Modelling Bio-Methane Production In Ruminant Livestock Farming

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Abstract - Methane from ruminants is a principal contributor to greenhouse gases. Consequently, sustainable mitigation strategies for enteric emission are in high demand. This study is aimed at modeling bio-methane production process in the bio-digesters using a combination of correspondent feed additives for methane emissions reduction. In this study, each of the experimental animals were exposed to 5 different feeding trials and theirding were collected after the feeding trials. A set up of 5 units of 50litres biogas digesters to cater for the digestion of 4 animal waste substrate and 1 control sample was used as experimental facility for biogas generation and collection. Biogas yield was measured at the end of 14 days. Bio-gas samples collected from each bio reactor was analyzed using the 263-50 Gas chromatograph and the result was displayed by the aid of D2500 Gas Chromatomo-Integrator. A first order linear model was developed using XL STAT Software, 2021 premium version for the prediction of methane emission from different animal feed additives. Comparison was carried out between predicted and observed bio-methane emission values for the different feed additives. Performance of the model was evaluated using model evaluation metrics in order to determine the consistency of the predicted values with observed values. Specific analyses were performed to validate the model outputs against measured data. Predicted values were paired against measured values using mean square error (MSE), root mean square error (RMSE) and mean absolute percentage error (MAPE). In addition, a measure of goodness of fit known as coefficient of determination ($R^2$) was used to determine the closeness of the predicted values to the measured values. The results indicate that all the developed first order linear models adequately fit the measured data set with goodness of fits greater than 95% ($R^2 > 0.95$). Test Unit 1 model explained 99.11% of the measured values; Test Unit 2 model explained 98.96% of the measured values; Test Unit 3 model explained 98.19% of the measured values; Test Unit 4 model explained 97.73% of the measured values; while Test Unit 5 model explained 97.93% of the measured values. Modeling error metrics shows that Test Unit 1 has that lowest mean prediction errors; this is followed by Test Units 2 and 5. This suggests that the first order linear model accurately predicts that naturally occurring of methane emission in the control group; while the feed additives in the other Test Units are variables that influence the potential of the first order linear models to accurately predict methane emission in the substrate degradation or utilization. This study shows that the derived first order linear model significantly predicted methane emission in substrate degradation and therefore can be used to forecast methane production from animal feeds. Result further revealed that all the developed first order linear models significantly predicted the methane emission with probability $p$-values < 0.05, 95% confidence interval/ level- (CI) and coefficient of determination ($R^2$) > 0.95. Therefore, mixed additives could be used as effective anti-methanogenic compounds to efficiently reduce enteric methane production.

Index Terms - Modeling Bio-methane, Nutritional Strategies, Ruminant Livestock

I. INTRODUCTION

Methane ($\text{CH}_4$) is a greenhouse gas that is less prominent but a key component of natural gas. Chemical name for methane is carbon tetra hydride or hydrogen carbide (Haynes, 2016) and other common names are methyl hydride, marsh gas and fire damp. Methane is a significant greenhouse gas due to its interaction with planetary infrared emissions. It is a Short-Lived Climate Pollutant (SLCP) with a half-life of 12 years, parts of which persist in the environment for several hundreds to thousands of years. $\text{CH}_4$ is the second most important anthropogenic GHGs in terms of global warming potential (GWP) with an estimated increase of 0.3% in 2016 to a total of 9.2 Gt CO$_2$ eq (Olivier et al., 2017). According to Climate and clean Air Coalition (2012), methane is incredibly effective at trapping the sun’s heat, making it responsible for at least a quarter of global warming. Thus, it is adverse for ambient air quality and contribute strongly to climate change.
About 70% of the CH$_4$ emissions from agriculture are attributed to enteric fermentation in ruminant livestock (Jackson et al., 2020). Current environmental impact or life-cycle assessments of beef cattle sector in USA has highlighted the need to focus on the grazing sector which has contributed 70-80% of total greenhouse gas from the US beef sector (Rotz et al., 2019). A farm gate life cycle assessment was used to quantify resource use and the annual greenhouse gas emissions for all production were analyzed to determine environmental intensities of emission from the US beef cattle sector (Rotz et al., 2019).

The current situation according to Jackson et al. (2020) is that global emissions of methane have reached the highest levels on record. Increases are being driven primarily by growth of emissions from coal mining, oil and natural gas production, cattle and sheep ranching, and landfills. Between 2000 and 2017, levels of the potent greenhouse gas barreled up toward pathways that climate models suggest that it will lead to 3-4 degrees Celsius of warming before the end of this century.

Methane is the low-hanging fruit in the effort to combat planetary warming. With global demand for livestock products continuing to grow strongly in almost all developing countries, it is imperative that the sector starts working now to achieve these reductions, to help offset the increases in overall emissions that future growth in livestock production will entail. Reversing this trend in methane emissions is now probably the most urgent challenge in the fight against global warming, even more than the ongoing need to tackle CO$_2$ emissions. Additional attention is urgently needed to quantify and reduce methane emissions.

