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Empirical analysis of methane gas yield dependence on organic loading rate during microbial treatment of fruit wastes in digester

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ABSTRACT

This paper presents a model development for predictive analysis of methane gas yield during bio-treatment of fruit wastes in the digester; aimed at producing biogas for heat and electricity generation. The overall validity of the derived model was established using the 4th Degree Model Validity Test Technique (4th DMVTT); computational, graphical, statistical and deviational analysis. Computational analysis of the model-predicted and experimental results indicates that methane gas yield per unit organic loading rate are - 0.0421 (VS)² d⁻¹ and - 0.0395 (VS)² d⁻¹ as obtained from experiment and derived model respectively. The graphical analysis, apart from showing very close alignment of curves from both experimental and model-predicted results, indicates 0.9923 and 1.0000 as the correlation between methane yield and organic loading rate as obtained from experiment and derived model are respectively. Statistical analysis of the results indicate that the variance and standard deviation as obtained from experiment and derived model are 9.1004 x 10⁻⁴ and 0.0302 as well as 8.0934 x10⁻⁴ and 0.0284 respectively, indicating proximate agreement. Deviational analysis indicates that the maximum deviation of the model-predicted methane yield from the corresponding experimental value is less than 6%. It was also found that the validity of the model is rooted on the expression (Log α)/N = Log (γ)⁻¹ where both sides of the expression are correspondingly approximately equal.

Keywords: Model, Methane Gas Yield, Microbial Treatment, Fruit Wastes.

INTRODUCTION

Rapid dwindling of fossil fuel reserves has presented a scenario, which sues for alternative energy sources to be renewable, sustainable, efficient, cost-effective, convenient and safe. An eco-friendly bio-ethanol is one of such alternate fuel that can be used in unmodified petrol engines with current fueling infrastructure and it is easily applicable in the present day combustion engine, as mixing with gasoline [1]. It is of paramount importance to generate a quantity of biofuel that can represent up to 40% of the country's fuel consumption and become 80% independent from foreign oil. There is need for most of the new cars manufactured and sold to be flexible-fuel vehicles that can run on ethanol, gasoline, or any blend of the two.

Over dependence of first generation biofuel on edible crops as feed stocks has lead to Food-Energy crisis thereby causing ecosystem instability. This has consequently, metamorphosed the second generation biofuel which is significantly dependent on non-food sugary materials as feedstocks. Various raw materials like sugarcane juice and molasses [2,3] sugar beet, beet molasses [3,4], Sweet sorghum [5] and starchy materials like sweet potato [6], Corn

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cobs and hulls [7,8], cellulosic materials like cocoa, pineapples and sugarcane waste [9] and milk, cheese, and whey using lactose hydrolyzing fermenting strains [10] have been reported in ethanol production.

Gases such as methane, hydrogen and carbon monoxide can be combusted or oxidized with oxygen, air containing 21% oxygen. Energy release as a result of the combustion process presents biogas as a very potent fuel. Biogas can be used as a low-cost fuel in any country for any heating purpose, such as cooking and in modern waste management facilities where it can be used to run any type of heat engine, to generate either mechanical or electrical power. Biogas can be compressed, much like natural gas, and used to power motor vehicles. Biogas is a renewable fuel, so it qualifies for renewable energy subsidies in some parts of the world.

