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BIOGAS GENERATION FROM ANAEROBIC FERMENTATION OF ANIMAL MANURES AND THE NUTRIENT DYNAMICS IN THE RESIDUES

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Abstract

Biogas technology helps to generate energy from waste treatment, reduce global warming, and earn carbon credits. The biogas residues (BRs), which contain all available plant nutrients, would be good sources of organic fertilizer for crop production. A Chinese fixed dome biogas digester has been successfully adopted in Asian countries recently but not in Thailand. The objectives of this study were to compare biogas generated from domestic animal manures (pig, chicken, and cow) in the Chinese fixed dome digesters and to determine the nutrient dynamics in both biogas liquid residues (BLRs) and biogas solid residues (BSRs). The results showed that from 1000 kg dry matter, the duration of biogas production from pig, chicken, and cow manures was 150, 90, and 90 days, and gas volume was 250, 150, and 70 m^3 with maximum CH_4 compositions of 76.1, 79.9, and 62.0%, respectively. Nutrient dynamics were analyzed regularly and it was found that all manures had similar nutrient dynamics but cow manure BLR had a lower N content. Most of the N in all the BRs was in NH_4^+ form. NH_4^+ increased in all the BLRs while NO_3^- decreased after the hydrolysis phase due to the absence of O_2. All other nutrients increased in the BLRs but decreased in the BSRs due to the digestion and dissolution into the BLRs. Available P was relatively low in all the BLRs. It could be concluded that the Chinese fixed dome biogas digester could be successfully applied in Thailand's environmental conditions. Among the 3 manures (pig, chicken, and cow), pig manure was the best material for biogas generation.

Keywords: Anaerobic fermentation, animal manures, biogas, residue, nutrient dynamics

Introduction

Biogas technology has been developed fast in the world. It helps to generate energy from waste treatment, reduce global warming, and earn carbon credits. Biogas is used for cooking, heating, lighting, electricity generation, and even running engines of vehicles and trains in many

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European countries (Dieter and Steinhauser, 2008). Biogas household application has been developed very fast in China in recent years (17 million biogas tanks, 6.5 billion m^3 of biogas produced annually) (Li and Mae, 2002; Liu *et al*., 2009). However, the Chinese fixed dome biogas digester which has been successfully adopted in most Asian countries recently has not been adopted in Thailand yet.

The residues from the biogas digester contain all available plant nutrients. Biogas liquid residues (BLRs) contain readily available plant nutrient elements which could be applied to crops. Most organic matter was digested by the bacteria and available plant nutrients were dissolved in the BLRs. Biogas solid residues (BSRs) are the organic matter left that could not be digested during the biogas generation. They could still be digested by the combination of aerobic and anaerobic bacteria when applied to the field, and they also can be used as organic fertilizers for crop production.

Understanding the amount of gas generated and quality of organic fertilizer (the plant nutrient elements content in BRs) could help the organic grower to choose suitable animal manure in the organic agricultural system. Knowing the nutrient dynamics also could help with managing when and how to apply the BRs as organic fertilizer.

The objectives of this study were to compare biogas generated from 3 different kinds of animal manures in the Chinese fixed dome digesters and to determine the plant nutrient dynamics of both the liquid and solid residues.

Materials and Methods

One thousand kg (dry weight) of fresh animal manures (pig, chicken, and cow) were digested in Chinese fixed dome biogas digesters (10 m^3) built in the Suranaree University of Technology (SUT) organic farm. The digesters were filled up with 6 m^3 of water. Gas generation was recorded daily with a gas meter. Biogas samples were analyzed for gas compositions by gas chromatography (GC-14) every 5 days. The temperature of the air, soil, inlet and outlet of the tank, pH, and electrical conductivity (EC) of the digestion solution were measured daily.