Many studies have proved that methane can be generated from livestock manure such as cow dung, poultry litter, horse dung, swine dung, sheep and goat dung and many others. Kafle et al., 2016 investigated the production of methane from five different livestock manure (dairy manure (DM), horse manure (HM), goat manure (GM), chicken manure (CM) and swine manure (SM). Other researchers generated biogas from horse manure (Van et al., 2018); poultry manure (Nwosu et al., 2020; co-digestion of cattle manure with food waste and pig manure (Baek et al., 2020).

The management of livestock manure (LM) has become increasingly challenging because its production continues to rise, while the regulations on manure management have become increasingly stringent especially in developed countries. According to the Department of Primary Industries and Regional Development (DPIRD) (2020), improved forage quality with lower fibre and higher soluble carbohydrates can reduce methane production in livestock. A critical review of the recent progress made toward the development of nutritional additives for reducing methane production in ruminant livestock farming especially cattle has shown that sea weed, aged garlic, organic acid (orange peel), Aloe vera is a medicinal plant cultivated for various applications in medical, food and health products.

Kafrin et al., (2012) researched on Garlic as a rumen modifier for eco-friendly and economic livestock production. The results reported so far indicate that garlic and its essential oils inhibit methanogenesis significantly accompanied with a lower acetate to propionate ratio indicating a diversion of fermentation in a favorable direction. As methanogenesis is the major hydrogen sink in the rumen, its inhibition requires reducing equivalents produced during fermentation of feed. The anti-microbial compounds present in garlic appear to be selective inhibitors of methanogenesis, as there is no adverse effect on feed degradation in the rumen. Garlic and its oil adversely affect the protein degrading bacteria and deamination activity of the rumen contents. Only a few in vivo experiments have been conducted using garlic as a feed additive, and it appears to have good potential for rumen manipulation for ecofriendly (with minimum methane emission) and economic livestock production.

Singh et al. (2013) investigated the effects of dietary supplementation of Aloe-vera waste (AVW) on ruminal fermentation, methane production, nutrient utilization, and milk production performance in lactating cows. The results showed that inclusion of AVW at 20g/kg substrate decreased methane production, increased milk production, increased feed digestibility and total volatile fatty acid concentration in vitro. Aloe-vera is a medicinal plant cultivated for various applications in medical, food and health products. The study is concerned with reducing biogenic methane emission in livestock farming using nutritional strategies. Methane-reducing feed additives and supplements inhibit methanogens in the rumen, and subsequently reduce enteric methane emissions. Modeling biomethane production in ruminant livestock farming could help to achieve widespread utilization of the large body of knowledge of anaerobic process available from research studies and operational experience in small agricultural farms. Indeed, this is one of the areas where most benefits from the application of a simple model can be gained. Assumptions are taken into account, simplifications are made and the results for different feedstock may vary, and the model provides basic predictions that can aid agricultural farmer decisions. The aim of this study is to model bio-methane production process in the bio-digesters using a combination of correspondent feed additives for methane emissions reduction.

**Research Design:** Experimental research design was adopted for this study. Purposive sampling technique was used in this study because the population of livestock is heterogeneous in nature. Five white Fulani cows (aged 3 years) were selected and used for the study. To achieve a reasonable sample size, animal replicates were used for this study. The animals were exposed to 4 different feeding trials sequentially with resting intervals of 2 weeks.
This research used both primary data and secondary data. Secondary data was collected from literatures on the use of feed additives to modulate or adjust rumen fermentation in order to reduce enteric methane (EC\textsubscript{H\textsubscript{4}}) emissions, improve feed efficiency, and the quantity and quality of animal products. This was sourced from secondary sources like workshop proceedings, journals, research publications and conference monographs.

**Study Area**: Uyo, capital of Akwa-Ibom State, Nigeria, lies between latitudes 0502’ North and longitudes 07°56’ East. It has a natural day length of 12-13 hours and a total area of 362 km\textsuperscript{2} with an annual rainfall range from 78-93\% and relative humidity of 60-90\%. The annual temperature range from 28.4\degree C-34.5\degree C (Meteorological Station Department of Geography, University of Uyo). Akwa-Ibom is one of the states in Nigeria, with a population of 5.451 million people by 2016. Rearing system of livestock predominant in this area is intensive and semi-intensive system (for goat and sheep) and extensive system for cattle. The experimental research (feeding trial and manure sample collection) was carried out at the teaching and research farm unit of the Department of Animal Science University of Uyo, annex campus, Uyo, Akwa-Ibom State, Nigeria while the cross-sectional analytical research involved all ruminant livestock farmers in Uyo L.G.A. The population of the study includes all livestock at the teaching and research farm unit of the Department of Animal Science University of Uyo in Uyo Local government area.

**Nature/ Sources of Data**: This research used both primary data and secondary data. Secondary data was collected on each of the stated objectives. Literatures on the use of feed additives to modulate or adjust rumen fermentation in order to reduce enteric methane (EC\textsubscript{H\textsubscript{4}}) emissions, improve feed efficiency, and the quantity and quality of animal products was sourced from secondary sources like workshop proceedings, journals, research publications and conference monographs.