Studies [11] have shown the possibility and potentialities in fruit wastes microbial treatment, to produce methane gas used as energy source. It has been reported [11] that tomato, mango, pineapple, lemon, and orange processing waste, yielded 0.62, 0.56, 0.77, 0.72 and 0.63 m³ of methane gas/kg of VS respectively. Mango peel supplemented with urea was found [12] to adjust the C: N ratio to 20-30: 1 resulting in the stability of the digester. Further research [12] reported that addition of nitrogen in the form of silkworm waste and oilseed extracts, such as neem and castor, increased the methane content. Successive addition of fruit and vegetable solid wastes on the performance of biogas digester shows that the digester was stable at a loading rate of 3.8 kg VS $m^{-3} d^{-1}$ [13]. The researchers further observed that no noticeable changes in the rates and yields of biogas occurred as a result of minor manipulation in nutritional and operational parameters which practically helped in the functioning of the digester fed with different fruits (mango, pineapple, tomato, jack fruit, banana, and orange) and vegetable wastes for a considerably long time. Studies carried out on Pilot plant (of volumetric capacity 1.5 m³ and digester type KVIC) with mango peel showed that supplementation with essential nutrients improved the digestibility of feedstock, yielding as high as $0.6 \text{ m}^3/\text{kg}$ VS with a methane gas content of 52% at a loading rate of 8–10%. Also, addition of sugarcane filter mud at a rate of 200 g/4 kg of mango peel in 1.5 m³ digester increased biogas yield substantially with a methane content of 60%. Addition of extract of nirmali seeds, hybrid beans, black gram, and guar gum seeds (as additives) at 2-3% level increased the biogas production significantly [12]. This increment was attributed to the galactomannan constituent of the leguminous seeds which increased the floc formation, thereby retaining the organisms in the digester.

The microbiology of digesters fed with tomato-processing waste, was studied [14] and the results of the investigation revealed that in batch digestion, the population of methanogens was less due to the drop in pH of slurry. However in semi-continuous digestion, biogas yield of $0.42 \text{ m}^3 \text{ kg}^{-1} \text{ VS}$ was reported following increase in the population of cellulolysers, xylanolysers, pectinolysers, proteolysers, lipolysers, and methanogens with increase in hydraulic retention time (HRT). Results of previous studies [15] on the feasibility of mango processing waste for biogas production indicates a biogas output of $0.21 \text{ m}^3 \text{ kg}^{-1} \text{ TS}$.

Studies [16] have shown that the earliest attempt to understanding material behavior is through observation via experiments. The researchers further posited that careful measurements of observed data are subsequently used for the development of models that predict the observed behavior under the corresponding conditions. The models are necessary to develop the theory. The theory is then used to compare predicted behavior to experiments via simulation. This comparison serves to either validate the theory, or to provide a feedback loop to improve the theory using modeling data [16]. Based on the foregoing, it is clear that development of a realistic theory of describing the structure and behavior of materials is highly dependent on accurate modeling and simulation techniques.



Fig. 1: Schematic of the process of developing theory and the validation of experimental data [17]

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The aim of this work is to develop a model for the prediction of methane gas yield from microbial treatment of fruit wastes. The model is expected to predict the methane yield based on the organic loading rate during the bio-treatment process.

Biomethane Production Process Analysis

The solid phase (wastes) is assumed to be stationary, contains some un-reacted fruit seeds remaining in the prepared waste. Conversion of organic matter to methane was by microbes. This process is anaerobic and is carried out by action of various groups of anaerobic bacteria. Complex polymers are broken down to soluble products by enzymes produced by fermentative bacteria which ferment the substrate to short-chain fatty acids, hydrogen and carbon dioxide. Obligate hydrogen-producing acetogenic bacteria metabolized fatty acids. Hydrogen, carbon dioxide, and acetate are the major products after digestion of the substrate by the two groups are. Hydrogen-oxidizing acetogens converts hydrogen and carbon dioxide to acetate or to methane by carbon-dioxide-reducing, hydrogen-oxidizing methanogens. Aceticlastic methanogens also converts acetate to methane.



Fig. 2: Pathway of methane formation by Methanobacterium thermoautotrophicum [18]

MATERIALS AND METHODS

A weighed quantity of prepared fruit wastes was put in the digested containing the appropriate microbes. Details of the experimental procedure and associated process conditions are as stated in the past report [13].

Model Formulation

Experimental data obtained from research work [13] were used for this work. Computational analysis of the experimental data [13] shown in Table 1, gave rise to Table 2 which indicate that;

$$\left(\frac{\log \alpha}{N} \right)^{=} \log \left(\gamma \right)^{-1} \quad (approximately) \qquad 1$$

$$\left(\log \alpha \right)^{=} \left(N \log \left(\gamma \right)^{-1} \right) \qquad 2$$

$$\left(\text{Log }\alpha\right) = \text{Log }\left(\left(\gamma \right)^{1}\right)^{N}$$
 3

$$\left[\text{Log } \alpha \right] = \text{Log } \left[\gamma \right]^{-N}$$

Introducing the value of N into equation (4) reduces it to;

$$\alpha = \left(\gamma \right)^{-1.25} 5$$

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Where

 $(\gamma) = \text{Organic loading rate } (\text{kg VS m}^{-3} \text{ d}^{-1})$

(α) = Methane yield (m³ kg⁻¹ VS)