BLR and BSR samples in the digesters were taken from the inlet after half an hour of solution mixture using a pump in the digesters every 5 days for chemical analysis. The BLR samples were filtered and the BSRs were oven-dried at 70°C for 2-3 days until they were dry before nutrient analysis. Both the BLRs and BSRs were analyzed for organic matter (OM) and plant nutrients (total N, inorganic N, P, K, Ca, and Mg). OM in both the BLRs and BSRs was analyzed by Walkley-Black acid digestion (Jackson, 1960). N was analyzed by wet digestion (H_2SO_4 + mixed catalyst digestion) in the Kjeldahl method (Soil and Plant Analysis Council, 2000). P and other nutrient elements were analyzed in the filtrated solution. P was analyzed by spectrophotometer with Baton's reagent. K and Ca were analyzed by flame spectrophotometer. Mg was analyzed by Atomic Absorption Spectrophotometer (AAS).

Results and Discussion

Biogas Generation

Duration and Amount of Biogas Generation

Unlike the aerobic digestion, the temperature of the fermented solution was not directly affected by air temperature since the digesters were underground. It was constant (30 ± 2°C) throughout the fermentation period.

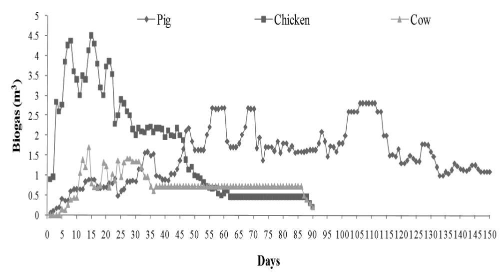

Figure 1. The daily gas generated from the anaerobic fermentation of pig, chicken, and cow manures in 150 days

Figure 1 showed the daily gas generation from the pig, chicken, and cow manures in 150 days. The chicken manure generated gas on the first day and a large amount of gas was produced within 25 days, but it decreased after 25 days to less than 1 m^3 within 50 days and could not produce significant amount of gas after 90 days. Due to the digestibility of the chicken manure during hydrolysis phase, gas generated rapid, but amount of CO_2 was higher than CH_4. The gas generation rapidly dropped from about 4.5 m^3 at 8^{th} day of fermentation to 3 m^3 at 11^{th} day. This might be due to the low pH, high EC, and high NH_4^+ content in the hydrolysis phase. Then along with the increase in pH, the gas generation grew up again to nearly 3.5 m^3 at 13^{th} day. The pig manure had a tendency to produce a stable gas amount; the gas generation increased to more than 1 m^3 after 30 days, and it was able to generate gas until 150 days (60 days longer than the chicken and cow manures). The cow manure could not generate gas for the first 5 days; gas increased after 10 days, but after 35 days the gas generation was relatively low and it could not produce a significant amount of gas after 90 days. The same gas generation tendency was also found by Chen *et al*. (2009) and Zeng *et al.* (2009). In their experiments, chicken and cow manures showed similar tendencies in that they generated more gas within 30 days, but decreased and were stable afterwards. Pig manure generated a small amount of gas within 30 days, but increased afterwards, and then stably generated gas until 150 days.

The total amount of biogas generated in 50 and 90 days showed that the chicken manure had the highest amount of gas (132 m^3 and 153 m^3) followed by the pig (50 m^3 and 125 m^3) and cow manure (40 m^3 and 70 m^3) (Table 1). However, the chicken and cow manures could not produce biogas longer than 90 days. The reasons for the short duration of gas generation in the chicken manure might be due to the high EC level and NH_4^+ in the chicken BLR which could prohibit the microbial activities for biogas generation. Starkenburg (1997) found that biogas generation was inhibited when NH_4^+ reached 1700 mg/L. In this study, the concentration of NH_4^+ was 2465 mg/L; therefore, the chicken manure might need more water to dilute the NH_4^+ and reduce the high EC. The low gas generation in the cow manure might be caused by the high C/N ratio and low N content which could not provide enough nutrients for anaerobic bacteria to digest the leftover organic C (lignin, fibers, and cellulose). On the other hand, the pig manure could continuously and significantly produce biogas until 150 days which might be due to its suitable C/N ratio and digestibility.

