International Journal of Engineering & Technology, 7 (4.38) (2018) 1380-1383

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Methane Production in Batch Anaerobic Digestion of Livestock Manures with Different Substrate Concentrations

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Abstract

This research aimed to evaluate the biochemical methane potential (BMP) of three livestock manures including swine manure (SM), chicken manure (CM), and dairy manure (DM) under the same conditions in batch anaerobic digestion (AD) including inoculum to substrate ratio, temperature, digestion time, concentration of total solids in the system, and reactor size. The experiments were performed on individual manure, 2-manure mixture, and 3-manure mixture. For the individual manure experiments, BMP of SM, CM, and DM were 326.97, 306.60, and 105.30 mL/gVSadded; and volatile solids (VS) removal values were 66.31, 62.47, and 52.02%, respectively. In the 2-manure mixture; SM: DM, SM: CM, and CM: DM ratios of 90:10%TS, the BMP were 278.15, 264.47, and 252.80 mL/gVSadded, respectively. In the 3-manure mixture, the maximum BMP was 200.82 mL/gVSadded under the SM: CM: DM combination of 74:20:6%TS. The conditions of the 3 experiments were similar: the total solids concentration at 20% of working volume and the temperature of 37°C. It could be concluded that each manure i.e., SM, CM, and DM could be used as raw material for methane production by anaerobic digestion. SM generated the highest BMP, followed by CM and DM, respectively. However, DM should not be used as raw material alone, except combining it with SM or CM for better methane production.

Keywords: *Anaerobic digestion, Biochemical methane potential, Livestock manure, Mixture design*

1. Introduction

Livestock has continually grown in order to support the consumption worldwide while the wastes, its manure, also increased. If the manure could not be properly disposed of, it may induce air and water pollution which brings further impact to human health (Abouelenien al et, 2014). In addition, Food and Agricultural Organization (FAO) reports that livestock accounts for as high as 40% of greenhouse gas emission among other agricultural activities. This raises the awareness for treatment/disposal; which in this regard livestock manure has been used as raw material for methane production through anaerobic digestion.

Anaerobic digestion (AD) is one of the processes that generate methane and is considered an environmental friendly process. It can minimize air and water pollution caused by livestock manure. In the meantime, AD is potential for producing methane which can be reused as alternative energy to mitigate energy shortage problem. AD has been used for the livestock sector since the past century (Kafle, G.K and Chen, L, 2016). Improvement of AD has been extensively researched since the potential methane production depends on manure components, which are different owing to the different feeds and raising methods as well as medicine and manure-collecting procedures (Wang et al., 2014; Garcia-Launay et al., 2014). In addition, the manures are contaminated with feathers, floor-laying materials, food residues, etc. These matters have affected the manure components that in turn brought impacts on anaerobic digestion and methane production (Garcia-Launay et al., 2014). Besides the manure components, the concentration of manure, source of inoculum and substrate used in AD, reactor size, temperature are factors influencing methane production (Browne and Murphy, 2013). The same substrate can give different BMP as it is dependent on conditions used for anaerobic digestion. Although there are various research studies on methane production from different kinds of manure (Kafle, G.K and Chen, L, 2016), they have not mixed any two or three manures together in order to find the maximum methane production capacity. This research would be useful when there is requirement for managing many types of manure from a large-scale farm or a community where many villagers raise various kinds of livestock.

Therefore, the aim of this research is to study the biochemical methane potential of SM, CM, and DM through anaerobic digestion by application of DOE (Mixture Design) through the Minitab program.

2. Materials and methods

2.1 Manures and inoculum

Fresh CM was taken from a chicken farm located in Khon Kaen Province, Thailand. Fresh DM and fresh SM were taken from the dairy farm and swine farm of the Faculty of Agriculture, Khon Kaen University, Thailand. Inoculum was taken from a biogas lagoon located in Khon Kaen Province, Thailand. The characteristics of the three livestock manures and inoculum are presented in Table 1.

2.2 Experimental design and set-up

Batch AD was performed by using 120 mL glass bottles, working volume of 80 mL, total solids concentration in the system of 1-20%, inoculum to substrate of 30:70, and temperature of 37°C. After adding inoculum and manure into the bottle, water was filled to

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increase the volume to 80 mL. The free space in the bottle was purged with nitrogen 99.999% for 2 minutes to expel oxygen. Measurement of biogas and methane production was taken everyday for 35 days.