**Methods of Data Collection / Instrumentation**: Methane was measured by methanization of manure obtained from animals used for the feeding trials. This was done by measuring and comparing biomethane produced from the animal manure before and after the feeding trial. For collection of manure sample, the experiment was conducted through a period of 58days. This includes 7 days of adaptation and collection of control samples, 14 days of exposure to experimental diets or feed additives, 7 days of sample collection and 30 days of sample analysis excluding resting intervals. The animals for the trial were tagged for ease of identification. Feeding of ration with additives was made available twice a day/ad-libitum, with continued exposure for 14 days. Fresh Clean water was provided ad-libitum. Manure samples were collected after 14 days. Animals were housed in individual half-walled pen throughout the duration of this experiment.

The animals were exposed to four (4) feeding trials with suggested experimental diets or feed additives for mitigation of methanogenesis in ruminants’ livestock. Feeds that is readily available or can be easily sourced locally were used for feeding trials and they includes: Garlic powder---20g/kg, Blended Aloevera waste---20g/kg, Organic / citrus acid (Blended Orange peel)---- 20g/kg and Mixed Feed additives: Garlic + Orange peel + Coconut oil--20g/kg. This research adopted the feeding methodology used by Hilary-Udoh and Ezekiel-Udoh (2019) by supplementing feeding with common grasses such as Guinea grass (Panicum maximum), Giant star grass (Cynodonplectostachium), Elephant Grass (Pennisetum purpureum), and legume forages such as Centro (Centresmapubecens), Moringa leaves and Sweetpotatoes vines. Feed additives was added to concentrate feed consisting of 16\% crude protein and 3500kcal/kg. Six kilograms (6kg) of each grade of animal manures were collected, properly labeled and sent to the bio-digesters. 6kg of each of the dried dung was mixed simultaneously with 32 litres of water in five 50 litres biogas digesters constructed for the experiment simultaneously to give a 0.19kg/litre slurry volume of each biomass.

**Experimental Procedures**: 5 units of 50 litres biogas digesters (labelled Test unit 1 to Test unit 5) was set up to cater for the digestion of 4 animal waste substrate and 1 control sample. The bio-digesters were constructed with the following components, namely: Digestion chamber, slurry inlet and outlet, gas outlet / gas control valve, thermometer installed on top of the digester to monitor the temperature inside the digester as well as gas collecting apparatus. The Digestion chamber has an opening at the top with a removable cover where the feedstock or slurry is fed into the digester chamber. The digesters were located outdoors at an ambient temperature of 33\degree C as high temperature facilitates the emission of biogas. Digesters were implemented simultaneously under anaerobic environment, adopting the methodology by Abayomi, et.al (2019). Each of the digesters has an opening on top for loading of the substrate/feedstock/ slurry into the digester and a top cover with a plastic hose connected to it which is being held fixed with adhesive gum to prevent leakage. The digesters are designed to displace excess slurry or water through the downward displacement technique with a container provided to collect the displaced slurry. Each of the digesters is connected to the gas collecting apparatus through a plastic hose with a control valve positioned at the end of the hose to keep the digester air tight as much as possible when closed to create the desired anaerobic environment. Each of the digester has a thermometer installed on top of the digester to monitor the temperature inside the digester. Optimum temperature of 30\degree C- 40\degree C was maintained for each of digester and the pH of spent substrate from the outlet was measured daily using portable digital pH meter (PHMETER, PH_009 (I)). Retention period of 5-7 days before the start time of the anaerobic digestion processor biogas generation commenced. Anaerobic digestion occurs when organic
material decomposes biologically in the absence of oxygen. The gas was collected through the upward delivery gas method. The biogas yield was measured at the end of 14 days. Plate 1 shows the biogas digester set up for one of the digesters.

Plate 1: Bio-digesting Unit

The digesters were located outdoors at an ambient temperature of 33°C as high temperature facilitates the emission of biogas. Digesters were implemented simultaneously under anaerobic environment, adopting the methodology by Abayomi, et.al (2019). Each of the digester has an opening on top for loading of the substrate/feedstock/ slurry into the digester. Each of the digesters has a top cover with a plastic hose connected to it and being held fixed with adhesive gum to prevent leakage but designed to displace excess slurry or water through the downward displacement technique with a container provided to collect the displaced slurry. Each of the digesters is connected to the gas collecting apparatus through a plastic hose with a control valve positioned at the end of the hose to keep the digester air tight as much as possible when closed to create the desired anaerobic environment. Each of the digester has a thermometer installed on top of the digester to monitor the temperature inside the digester. Optimum temperature of 30°C- 40°C was maintained for digestion to proceed by conducting the experiment during the dry season to attain optimum temperature. The pH of spent substrate from the outlet was measured daily using portable digital pH meter (PHMETER, PH_009 (I)). Retention period of 5-7 days before the start time of the anaerobic digestion processor biogas generation commenced. Anaerobic digestion occurs when organic material decomposes biologically in the absence of oxygen. The gas was collected through the upward delivery gas method. The biogas yield was measured at the end of 14 days.