Chen *et al*. (2009) had studied biogas generation by fermenting pig, chicken, and cow manure at 35°C, 25°C, and room temperature for 60 days. They reported that predigested manure could generate gas earlier. Gas from pig manure reached peaks on the 6^{th}, 10^{th}, and 21^{st} days at 35°C, 25°C, and room temperature, respectively while chicken manure reached peaks on the 6^{th}, 8^{th}, and 21^{st} days and cow manure reached peaks on the 7^{th}, 7^{th}, and 20^{th} days at the above temperatures. Shi *et al*. (2010) fermented 100 g of dry pig, chicken, and cow manures in 1000 ml glass digesters for 20 days. They found that the biogas generated amounted to 1964, 1278, and 2649 ml in pig, chicken, and cow manures, respectively (equivalent to 19.6, 12.8, and 26.5 m^3 per 1000 kg). Their results were different from the results of this study which might be attributed to the quality of the manures. The

Table 1. Biogas generated, generation duration, and dry matter changed from the anaerobic fermentation of pig, chicken, and cow manures in the Chinese fixed dome digester

Manures	C/N	Initial dry matter (kg)	50 days gas generated (m^3)	90 days gas generated (m^3)	Total gas generated (m^3)	Duration (days)	Dry matter left (kg)
Pig	10:1	1000	50	125	256	150	250
Chicken	5:1	1000	132	153	153	90	450
Cow	20:1	1000	40	70	70	90	600

manures in their study were predigested, while in this study all manures were fresh. More importantly, 20 days of data records in their study could not represent the total gas generation for pig manure. Therefore, the gas generation of pig manure was less than the others in their report. Ninety days of fermentation time was adopted by early study of Tanusri and Mandal (1997) to compare the biogas generation capacity of some animal manures. According to Zeng *et al.* (2009), CH_4 emission from pig, chicken, dairy cow, and beef cow manures were 3.3, 0.26, 21, and 15 kg per head per year, respectively, but the gas generation from cow manure digestion took time. According to Weiland (2006), biogas generation could be 30 and 25 m^3 per 1000 kg of wet pig and cow manure. The differences of reported data among research studies might be due to several factors such as digester types, manure/water ratios, environmental conditions, and predigestion.

According to the literature, 1 m^3 of biogas is equivalent to 0.43-0.44 kg of liquefied petroleum gas (LPG), 0.6 Lt of diesel oil, 0.64 Lt of kerosene, and 1.25 Kw of electricity (Chen, 2009; India Development Gateway, 2010; Shri, 2010). Generally, 1 household with 3-4 people uses 0.50 kg of LPG per day which is equivalent to 1.1 m^3 of biogas (15 kg of LPG could be used for 30 days). The 10 m^3 of the Chinese fixed dome biogas digester is large enough to meet the gas needs for the daily use of each household. The amount of animal manure could be adjusted depending on the biogas consumption ability of the beneficial families.

Gas Composition in the Biogas Generated from Pig, Chicken, and Cow Manures

CH_4 increased rapidly in the first 10 days and was relatively constant after that until the end of digestion. During the peak, the chicken manure had the highest methane composition (79.9%) followed by the pig (76.1%), and cow manure (61.9%) (Figure 2). Zhang *et al.* (2005) also found high methane content in chicken manure digestion (73.1-76.4%). However, with the fermentation in the Chinese fixed dome digesters, all 3 manures produced a high enough CH_4 composition for gas utilization. The quality of biogas is higher when the CH_4 composition is more than 50%.

Other investigations reported that for the ignition point, the biogas should have a minimum CH_4 content of 20-30% (Constant *et al.*, 1989). In this experiment, the CH_4 content reached the ignition point (30%) within 10 days in all manures. The burning of the biogas could confirm the gas purity. For the pig manure, ignition could be started on the 7th day using a flame and the 14th day using a starter; for chicken manure and cow manure on the 10th day using flame and the 14th day using starter.