N = 1.25; Overall microbe- substrate interaction factor (determined using C-NIKBRAN [19]

Table 1: Variation of methane yield with organic loading rate [13]

(a) [13]	(γ)
0.1900	3.8
0.1820	4.0
0.1563	4.6
0.1310	5.2
0.1100	5.7

Boundary and Initial Condition

Consider prepared fruit wastes (in a digester) interacting with microbes. The digester atmosphere is not contaminated i.e (free of unwanted gases and dusts). Range of organic loading rate used: $3.8-5.7 \text{ kgVS m}^{-3} \text{ d}^{-1}$. Mass of wastes used, resident time, treatment temperature, growth rate of microbes and other process conditions are as stated in the experimental technique [13].

The boundary conditions are: anaerobic atmosphere to enhance bacterial action on the wastes (since the digester was air-tight closed). At the bottom of the particles, a zero gradient for the gas scalar are assumed and also for the gas phase at the top of the waste particles. The biodegraded waste is stationary. The sides of the waste particles are taken to be symmetries.

RESULTS AND DISCUSSION

The derived model is equation (5). The computational analysis of Table 1 gave rise to Table 2

Table 2: Variation of $(\text{Log }\alpha)/N$ with $\text{Log }(\gamma)^{-1}$

(Log α)/N	$Log (\gamma)^{-1}$
-0.5770	-0.5798
-0.5919	-0.6021
-0.6448	-0.6628
-0.7062	-0.7160
-0.7669	-0.7559

Model Validation

The validity of the model is strongly rooted on equation (1) where both sides of the equation are correspondingly approximately equal. Table 2 also agrees with equation (1) following the values of $(\text{Log } \alpha)/N$ and $\text{Log } (\gamma)^{-1}$ evaluated from the experimental results in Table 1.

Furthermore, the derived model was validated by comparing the methane gas yield predicted by the model and that obtained from the experiment [13]. This was done using various analytical techniques.

Computational Analysis

A comparative computational analysis of the experimental and model-predicted methane gas yield was carried to ascertain the degree of the derived model. This was done by comparing methane gas yield per unit organic loading rate obtained by calculations involving experimental results, and model-predicted results obtained directly from the model.

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Methane gas yield per unit organic loading rate $\alpha_R (VS)^2 d^{-1}$ was calculated from the equation;

 $\alpha_{\rm R} = \alpha / \gamma$



Fig. 3: Coefficient of determination between methane yield and organic loading rate as obtained from the experiment [13].



Fig. 4: Coefficient of determination between methane yield and organic loading rate as predicted by model

Therefore, a plot of methane gas yield against organic loading rate as in Fig. 3 using experimental results in Table 1, gives a slope, S at points (3.8, 0.19) and (5.7, 0.11) following their substitution into the mathematical expression;

$$S = \Delta \alpha / \Delta \gamma$$
 7

Equation (7) is detailed as

$$\mathbf{S} = \boldsymbol{\alpha}_2 - \boldsymbol{\alpha}_1 / \boldsymbol{\gamma}_2 - \boldsymbol{\gamma}_1 \qquad \mathbf{8}$$

Where $\Delta \alpha$ = Change in the methane yield α_2 , α_1 at two organic loading rates values γ_2 , γ_1 . Considering the points (3.8, 0.19) and (5.7, 0.11) for (γ_1 , α_1) and (γ_2 , α_2) respectively, and substituting them into equation (8), gives the slope as - 0.0421 (VS)² d⁻¹ which is the methane gas yield per unit organic loading rate during the actual experimental process. Also similar plot (as in Fig. 4) using model-predicted results gives a slope. Considering points (3.8, 0.1885) and (5.7, 0.1135) for (γ_1 , α_1) and (γ_2 , α_2) respectively and substituting them into equation (8) gives the value of slope, S as - 0.0395 (VS)² d⁻¹. This is the model-predicted methane gas yield per unit organic loading rate. A comparison of these two values of the methane gas yield per unit organic loading rate.