Model development
The popular modified Gompertz equation was used to model the biogas production (Yusuf, et al., 2011; Van, et al., 2018; Zhang, et al., 2021). The modified Gompertz model is a Statistical Regression Model which describes the cumulative biogas production in batch digestion. It assumes that methane production is a function of bacterial growth or that methane production is a composite function of substrate levels limit growth in a logarithmic relationship (Van et al., 2018; Zhang et al., 2021). The modified Gompertz model is given in Equation 1.

$$G_t = A \exp \left[ - \exp \left( \frac{R_{\text{max}} x e}{A} (\lambda - t) + 1 \right) \right]$$

(1)

where:

- $G_t$ is the cumulative of biogas produced (ml) at any time (t)
- $A$ is the biogas production potential (ml)
R\(_{\text{max}}\) is the maximum biogas production rate (ml/day)
λ is the lag phase (days), which is the minimum time taken to produce biogas or time taken for bacteria to acclimatize to the environment in days.

**Modeling methane production kinetics using first-order kinetic method**

This study further modeled biogas methane gas yield using first order linear approach derived from first order exponential kinetic models (Nwosu-obieogu, et al., 2020). The purpose of this modeling approach is to determine the optimal methane production with the correspondent feed additives for methane emissions reduction. The study modeled methane production process in the digesters using a combination of feed additives. A set of linear equations (models) to predict methane production from variables that describe the different feed additives are derived. Extant methane prediction equations were also evaluated. The model describing methane production process in digesters with volume (V) by feed additives is developed using mass balance method. The governing mass balance equation based on changes in the substrate concentration (C) is expressed in Equation 2 as: (Yusuf & Nwaogazie, 2009).

\[
V \frac{dC}{dt} = Q_0 C_0 - Q_0 C + V rC
\]

Where \(C_0\) is the input flow volatile solids
\(C\) is the output flow volatile solids

However, for a batch system flow of input, \(Q_0 = 0\), thus, Equation 2 can be written as follows:

\[
V \frac{dC}{dt} = V rC
\]

Where:
\(r\) is the substrate removal rate as a function of \((C)\),
\(t\) is the time in day
\(r\) is the rate of reaction (concentration unit per time).

The order of kinetic reaction can be determined by writing Equation 3 as:

\[
r = \frac{dC}{dt} = -k C^n
\]

Where:
\(C\) is the concentration of substrate remaining at any time, \(t\),
\(n\) is the reaction order,
\(k\) is the kinetic rate constant.

For first-order kinetic reaction, \(n = 1\)

Then, Equation 4 becomes

\[
\frac{dC}{dt} = -k C
\]

Taking the derivative of Equation (3.5) with respect to time, \(t\) gives

\[
\frac{dC}{dt} = -k C
\]

\[
\frac{dC}{C} = -k dt
\]

Where:
\(C\) is the concentration of volatile solids remaining at time \(t\) and
\(k\) is the first-order rate constant

Integrating Equation 7 with initial conditions, \(t = 0, t = t; C = 0, C = C_i\).

\[
\int_{C_0}^{C_i} \frac{dC}{C} = -k \int_0^t dt
\]

\[
\ln(C_i) - \ln(C_0) = -kt
\]

\[
\ln(C_i) = \ln(C_0) - kt
\]
Equation (9) can also be expressed as

\[ \ln \left( \frac{C_t}{C_0} \right) = kt \]  \hspace{1cm} (10)

\[ \frac{C_t}{C_0} = e^{kt} \]  \hspace{1cm} (11)

\[ C_t = C_0 e^{kt} \]  \hspace{1cm} (12)

Generally, Equations (10) to (12) apply to substrate degradation only without information about methane gas production or yield in the substrate utilization process (Yusuf & Nwaogzie, 2009).

The development of a biogas of methane gas yield model is based on the assumption that all substrates (biomass) are converted into biogas as shown in Plate 1 (Linke, 2006; Yusuf et al., 2009). The methane gas production or yield model in this study is derived from Equations (10) to (12) and Figure 2. Therefore, the substrate degradation and methane gas yield are correlated from Equation (10) and Plate 1 as follows:

\[ \frac{C_0 - C_t}{C_0} = \frac{y_t}{y_m} \]  \hspace{1cm} (13)

Taking like terms, Equation (13) becomes

\[ \frac{C_0}{C_t} = \frac{y_m}{y_m - y_t} \]  \hspace{1cm} (14)

Where:
- \( y_m \) - is the maximum biomethane yield obtained over the digestion period (ml/g/day),
- \( y_t \) - is the ultimate or total biomethane yield obtained at the time, \( t \) (ml/g/day),
- \( k \) - is the first order rate constant (l/day),
- \( t \) - is the biomethane production time.