CO_2 for the pig and chicken manure increased in the first few weeks, then decreased after the peak of the CH_4 production. The initial CO_2 composition in the cow manure was higher,

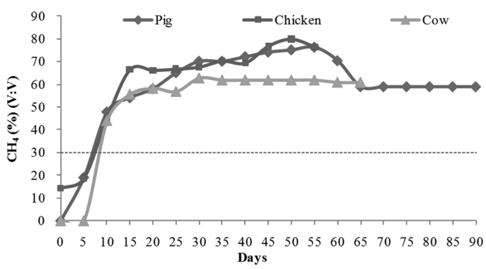

Figure 2. CH_4 composition in the biogas generated from the anaerobic fermentation of pig, chicken, and cow manurs

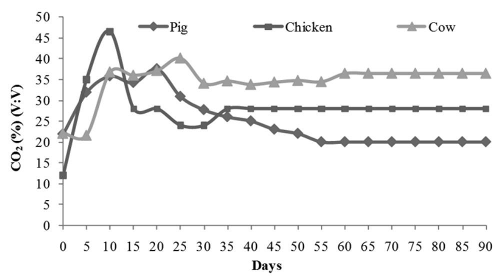

Figure 3. CO_2 composition in the biogas generated from the anaerobic fermentation of pig, chicken, and cow manurs

and it decreased afterwards along with the CH_4 production, and then maintained a constant level (Figure 3). $N_2 + O_2$ were high at the beginning, but then were emitted with the CH_4 from the digesters, and consequently decreased to a relatively low level (around 2%) along with the CH_4 production process.

Plant Nutrient Dynamics

Nutrient analysis indicated that the nutrients had dynamics in both the BLRs and BSRs. All nutrients had the tendency to increase in the BLRs and decrease in the BSRs.

Plant Nutrient Dynamics in Biogas Liquid Residue (BLRs)

Acidity (pH) and Electrical Conductivity (EC)

The pH dynamic confirmed the theory of hydrolysis and the acetogenesis/acidification stages. In all the manures, the pH dropped on the 5th day, and constantly increased after the 10th day (Figure 4). Most studies have confirmed the pH dynamic trend in many kinds of manures. Chen *et al.* (2009) found that pH decreased from 7.41 to 6.45, 6.91 to 6.32, and 7.21 to 6.66 in 8 days at room temperature for pig, chicken, and cow manures, respectively. Okoroigwe *et al.* (2010) also found the pH decreased to 6.0 at the beginning, and increased after 7 days in the experiment of dog waste treatment.

In all the manures, EC was relatively low initially and increased during the digestion. The chicken BLR had very high salinity with the highest EC (25.8 dS/m) at the end of digestion (Figure 5). Few people have reported the EC dynamics, but it was an important indicator of salinity and nutrient concentration. In this study the EC values were closely related to the nutrient contents in the BLRs.

Organic Matter and Nitrogen (N)

Organic matter was the major digested material and was broken down by the anaerobic bacteria. Small particles of organic matter dissolved into the BLRs (Figure 6). It increased and reached the highest amount between 30-35 days in all manures, then it continued to be digested and decreased in the BLRs afterwards. The BLRs of all manures became clear when the digestion was complete. It also could be observed with the turbidity from the BLRs.

Total N increased very fast in the chicken BLR after the hydrolysis phase (from 140 to 3690 mg/L), moderately increased in the pig manure (from 230 to 1660 mg/L), while it slowly increased and was very much less in the cow BLR (from 60 to 300 mg/L) (Figure 7). Gupta (1991) mentioned that total N in pig manure BLR could reach 1.6% if the BLR is digested by mixing it with various dry organic materials such as dry leaves, straw, etc.