2.3 Biogas and methane measurement and calculation

Biogas production per day of each AD bottle was determined by displacement of water. Methane concentration (CH_4, %) in biogas was analyzed by gas chromatograph (GC) (2014 Shimashu). For this study, the formula of Buswell (Chae at al., 2008b) was applied for calculation of the theoretical methane potential(TMP). TMP of three livestock manures from elemental composition of substrates as follows:

$$C_nH_aO_bN_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{8}\right) H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right) CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3C}{8}\right) CO_2 + cNH_3 \quad (1)$$

$$TMP\left(\frac{mL\ CH_4}{g_{VS}}\right) = \frac{22.4 \times 1000 \times \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)}{12n+a+16b+14c} \quad (2)$$

2.4 Analysis methods

Total solids (TS), volatile solids (VS), total chemical oxygen demand (TCOD), total Kjeldahl nitrogen (TKN) and total ammonia nitrogen (TAN), alkalinity and volatile fatty acids (VFA) were analyzed based on Standard Methods (APHA, 2005). Carbon (C), Nitrogen (N), Hydrogen (H) and Oxygen (O) were analyzed using elemental analyzer (CHNS628, 628S Truspec Micro O).

Table1. Characteristics of three different manures and inoculum

Characteristics	Units	Manures			Inoculum
		SM	CM	DM	
Total solids (TS)	%	66.99	79.28	20.52	2.86
Volatile solids (VS)	%	24.70	11.15	35.26	1.09
pH	-	7.08	7.47	8.47	8.22
TCOD	mg/l	11,076.80	15,032.80	7,120.80	19,636.36
TKN	mg/l	1,302	1,526	1,134	5,782
TAN	mg/l	654.50	724.50	563.50	2,751.00
Alkalinity	mg/l as $CaCO_3$	3,584	3,810	4,260	3,980
VFA	mg/l as $CaCO_3$	750.00	725.00	737.50	812.50
Carbon (C)	%TS	40.99	32.93	21.25	-
Nitrogen (N)	%TS	4.15	2.47	1.41	-
Hydrogen (H)	%TS	6.24	4.89	3.60	-
Oxygen (O)	%TS	36.93	43.55	19.33	-
C/N ratio	-	9.88	13.33	15.07	-

SM: swine manure, CM: chicken manure, DM: dairy manure

Statistical analysis
Analysis of methane production was conducted by using MINITAP for experimental design of each experimental set in order to find factors affecting methane production and to obtain the BMP predicting equation. The statistical analysis was considered at confidence level of 95% and p-value at 0.05.

3. 3. Results and discussion

3.1 Biogas and methane production of individual manure

As shown in Figure 1, biogas and methane yield higher volume at 20% TS of working volume than at the 1% TS of working volume for all of the three livestock manures. In the anaerobic digestion, digestion time of 35 days and 37°C, SM produced maximum biogas and methane production of 591.94 mL/gVSadded and 326.97 mL CH4/gVSadded; followed by CM with biogas production of 520.80 mL/gVSadded and methane production of 306.60 mL CH4/gVSadded. The minimum production was from DM, 212.04 mL/gVSadded and 105.30 mL CH4/gVSadded, for biogas and methane, respectively. In addition, the VS removal values were 62.47, 66.31 and 52.02% for SM, CM, and DM, respectively.
In comparison with the theoretical methane potential (TMP), TMP presents methane production by SM, CM, and DM at 456.50, 330.41, and 489.18 mL/gVSadded, respectively, which were higher than the BMP obtained from the experiments, indicating TMP was higher than the actual production. TMP was calculated from the substrates which were both biodegradable and non-biodegradable organic matters, whereas BMP was generated from the only biodegradable organic matter.