With respect to the linear equation, the rate of biogas production is directly proportional to time, Substituting \( C_0/C_t \) in equation (10) with respect to \( y_m/(y_m - y_t) \) we have,

\[ \ln \left( \frac{y_m}{y_m - y_t} \right) = kt \]  \hspace{1cm} (15)

Equation (15) can be translated into exponential form as follows,

\[ y_t = y_m \left( 1 - e^{-kt} \right) \]  \hspace{1cm} (16)

From Equations (15) and (16), the \( k \) rate constant is determined as:

\[ k = \frac{y_m}{(y_m - y_t)t} \]  \hspace{1cm} (17)
The linear analysis equation can be expressed as:

\[ y_t = \beta_0 + \beta_1 t \]  \hspace{1cm} (18)

Equation (18) indicates that the rate of bio-methane gas production is directly proportional to time, t. Applying the linear Equation (18) to the exponential Equation (16): Equation (16) is modified into a linear form as expressed in Equation (19). This indicates the rate of bio-methane gas production increase with the digestion time.

\[ y_t = \beta_0 + \beta_1 \times \text{Exp}(kt) \]  \hspace{1cm} (19)

Where:

- \( y_t \) is the biogas production rate (ml/gas/day);
- \( t \) is the biogas production time (day);
- \( \beta_0 \) is the intercept of the model (ml/g/day);
- \( \beta_1 \) is the material mixing ratio; and
- \( k \) is the kinetic rate constant (/day).

\( \beta_0 \) is the intercept of the model and represents the amount of methane yields expected to be achieved when the digestion time spent on feed additives is zero.

\( \beta_1 \) quantifies the relationships by the additive variables for the different units and the methane gas yields.

\( \beta_0 \) and \( \beta_1 \) in Equation (19) were calibrated using Equations (20) and (21) respectively.

\[ \beta_0 = \frac{\sum y_i - \bar{y} \sum x_i}{n} \]  \hspace{1cm} (20)

\[ \beta_1 = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x - \bar{x})^2} \]  \hspace{1cm} (21)

where,

- \( x_i \) is the \( i^{th} \) observed methane value,
- \( \bar{x} \) is the mean observed methane value;
- \( y_i \) is the \( i^{th} \) predicted methane yield,
- \( \bar{y} \) is the mean predicted methane yield and
- \( n \) is the total number of data points over the 14 days digestion period.
Model Evaluation Method
Since this study used a statistical regression to model bio-methane production process in the bio-digesters using a combination of correspondent feed additives for methane emissions reduction, model evaluation was carried out instead of model validation used in a deterministic model. Therefore, the performance of the model was evaluated using model evaluation metrics in order to determine the consistency of the predicted values with observed values.

Specific analyses were performed to validate the model outputs against measured data. Predicted values were paired against measured values using mean square error (MSE), root mean square error (RMSE) and mean absolute percentage error (MAPE). In addition, a measure of goodness of fit known as coefficient of determination, R-square ($R^2$) was used to determine the closeness of the predicted values to the measured values.

The mean square error (MSE) was computed as the mean difference between predicted and measured values using Equation (11), while the root mean square error was computed using Equation (12).

The mean square error (MSE) is given as:

$$MSE = \frac{1}{N} \sum_{i=1}^{n} (y_{pred,i} - x_{meas,i})^2$$

The root mean square error (RMSE) is given as:

$$RMSE = \left[ \frac{1}{N} \sum_{i=1}^{n} (y_{pred,i} - x_{meas,i})^2 \right]^{1/2}$$

The mean absolute percentage error (MAPE) is given as:

$$MAPE = \frac{\sum |y_{pred, i} - x_{meas, i}|}{N} \times 100$$

The coefficient of determination was computed using Equation (23).

$$R^2 = \frac{\sum (y_{pred, i} - \overline{X})^2}{\sum (x_{meas, i} - \overline{X})^2}$$

Where:
- $y_{pred}$ is the predicted value,
- $x_{meas}$ is the measured value.
- $N$ is the number of observations
- $\overline{X}$ is the mean of the measured values

MSE, RMSE, MAPE and $R^2$ were used to evaluate the performance of the predictive model; while t-test and F-test were used to statistically test the significance of the predicted values against the measured values. The t-test was also used to test the significance level of methane reduction by the different feed additives of the test units over the 14 days digestion period.

Model Calibration
The calibrated model developed is in Equation 19

$$y_t = \beta_0 + \beta_1 * \exp(kt)$$

Where:
- $y_t$ is the biogas production rate (ml/gas/day);
- $t$ is the biogas production time (day);
- $\beta_0$ is the intercept of the model (ml/g/day);
- $\beta_1$ is the material mixing ratio; and $k$ is the kinetic rate constant (day).

$\beta_0$ and $\beta_1$ in Equation (19) were calibrated using Equations (20) and (21) respectively.
\[
\beta_0 = \frac{\sum y_i - \beta_1 \sum x_i}{n}
\]

(20)

\[
\beta_1 = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x - \bar{x})^2}
\]

(21)

where, \(x_i\) is the \(i^{th}\) observed methane value,
\(\bar{x}\) is the mean observed methane value;
\(\bar{y}\) is the \(i^{th}\) predicted methane yield,
\(\bar{y}\) is the mean predicted methane yield and
\(n\) is the total number of data points over the 14 days digestion period.