NH_4^+ was the major form of inorganic N in the BLRs; it increased from 171 to 580 mg/L, 62 to 2465 mg/L, and 31 to 160 mg/L in the pig, chicken, and cow BLRs, respectively. NH_4^+ in

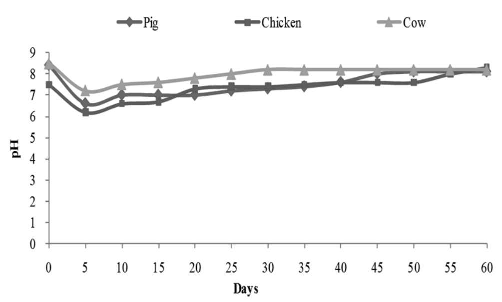

Figure 4. pH in BLRs digested from the anearobic fermentation of pig, chicken, and cow manures

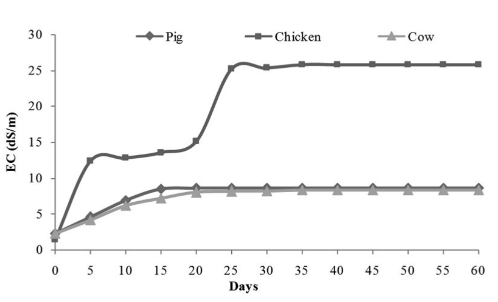

Figure 5. EC in BLRs digested from the anaerobic fermention of pig, chicken, and cow manures

the chicken BLR was 15 times higher than that in the cow BLR, and 4 times higher than in the pig BLR (Figure 8). Chen et al. (2009) reported the same dynamic trend of NH_4^+ in the digested BLRs since the organic N in the manure was digested and dissolved in the BLRs. Only Shi et al. (2010) reported that NH_4^+ decreased in the first 5 days. Starkenburg (1997) found that gas generation was inhibited when NH_4^+ reached 1700 mg/L. Feng and Fang (1989) also found gas generation inhibition when NH_4^+ was 1500-3000 mg/L due to the toxicity of NH_4^+ to the anaerobic bacteria. In this study, the high amount of NH_4^+ in the chicken BLR also inhibited the gas generation; therefore, additional water might be needed for the digestion of chicken manure.

NO_3^- in all the manure BLRs increased on the 10th day during the hydrolysis and acetogenesis stage, and then decreased and was constant after that due to the anaerobic conditions. It was 62, 93, and 31 mg/L in the pig, chicken, and cow BLRs, respectively (Figure 9).

Available Phosphorus (P) and Potassium (K)

P increased from 70 to 244, 10 to 146, and 34 to 105 mg/L, K from 250 to 1800, 320 to 4130, and 550 to 2520 mg/L in the pig, chicken, and cow BLRs, respectively (Figures 10-11). P was very low in the BLRs since it was very active in this pH condition (pH > 7 for all BLRs). It probably reacted with the high concentrated Ca and precipitated to the BSRs afterwards. The nutrients values in the pig BLR were in the same range as Xu *et al*. (2005) reported with totals of N 300-800 mg/L, P 200-300 mg/L, and K 490-700 mg/L. Gupta (1991) reported that total P in pig manure BLR could reach 1.6%, and K could reach 1.0% if the BLR is digested by mixing it with various dry organic materials such as dry leaves, straw, etc.

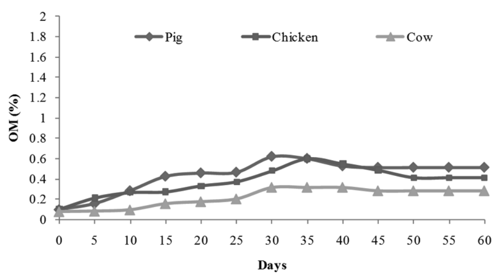

Figure 6. OM in BLRs digested from the anaerobic fermentation of pig, chicken, and cow manures