3.2 Methane production from mixture of manures

The result from the experiment performed on the 3-manure mixture for methane gas production based on the optimum conditions as follows: SM:CM:DM at 74:20:6%TS, the TS concentration in system of 20% of working volume, temperature of 37°C shows that this mixture could produce methane gas at 200.82 mL/gVSadded. For the 2-manure mixture for methane production, the ratio of SM: CM, SM: DM and CM: DM was 90:10% TS at the inoculum to substrate of 30:70, 20%TS concentration in the system, and temperature of 37°C. Methane production were 264.47, 278.15, and 252.80 mL/gVSadded, respectively. However, the AD of individual manure could produce higher biogas and methane than the combination of manure except in the case of DM because DM contains fiber (carbon component) and low nitrogen which means high C/N, in manure component not suitable for anaerobic digestion. In addition, lignin content of grass fiber is rather difficult to digest as previously reported that lignin content in DM, which was 9.8%TS, a higher value than CM and SM, which were 5.07%TS and 3.81%TS, respectively (Kafle, G.K and Chen, L, 2016).

3.3 Statistical analysis

3.3.1 Influential factors to methane production

In the statistical analysis, variance and linear regression were employed in order to study the influential factors affecting methane production by designating the significant level at 0.05. The factors including combination of CM: DM ($p = 0.213$), SM: DM ($p = 0.613$), DM and TS concentration in the system ($p = 0.272$), CM: DM and TS concentration in the system ($p = 0.167$), and SM: DM and TS concentration in system ($p = 0.302$) did not have any significant effect on methane production at the confident level of 95%. The factors having significant effect on methane production were CM: SM ($p = 0.041$), CM and TS concentration in system ($p = 0.001$), SM and TS concentration in system ($p = 0.003$), and CM: SM and TS concen- tration in system ($p = 0.050$).

3.3.2 Assessment the model validity

Figure 2 presents residual plots for methane production in order to assess the model validity. If the model is valid, the residuals will not have any pattern. The good model should demonstrate the following 4 aspects: 1) normal distribution, 2) average residual of 0, 3) constant distribution, and 4) independent residuals. For normal probability plot, the experiments are valid for the DOE (Mixture Desingn) application because the points on normal probability plot narrowly scattered around a straight line shows that the residuals follow a normal distribution and the derived methane production model will not be improved by a change in the transformation.

The histogram is an upside-down symmetrical bell and residuals value are at 0.000 which has high frequency indicating normal distribution. The versus fits presents normal distribution of data for both plus and minus sides showing that analyzed factors are independent and the model does not have multicollinearity. The plot of the residuals versus the order run for methane production, there present to be no evident trends or groupings visible. Residuals distribution does not have an actual pattern, indicating residuals not depending on the order of experiments. Based on the residual plots for methane production analysis, the experimental results and model are reliable and adequate to predict the methane production.

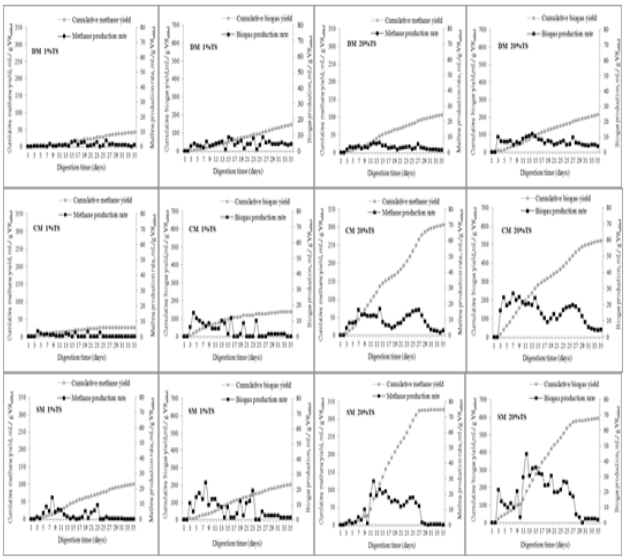


Figure 1. Biogas and methane production of manures at different substrate concentrations