Results: The developed bio-methane emission prediction first order linear models for Test Unit 1, Test Unit 2, Test Unit 3, Test Unit 4 and Test Unit 5 are shown in Equations (26) to (30) respectively. The summary statistical results of the predictive models for different feed additives is shown in Table 1; while the actual and predicted values of Methane emission for the different feed additives are shown in Tables 2 to 6. The plots of the correlation (goodness of fits) between the predicted and observed bio-methane gas emission values for the different feed additives are shown in Figures 2, 4, 6, 8 and 10; while the comparison between predicted and observed bio-methane emission values for the different feed additives are shown in Figures 3, 5, 7, 9 and 11. Finally, the variations of the methane yields with the digestion temperature levels are shown in Figure 12; while the cumulative plot of the predicted methane yield by the all the test units over the 14 days digestion period is shown in Figure 13.

<table>
<thead>
<tr>
<th>Experimental Unit</th>
<th>MSE (ml/g/day)</th>
<th>RMSE (ml/g/day)</th>
<th>MAPE (ml/g/day)</th>
<th>F-stat</th>
<th>P-value</th>
<th>(R^2)</th>
<th>(\beta_0) (ml/g/day)</th>
<th>(\beta_1)</th>
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<td>Test Unit 1</td>
<td>6123.25</td>
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<td>1343.243</td>
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</tbody>
</table>

Equation (19) was calibrated for Test Unit 1 as shown in Equation (26). The calibrated derived first order linear model of Equation (26) was used to predict the bio-methane emission for Test Unit 1 and the result presented as shown in Table 2. The modeling result for Test Unit 1 control group (Table 1) indicates a computed mean square error (MSE) of 6123.25ml/g/day, a root mean square error (RMSE) of 78.251ml/g/day and a mean absolute percentage error (MAPE) of 9.614%. The goodness of fit (Figure 3) between measured and predicted values indicates a coefficient of determination \(R^2\) of 0.9911. This implies that the linear model accurately predicted bio-methane emission for Test Unit 1 as shown in Figure 4.1.4. Also, the p-value shows that the linear model significantly predicted methane emission for Test Unit 1 (p-value < 0.05, 95%CI).
Table 2: Observed and predicted Methane emission for Test Unit 1

<table>
<thead>
<tr>
<th>Time (Day)</th>
<th>Measured $\text{CH}_4$ (ml/g/day)</th>
<th>Predicted $\text{CH}_4$ (ml/g/day)</th>
<th>k (/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>49.6</td>
<td>1.0000</td>
</tr>
<tr>
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<td>0.5000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>49.6</td>
<td>0.3333</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>49.6</td>
<td>0.2500</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>49.6</td>
<td>0.2000</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>49.6</td>
<td>0.1667</td>
</tr>
<tr>
<td>7</td>
<td>190</td>
<td>178.5</td>
<td>0.1461</td>
</tr>
<tr>
<td>8</td>
<td>280</td>
<td>242.7</td>
<td>0.1292</td>
</tr>
<tr>
<td>9</td>
<td>390</td>
<td>324.1</td>
<td>0.1164</td>
</tr>
<tr>
<td>10</td>
<td>780</td>
<td>641.6</td>
<td>0.1100</td>
</tr>
<tr>
<td>11</td>
<td>2000</td>
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<td>0.1187</td>
</tr>
<tr>
<td>12</td>
<td>2050</td>
<td>2128.3</td>
<td>0.1096</td>
</tr>
<tr>
<td>13</td>
<td>1850</td>
<td>1832.4</td>
<td>0.0982</td>
</tr>
<tr>
<td>14</td>
<td>1010</td>
<td>853.2</td>
<td>0.0810</td>
</tr>
</tbody>
</table>

$CH_4 = -5556.6506 + 2062.4275 \times \text{Exp}(kt) \quad (26)$

Figure 3: Correlation between predicted and observed bio-methane gas for Test Unit 1
Equation (19) was calibrated for Test Unit 2 as shown in Equation (27). The calibrated derived first order linear model of Equation (27) was used to predict the bio-methane emission for Test Unit 2 and the result presented as shown in Table 3. The modeling result for Test Unit 2 feed additive (Table 1) indicates a computed mean square error of 7091.02 ml/g/day, a root mean square error of 84.208 ml/g/day and a mean absolute percentage error of 11.329%. The goodness of fit (Figure 5) between measured and predicted values shows a coefficient of determination ($R^2$) of 0.9896. This suggests that the linear model highly predicted bio-methane emission for Test Unit 2 as shown in Figure 6. Also, the p-value shows that the linear model significantly predicted methane emission for Test Unit 2 (p-value < 0.05, 95% CI).