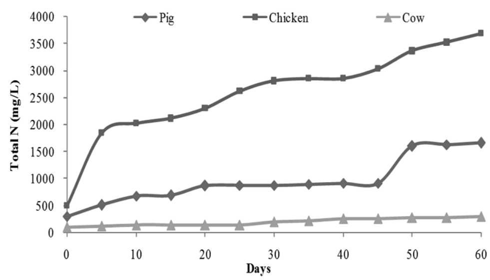

Figure 7. Total N in BLRs digested from the anaerobic fermentation of pig, chicken, and cow manures

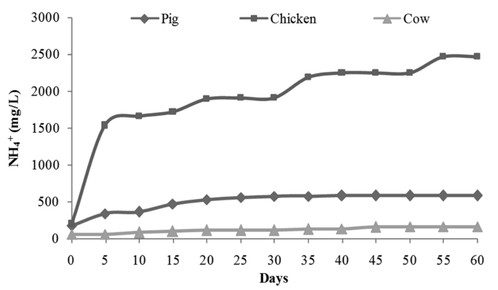

Figure 8. NH_4^+ in BLRs digested from the anaerobic fermentation of pig, chicken, and cow manures

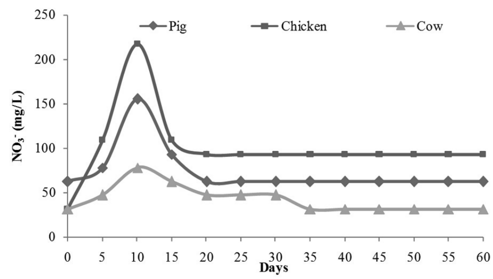

Figure 9. NO_3^- in BLRs digested from the anaerobic fermentation of pig, chicken, and cow manures

Nutrient Dynamics in Biogas Solid Residue (BSRs)

In the BSRs, all nutrients decreased due to the digestion, degradation, and dissolution into the BLRs solution.

Organic Matter and Nitrogen (N)

Organic matter was the major material digested by anaerobic bacteria; it decreased from 55.02% to 44.60%, 43.26% to 31.73%, and 49.63% to 30.35% in the pig, chicken, and cow BSRs, respectively (Figure 12).

Total N decreased from 3.2 to 1.7%, 6.3 to 2.2%, and 3.0 to 1.2% in the pig, chicken, and cow sludge, respectively (Figure 13). NH_4^+ increased during the first 30 days, but decreased after that since it dissolved into the liquid; consequently, it was 724 mg/L, 517 mg/L, and 517 mg/L in the pig, chicken, and cow BSRs, respectively (Figure 14). NO_3^- also increased during the first 10 days, but decreased after that due to the absence of O_2. It was 207, 310, and 310 mg/L in the pig, chicken, and cow BSRs, respectively (Figure 15).

Total Phosphorus (P) and Potassium (K)

P decreased from 3.94 to 1.81%, 2.76 to 0.84%, and 0.86 to 0.37%; K from 1.7 to 0.7%, 9.4 to 3.2%, and 1.5 to 0.8% in the pig, chicken, and cow BSRs, respectively (Figures 16-17). Results of the pig BSRs were also in the same range as Xu *et al.* (2005) mentioned (OM 36.0-49.9%, N 0.78-1.61%, P 0.4-0.6%, K 0.61-1.3%). P in this study was higher than their results.

Overall Nutrients Dynamics in BLRs and BSRs

Most nutrients in the initial raw manures which were in the organic form were digested and converted to the inorganic form. They were dissolved into BLRs during the fermentation process. Take N as an example and based on the calculation of nutrient balance: there was initial

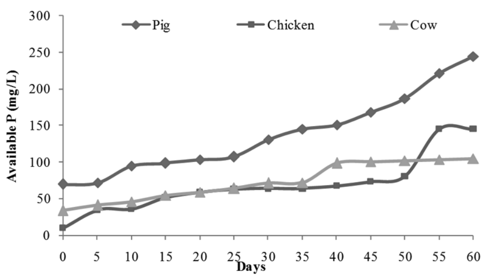

Figure 10. Available P in BLRs digested from the anaerobic fermentation of pig, chicken, and cow manures