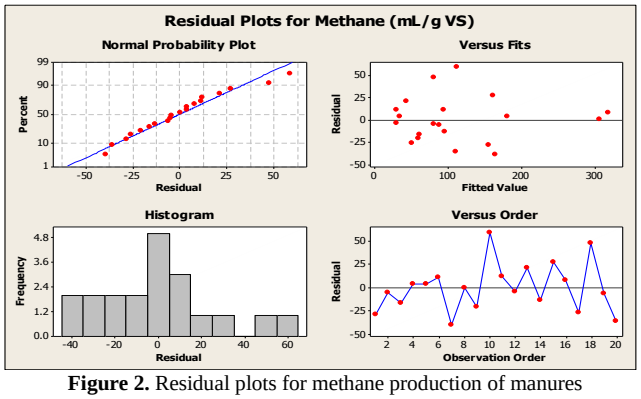


Figure 2. Residual plots for methane production of manures

3.3.3. Development of equation for BMP

Based on the experiment in accordance with the DOE (Mixture Design), the experimental results could be analyzed to determine factors affecting methane gas production at 95% of confidence level. Then the equation was developed to predict methane production as shown in Table 2. The decision coefficient (R2) was 91.0% and the adjusted decision coefficient (adj R2) was 78.83%, which was close to R2. Hu (1999) reported that the equation obtained from the regression coefficient should have R2 of at least 0.75; the value higher than 0.90 means reliable. R2 has value of 0-1; R2 equal to 0 means no relation between independent and dependent variables. R2 equal to 1 means complete relation between independent and dependent variables. In addition, adj R2 with value higher than 0.64 means the equation pattern is suitable and the effects of factors were consistent with methane production. Table 2 presents factors including CM: DM ($p = 0.213$), SM: DM ($p = 0.613$), DM and TS concentration in the system ($p = 0.272$), CM: DM and TS concentration in the system ($p = 0.167$), SM: DM and TS concentration in system ($p = 0.302$) did not have any significant effect on methane production at 95% of confidence leval. Thus these factors were deleted from the developed equation. The equation for methane production (Y) in unit of mL/gVSadded shows in Eq. 3; CM and SM are %TS of chicken manure and swine manure. The equation would be accurate for prediction under the temperature 37°C and retention time of 35 days. DM had no any significant effect on methane production since it did not include in the equation 3.

$$Y = -303.2(CM)(SM) + 138.2(CM)(TS) + 111.3(SM)(TS) - 288.0(CM)(SM)(TS) \quad (3)$$

Table 2. Data analysis for developing equation to predict methane gas production

Terms	Coef	SE Coef	T	p-value
CM	168.1	27.06	*	*
SM	207.7	27.06	*	*
DM	62.0	27.06	*	*
CM (%TS) * SM (%TS)	-303.2	124.70	-2.43	0.041
CM (%TS) * DM (%TS)	-168.8	124.70	-1.35	0.213
SM (%TS) * DM (%TS)	-65.7	124.70	-0.53	0.613
CM (%TS) * TS (%)	138.2	27.06	5.11	0.001
SM (%TS) * TS (%)	111.3	27.06	4.11	0.003
DM (%TS) * TS (%)	31.9	27.06	1.18	0.272
CM (%TS) * SM (%TS) * TS (%)	-288.0	124.70	-2.31	0.050
CM (%TS) * DM (%TS) * TS (%)	-189.5	124.70	-1.52	0.167
SM (%TS) * DM (%TS) * TS (%)	-137.7	124.70	-1.10	0.302
S = 39.6743	PRESS = 178877			
R^2 = 91.09%	adj R^2 = 78.83%			

4. Conclusion

Biochemical methane potential (BMP) generated from three livestock manures including swine manure (SM), chicken manure (CM), and dairy manure (DM) was evaluated under the same conditions in batch anaerobic digestion (AD): inoculum to substrate ratio was 30:70, temperature of 37°C, digestion time for 35 days, total solids concentration in the system of 20% of working volume and reactor size of 120 mL. It was found that individual of SM and CM could generate higher methane gas than the manure mixture. Maximum BMP generated by SM was 326.97 mL/gVSadded and VS removal value was 62.47%, followed by CM and DM, 306.60, and 105.30 mL/gVSadded, respectively. For the 2-manures mixture of SM: CM, SM: DM and CM: DM at 90:10%TS, BMP were 264.47, 278.15, and 252.80 mL/gVSadded, respectively. Regarding the mixture of 3-manures mixture: SM: CM: CM 74:20:6 %TS, BMP was 200.82 mL/gVSadded.

In addition, the statistical analysis performed at the confidence level of 95% shows that the experimental result and mixture model are reliable with the decision coefficient (R2) of 91.09% and the adjusted decision coefficient (adj R2) of 78.83% at p-value less than 0.05.

Acknowledgement

This research was financially supported by Farm Engineering and Automatic Control Technology Research Group, Faculty of Engineering, Khon Kaen University, Thailand.

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