Table 3: Observed and predicted Methane emission for Test Unit 2

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Measured $CH_4$ (ml/g/day)</th>
<th>Predicted $CH_4$ (ml/g/day)</th>
<th>$k$ (/day)</th>
</tr>
</thead>
<tbody>
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<td>41.98</td>
<td>1.000</td>
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<tr>
<td>2</td>
<td>0</td>
<td>41.98</td>
<td>0.5000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>41.98</td>
<td>0.3333</td>
</tr>
<tr>
<td>4</td>
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<td>0.2500</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>41.98</td>
<td>0.2000</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>41.98</td>
<td>0.1667</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>41.98</td>
<td>0.1429</td>
</tr>
<tr>
<td>8</td>
<td>220</td>
<td>189.2</td>
<td>0.1285</td>
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<tr>
<td>9</td>
<td>310</td>
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<td>0.1156</td>
</tr>
<tr>
<td>10</td>
<td>610</td>
<td>483.7</td>
<td>0.1083</td>
</tr>
<tr>
<td>11</td>
<td>1700</td>
<td>1632.75</td>
<td>0.1155</td>
</tr>
<tr>
<td>12</td>
<td>1900</td>
<td>1918.89</td>
<td>0.1093</td>
</tr>
<tr>
<td>13</td>
<td>2100</td>
<td>2237.93</td>
<td>0.1043</td>
</tr>
<tr>
<td>14</td>
<td>1150</td>
<td>980.54</td>
<td>0.0834</td>
</tr>
</tbody>
</table>

$CH_4 = -5084.2824 + 1885.8462 * Exp(kt)$

(27)
Figure 5: Correlation between predicted and observed bio-methane gas for Test Unit 2

\[ y = 0.9896x + 5.9314 \]
\[ R^2 = 0.9896 \]

Figure 6: Comparison between predicted and observed bio-methane gas for Test Unit 2
Equation (19) was calibrated for Test Unit 3 as shown in Equation (28). The calibrated derived first order linear model of Equation (28) was used to predict the bio-methane emission for Test Unit 3 and the result presented as shown in Table 4. The modeling result for Test Unit 3 feed additives (Table 1) shows a computed mean square error of 10279.6ml/g/day, a root mean square error of 101.388ml/g/day and a mean absolute percentage error of 12.405%. The goodness of fit (Figure 7) between measured and predicted values shows a coefficient of determination ($R^2$) of 0.9819. This shows that the linear model highly predicted bio-methane emission for Test Unit 3 as shown in Figure 8. Also, the p-value shows that the linear model significantly predicted methane emission for Test Unit 3 ($p$-value < 0.05, 95%CI).

Table 4: Observed and predicted Methane emission for Test Unit 3

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Measured $\text{CH}_4$ (ml/g/day)</th>
<th>Predicted $\text{CH}_4$ (ml/g/day)</th>
<th>$k$ (/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>48.25</td>
<td>1.0000</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>48.25</td>
<td>0.5000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>48.25</td>
<td>0.3333</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>48.25</td>
<td>0.2500</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>48.25</td>
<td>0.2000</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>48.25</td>
<td>0.1667</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>48.25</td>
<td>0.1429</td>
</tr>
<tr>
<td>8</td>
<td>150</td>
<td>141.43</td>
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<tr>
<td>9</td>
<td>260</td>
<td>213.85</td>
<td>0.1155</td>
</tr>
<tr>
<td>10</td>
<td>380</td>
<td>297.12</td>
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<tr>
<td>11</td>
<td>1250</td>
<td>1075.09</td>
<td>0.1110</td>
</tr>
<tr>
<td>12</td>
<td>1760</td>
<td>1741.56</td>
<td>0.1119</td>
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<tr>
<td>13</td>
<td>2050</td>
<td>2229.66</td>
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<tr>
<td>14</td>
<td>1050</td>
<td>863.53</td>
<td>0.0842</td>
</tr>
</tbody>
</table>

$$\text{CH}_4 = -4098.5539 + 1525.5243 \times \text{Exp}(kt) \quad (28)$$

![Figure 7: Correlation between predicted and observed bio-methane gas for Test Unit 3](image)
Equation (19) was calibrated for Test Unit 4 as shown in Equation (29). The calibrated derived first order linear model of Equation (29) was used to predict the bio-methane emission for Test Unit 4 and the result presented as shown in Table 5. The modeling result for Test Unit 4 feed additives (Table 1) indicates a computed mean square error of 9784.75ml/g/day, a root mean square error of 98.918ml/g/day and a mean absolute percentage error of 12.913%. The goodness of fit (Figure9) between measured and predicted values indicates a coefficient of determination ($R^2$) of 0.9773. This shows that the linear model highly predicted bio-methane emission for Test Unit 4 as shown in Figure10. Also, the p-value shows that the linear model (Equation 29) significantly predicted methane emission for Test Unit 4 (p-value < 0.05, 95%CI).