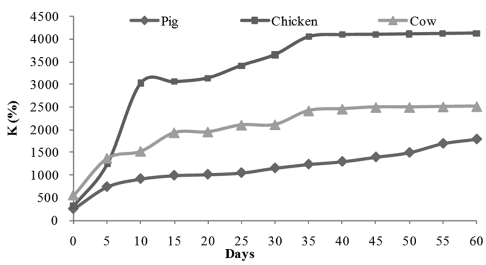

Figure 11. K in BLRs digested from the anaerobic fermentation of pig, chicken, and cow manures

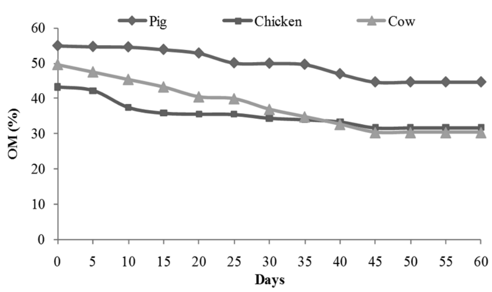

Figure 12. OM in BSRs digested from the anaerobic fermentation of pig, chicken, and cow manures

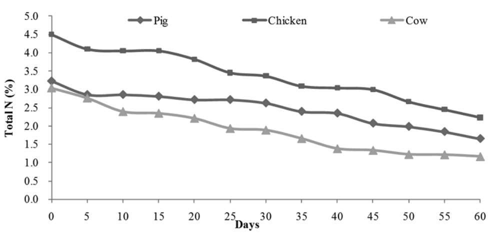

Figure 13. Total N in BSRs digested from the anaerobic fermentation of pig, chicken, and cow manures

Table 2. Nutrient concentration in the initial manures before anaerobic fermentation, and in BLRs and BSRs at the end of anaerobic fermentation of pig, chicken and cow manures

Residues	Total N (%)	NH_4^+ (mg/L)	NO_3^- (mg/L)	P (%)	K (%)	Ca (%)	Mg (%)
Manure							
Pig	3.230	517	310	3.940	1.700	1.130	0.285
Chicken	4.500	414	207	2.760	5.200	3.280	0.675
Cow	3.040	414	310	0.860	1.500	0.630	0.340
BLR							
Pig	0.166	580	62	0.024	0.180	0.022	0.017
Chicken	0.369	2465	93	0.015	0.413	0.030	0.015
Cow	0.030	160	31	0.011	0.252	0.050	0.019
BSR							
Pig	1.654	724	207	1.810	0.693	0.480	0.230
Chicken	2.235	517	310	0.840	3.233	2.150	0.280
Cow	1.168	517	310	0.370	0.975	0.310	0.240

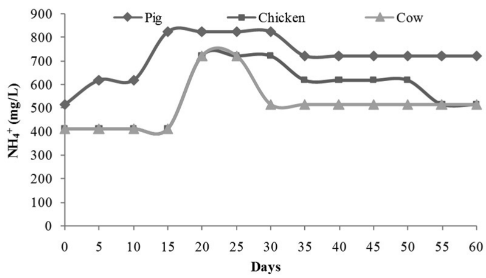

Figure 14. NH_4^+ **in BSRs digested from the anaerobic fermentation of pig, chicken, and cow manures**

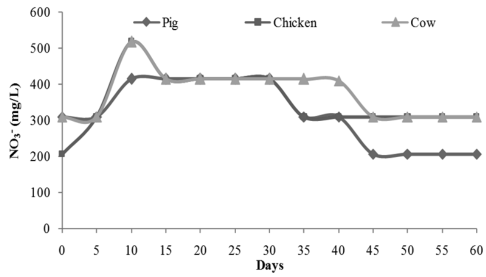

Figure 15. NO_3^- **in BSRs digested from the anaerobic fermentation of pig, chicken, and cow manures**