Graphical Analysis

Further comparison of methane gas yield per unit organic loading rate as obtained from experiment [13] and derived model for validity testing is achieved by considering the R^2 values (coefficient of determination). The values of the correlation coefficient, R calculated from the equation;

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$\mathbf{R} = \sqrt{\mathbf{R}^2} \qquad \qquad 9$

using the r-squared values (coefficient of determination) from Figs.1 and 2 show a better correlation (1.0000) for model-predicted values between methane yield and organic loading rate than that determined from experimental (0.9923) [62]. This suggests that the model predicts accurate and reliable methane gas yield which are in proximate agreement with values from actual experiment. This confirms the validity of the derived model.

Critical graphical analysis of Fig. 5 shows very close alignment of the curves from model-predicted methane gas yield per unit organic loading rate and that of the experiment (ExD). The degree of alignment of these curves is indicative of the proximate agreement between both experimental and model-predicted methane gas yield per unit organic loading rate, hence validity of the model.



Fig. 5: Comparison of the methane gas yield per unit organic loading rate as obtained from experiment [13] and derived model.

Statistical Analysis

The model was also validated statistically by comparing the values of the variance and standard deviation evaluated from experimental and model-predicted data.

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The variance V is given by

$$V = \left(\frac{\sum (x - x_a)^2}{\sum n}\right) [20]$$
10

Furthermore, standard deviation is given by

$$SD = [V]^{1/2}$$
 [20]

Substituting equation (10) into equation (11) reduces it to;

$$SD = \left(\frac{\sum(x - x_a)^2}{\sum n}\right)^{1/2}$$

$$x_a = \left(\frac{x_1 + x_2 + x_3 + x_4 \dots}{\sum n}\right)$$
12
13

Where

SD = Standard deviation

V = Variance

x = Variables representing methane yield

 x_a = Arithmetic mean (evaluated as average methane yield using experimental data, [13] and model-predicted data n = Number of samples

Standard deviation and variance as obtained from experiment [13]

Table 3: Variation of $(x-x_a)$ with $(x-x_a)^2$

	Experiment [62]	Model
SD	0.0302	0.0284
V	9.1004 x 10 ⁻⁴	8.0934 x10 ⁻⁴

$\sum n = 5$ $\sum (x - x_a)^2 = 4.5502 \text{ x} 10^{-3}$

Substituting the values of $\sum n$ and $\sum (x-x_a)^2$ into equations (10) and (12), where $x_a = 0.1539$ (as calculated from equation (13)) gives variance and standard deviation as 9.1004 x 10⁻⁴ and 0.0302 respectively.

Standard deviation and variance as predicted by derived model

Table 4: Variation of $(x-x_a)$ with $(x-x_a)^2$

n (Exp)	(x-x _a)	$(x-x_a)^2$ $(x \ 10^{-3})$
1	0.0361	1.3032
1	0.0281	0.7896
1	0.0024	0.0058
1	-0.0229	0.5244
1	-0.0439	1.9272

$\sum n = 5$ $\sum (x - x_a)^2 = 4.0467 \ x 10^{-3}$

Also substituting the values of $\sum n$ and $\sum (x-x_a)^2$ into equations (10) and (12), where $x_a = 0.1509$ (as calculated from equation (13)) gives variance and standard deviation as 8.0934 x 10⁻⁴ and 0.0284 respectively.

Table 5: Comparison of standard deviation (SD) and variance (V) from experimental and model-predicted results

n (Mod)	(x-x _a)	$(x-x_a)^2$ (x 10 ⁻³)
1	0.0376	1.4138
1	0.0259	0.6708
1	-0.0025	0.0063
1	-0.0236	0.5570
1	-0.0374	1.3988

The proximity of values of the standard deviation and variance (Table 5) as obtained from experiment [13] and derived model indicates agreement and validity for the model.