Table 5: Observed and predicted Methane emission for Test Unit 4

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Measured $CH_4$ (ml/g/day)</th>
<th>Predicted $CH_4$ (ml/g/day)</th>
<th>$k$ (/day)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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<td>1.0000</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>48.39</td>
<td>0.5000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>48.39</td>
<td>0.3333</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>48.39</td>
<td>0.2500</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>48.39</td>
<td>0.2000</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>48.39</td>
<td>0.1667</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>48.39</td>
<td>0.1429</td>
</tr>
<tr>
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<td>1850</td>
<td>2029.66</td>
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<tr>
<td>14</td>
<td>910</td>
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</tr>
</tbody>
</table>

$$CH_4 = -3484.0764 + 1299.5201^* \text{Exp}(kt) \quad (29)$$
Figure 9: Correlation between predicted and observed bio-methane gas for Test Unit 4

\[ y = 0.9773x + 9.7534 \]

\[ R^2 = 0.9773 \]

Figure 10: Comparison between predicted and observed bio-methane gas for Test Unit 4
Equation (19) was calibrated for Test Unit 5 as shown in Equation (30). The calibrated derived first order linear model of Equation (30) was used to predict the bio-methane emission for Test Unit 5 and the result presented as shown in Table 6. The modeling result for Test Unit 5 mixed feed additives (Table 1) indicates a computed mean square error of 7745.89ml/g/day, a root mean square error of 88.011ml/g/day and a mean absolute percentage error of 12.516%. The goodness of fit (Figure 11) between measured and predicted values indicates a coefficient of determination ($R^2$) of 0.9793. This shows that the linear model highly predicted bio-methane emission for Test Unit 5 as shown in Figure 12. Also, the p-value shows that the linear model (Equation (30)) significantly predicted methane emission for Test Unit 4 (p-value < 0.05, 95%CI).

Table 6: Observed and predicted Methane emission for Test Unit 5

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Measured CH$_4$ (ml/g/day)</th>
<th>Predicted CH$_4$ (ml/g/day)</th>
<th>k (/day)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>2</td>
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<td>42.12</td>
<td>0.5000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>42.12</td>
<td>0.3333</td>
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<td>4</td>
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<td>42.12</td>
<td>0.2500</td>
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<tr>
<td>5</td>
<td>0</td>
<td>42.12</td>
<td>0.2000</td>
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<td>0</td>
<td>42.12</td>
<td>0.1667</td>
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<tr>
<td>7</td>
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<td>0.1429</td>
</tr>
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</table>

\[
CH_4 = -3290.4351 + 1225.9780 \times Exp(kt) \quad (30)
\]

Figure 11: Correlation between predicted and observed bio-methane gas for Test Unit 5
Figure 12: Comparison between predicted and observed bio-methane gas for Test Unit 5

Figure 13: Plot of predicted methane yield for the all the test units
The cumulative curves for the different co-digestions (Figure 14) indicates that the methane yields of the control group (Test Unit 1) shows the highest methane emission with a total cumulative value 16090ml/g over the 14 days digestion period. The cumulative methane yield of the cow manure from mixed additives group (Test Unit- 5) shows the lowest methane emission with a cumulative value of 10350ml/g over the 14 days digestion period. This implies that cow manure from mixed additives feed additives reduces methane emissions in livestock farming. A test of significance indicates that cow manure from mixed feed additives significantly reduce methane emission over the 14 days digestion period compared to the control group (p-value = 0.009, 95%CI).

Discussion of Findings:
The results (Table 1) indicate that all the developed first order linear models adequately fit the measured data set with goodness of fits greater than 95% (R² > 0.95). Test Unit 1 model explained 99.11% of the measured values; Test Unit 2 model explained 98.96% of the measured values; Test Unit 3 model explained 98.19% of the measured values; Test Unit 4 model explained 97.73% of the measured values; while Test Unit 5 model explained 97.93% of the measured values. Modeling error metrics show that Test Unit 1 has that lowest mean prediction errors; this is followed by Test Units 2 and 5. This suggests that the first order linear model accurately predicts that naturally occurring of methane emission in the control group; while the feed additives in the other Test Units are variables that influence that potential of the first order linear models to accurately predict methane emission in the substrate degradation or utilization. Therefore, it is necessary to investigate relative proportions of feed additives as variables that determine methane emission in experimental animals. The study shows that all the developed first order linear models significantly predicted the methane emission with p-values < 0.05, 95%CI and R² > 0.95. This agrees with the study of Ali et al., (2018) who obtained R² values between 0.979 and 0.991 for the kinetic modeling of methane emission from slaughterhouse waste and salviniamolesta using Logistic modeling method. In a similarly study, Nwosu et al., (2020) used the same linear modeling approach and obtained a coefficient of determination (R²) of 0.9476 in the kinetic modeling of biogas production from poultry manure and banana peels. This study also strengthens the work of Yusuf & Nwaogazie (2009) who obtained goodness of fit (R²) values between 0.889 and 0.995 for the modeling of biogas yield from the co-digestion of cow dung and water hyacinth using first order kinetic method.

Conclusion
A first order linear model has been developed for the prediction of methane emission from different animal feed additives. The study showed that the derived first order linear model significantly predicted methane emission in substrate degradation and therefore can be used to forecast methane production from animal feeds. Result further revealed that all the developed first order linear models significantly predicted the methane emission with probability p-values < 0.05, 95% confidence interval/ level- (CI) and coefficient of determination (R²)> 0.95. Therefore, mixed additives could be used as effective anti-methanogenic compounds to efficiently reduce enteric methane production.
REFERENCES