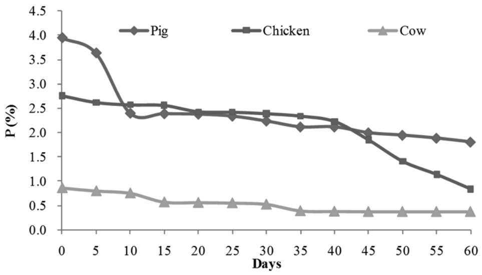

Figure 16. P in BSRs digested from the anaerobic fermentation of pig, chicken, and cow manures

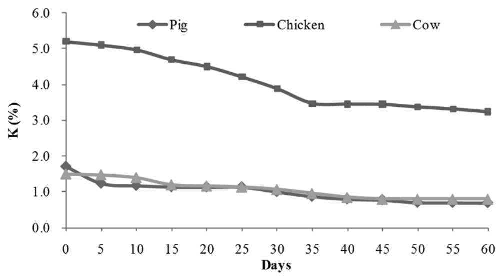

Figure 17. K in BSRs digested from the anaerobic fermentation of pig, chicken, and cow manures

N of 32, 45, and 30 kg in the pig, chicken, and cow manures (3.2, 4.5, and 3.0% in 1000 kg dry matter) (Table 2). After the fermentation was completed, there were about 27, 35, and 23 kg of N in the BLRs. Among them, 17, 30, and 3 kg of N were in the inorganic form and were dissolved, and 10, 5, and 20 kg of N were in the organic form suspended in the BLRs. There were about 5, 10, and 7 kg of N left in the pig, chicken, and cow BSRs, respectively, and most of them were in the organic form. In principle, the nutrient elements, especially P, K, Ca, and Mg content in the BSRs should be higher than the data presented in the study, nutrients content in BLRs and BSRs should be match with that in the initial manures. However, the nutrients in the BLRs were analysed as the available form (inorganic forms). The BLRs were filtrated. The P, K, Ca and Mg were analysed directly in the filtrated solution. There would be some nutrients left in the organic form (in the organic molecules and in the microbial cells) suspended in the BLRs and in the filtrated solid material. Therefore, the amount of nutrients in both residues was smaller than those in the initial manures (Figure 2). This experiment showed there was low N loss to the atmosphere. The values of BRs as fertilizer depend on animal feed contents, the amount of the residues, their nutrients concentration and balance, and the availability of the nutrients. This might be confirmed by further field crops' studies.

Conclusions

The Chinese fixed dome digester was successfully applied in the tropical conditions of Northeast Thailand for manure treatment and organic fertilizer production. Comparing the fixed dome digester with the plastic dome digester which is generally used in modern biogas production, the advantage of plastic dome is its cheaper price. The disadvantages are easily damaged by ultraviolet and animal and low gas generation efficiency. The only disadvantage for Chinese fix dome digester is its high cost, but it can last much longer. The gas generation efficiency is very high and it is very safe for operation.

It was found that pig manure had the longest biogas generation duration and produced the highest amount of gas. Therefore, it could be concluded that pig manure was the best material for biogas generation in the Chinese fixead dome digesters.

BLRs digested from the pig and chicken manures contained high amounts of available N. During the digestion, NH_4^+ increased, while NO_3^- decreased after the hydrolysis phase; most N was in NH_4^+ form. P, K, Ca, Mg, and other micronutrients also increased in the BLRs. All nutrients decreased in the BSRs due to the digestion, degradation, and dissolution into the liquid solution.

P was relatively low in all the BLRs. The balance of P in the application of liquid as an organic fertilizer should be considered. However, the biogas residues from the pig and chicken manures had relatively more balanced nutrients than the cow manure which had a very low N content. Both of them would be good sources of organic fertilizers for crop production.

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