Deviational Analysis

Comparative analysis of methane yield from experiment [13] and derived model revealed insignificant deviations on the part of the model-predicted values relative to values obtained from the experiment. This is attributed to the fact that the surface properties of the waste material and the physiochemical interactions between the waste material and the microbes (under the influence of the treatment temperature) which were found to have played vital roles during the process [13] were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted methane yield to those of the corresponding experimental values.

Deviation (Dn) of model-predicted methane yield from that of the experiment [6] is given by

$$Dn = \left(\frac{Pe - Ee}{Ee}\right) \times 100$$
 14

Correction factor (Cr) is the negative of the deviation i.e

Therefore

$$Cr = -\left(\frac{Pe - Ee}{Ee}\right) x \ 100$$
 16

Where

$$\begin{split} Pe &= Model-predicted methane yield (m^3 kg^{-1} VS) \\ Ee &= methane yield from experiment (m^3 kg^{-1} VS) \\ Cr &= Correction factor (\%) \\ Dn &= Deviation (\%) \end{split}$$

Introduction of the corresponding values of Cr from equation (16) into the model gives exactly the corresponding experimental methane yield.

Figs. 6 and 7 show that the maximum deviation of the mode-predicted methane yield from the corresponding experimental values is less than 6% and quite within the acceptable deviation limit of experimental results.



Fig. 6: Variation of model-predicted methane yield with its associated deviation from experimental values



Fig. 7: Variation of deviation (of model-predicted methane yield) with organic loading rate

The figures show that least and highest magnitudes of deviation of the model-predicted methane yield (from the corresponding experimental values) are -0.79 and -5.05% which corresponds to methane yield: 0.1885 and 0.1484 $m^3 kg^{-1} VS$ and organic loading rate; 3.8 and 4.6 kg VS $m^{-3} d^{-1}$ respectively.



Fig. 8: Variation of model-predicted methane yield with its associated correction factor



Fig. 9: Variation of correction factor (to model-predicted methane yield) with organic loading rate

Comparative analysis of Figs. 6-9 indicates that the orientation of the curve in Fig. 9 is opposite that of the deviation of model-predicted methane yield. This is because correction factor is the negative of the deviation as shown in equations (15) and (16). It is believed that the correction factor takes care of the effects of the surface properties of the waste material and the physiochemical interaction between the waste material and the microbes which (affected experimental results) were not considered during the model formulation. Figs. 8 and 9 indicate that the least and highest magnitudes of correction factor to the model-predicted methane yield are +0.79 and +5.05% which corresponds to methane yield: 0.1885 and 0.1484 m³ kg⁻¹ VS and organic loading rate; 3.8 and 4.6 kg VS m⁻³ d⁻¹ respectively.

Based on the foregoing, validation of the derived model using computational, graphical, statistical and deviational analysis has shown very proximate agreement between experimental and model-predicted result and is referred to as 4^{th} Degree Model Validity Test Techniques (4^{th} DMVTT). Assessment of the results generated from comparative evaluation between data from experiment [13] and derived model shows that any of the routes or techniques as shown in Fig. 10 can be used to establish the validity of the model. Consequently, the degree of model validity obtained on taking *n* number of routes or techniques to establish the validity of the model is referred to as n^{th} DMVTT.



Fig. 10: Flow process for establishment of model validity using the 4th DMVTT

CONCLUSION

The model predicts methane gas yield during the activities of microbes in digester aimed at producing biogas. It was found that the validity of the model is rooted on the expression (Log α)/N = Log (γ)⁻¹ where both sides of the expression are correspondingly approximately equal. The maximum deviation of the model-predicted methane yield from the corresponding experimental value is less than 6% which is quite within the acceptable deviation range of experimental results. Methane gas yield per unit organic loading rate as obtained from experiment and derived model were evaluated to be - 0.0421 (VS)² d⁻¹ and - 0.0395 (VS)² d⁻¹ respectively. The correlation between methane yield and organic loading rate as obtained from experiment and derived model were also evaluated 0.9923 and 1.0000 respectively, indicating proximate agreement. The evaluated values of variance and standard deviation as obtained from experiment and derived model are 9.1004 x 10⁻⁴ and 0.0302 as well as 8.0934 x 10⁻⁴ and 0.0284 respectively.

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