fermentation of *Ganoderma lucidum*, *Bioresource Technology*, 91(1): 105-109.

Jabatan Perkhidmatan Haiwan (2003). *Manual Perternakan Lembu Fidlot*. Malaysia Ministry of Agriculture.

Jabatan Perkhidmatan Veterinar Negeri Pulau Pinang (2001). *Garis Panduan Penternakan Khinzir Negeri Pulau Pinang.* Penang State Government. Malaysia.

Karim, K., Hoffmann, R., Klasson, K. T. and Dahhan, M. H. (2005). Anaerobic digestion of animal waste: effect of mode of mixing, Water Research 39, 3597-3606.

Kiely, P.V. (1985). Anaerobic digestion of slurry from cattle fed high roughage diet, Proceedings of the Symposium under EEC programme on recycling urban and industrial waste, 251-258.

Lim, H. K. (1967). Animal feeding stuffs compositional data of feeds and concentrates, *The Malaysian Agricultural Journal*, 46(1): 63-70.

Lo, K.V., Bulley, N.R., Liao, P.H. and Whitehead, A.J. (1983). The effect of solid-separation pretreatment on biogas production from dairy manure. *Agricultural Wastes,* 8: 155-165.

Noike, T., Takabatake, H., Mizuno, O. and Ohba, M. (2002). Inhibition of hydrogen fermentation of organic wastes by lactic acid bacteria, *Int. J. Hydrogen Energy*, 27: 1367-1371.

Rodriguez, L. and An, B.X. (1997). Installation and performance of low cost polyethylene tube digesters on small scale farms*. World Animal Review,* 88: 38 – 47.

Shyam, M. and Sharma, P.K. (1994). Solid state anaerobic digestion of cattle dung and agroresidues in small capacity field digester, *J. Biores. Technol*., 48:203–207.

Sung, S. and Liu, T. (2003), Ammonia inhibition on thermophilic anaerobic digestion. *Chemosphere*, 53: 43-52.

Symons, G. E. and Bushwell, A. M. (1933). The methane fermentation of carbohydrate, *Journal of the American Chemical Society*, 55: 2028-2039.

Van Der Vlugt, A. J., and Rulkens, W. H. (1985). Biogas production from a domestic waste fraction, Proceedings of the Symposium under EEC programme on recycling urban and industrial waste, 245-250.

Zábranská, J., Dohányos, M., Jeníček, P. and Kutil, J. (2000). Thermophilic process and enhancement of excess activated sludge degradability—two ways of intensification sludge treatment in Prague central wastewater treatment plant, *Water Sci. Technol.* 41: 265–272.