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Kinetic Modeling of Biogas Yield from Anaerobic Co-Digestion of Non-Uniform Multiple Feedstock Typically Available in Nigeria

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Abstract The kinetic models represent the basic framework for linear and non-linear relation between feedstock concentration and specific growth rate. This research work is focused on the kinetic modeling of biogas yield from anaerobic co-digestion of non-uniform multiple feedstock composition typically available in Nigeria. The collected feedstock was divided into different mass composition (i.e., S_1= 40 kg, S_2 = 48 kg, S_3 = 60 kg, S_4 = 65, S_5 = 75, S_6 = 87, S_7= 95 kg). Each composition of feedstock used was ground into fine particles to increase its surface area, and then mixed with waste water collected from slaughter house and ice fish cold room in a ratio of 1:2. An anaerobic digestion plant with a total capacity of 0.3m^3 was used to co-digest the slurry formed from the feedstock under optimum biogas yield conditions of process and operation parameters used in this research work. The actual cumulative biogas yield was compared to cumulative biogas yield predicted by modified Gompertz kinetic model. The results obtained show that biogas yield can be enhanced efficiently through co-digestion process. Besides, modified Gompertz kinetic model showed high coefficient of determination (R^2) (0.9986, 0.9993, 0.9630, 0.9963, 0.996, 0.998, 0.9985) for each substrate composition (S_1, S_2, S_3, S_4, S_5, S_6, and S_7) used. The high values of coefficient of determination (R^2), demonstrates the appropriateness of the modified Gompertz kinetic model for accurate prediction of anaerobic digestion of the substrate.

Keywords Kinetic model, anaerobic co-digestion, biogas yield, non-uniform multiple feedstock

1. Introduction

The anaerobic digestion process is a technology that recovers energy and nutrients from organic waste streams in useable forms in the absence of oxygen [1-3]. It is sustainable, renewable and a zero-carbon form of energy supply. The anaerobic digestion process can be used to recover energy in the form of biogas typically as a mixture of methane (CH_4), carbon (IV) oxide (CO_2), hydrogen sulphide (H_2S), hydrogen gas (H_2), water vapour (H_2O), nitrogen gas (N_2) and siloxane [4]. In the absence of the process, there is an uncontrolled released of methane to the atmosphere due to biodegradation of organic matter from open waste dump sites. Use of fossil fuels is one of the main reasons for the emission of greenhouse gases (GHGs). Yearly, 590-880 million tons of methane is released worldwide into the atmosphere through microbial activity. According to the report of Intergovernmental Panel on Climate Change (IPCC), greenhouse gas emissions must be reduced to less than half of global emission levels of 1990 in order to minimize climate change impacts and global warming. Biogas technology is considered to provide the benefits of reducing the emission of greenhouse gases and then mitigating global warming in ways of replacing firewood for cooking, replacing kerosene for lighting and cooking, replacing chemical fertilizers and saving trees from deforestation [5].

Anaerobic co-digestion simply means processing of different compositions of biodegradable organic waste in an anaerobic digester (AD) in the absence of oxygen. Vegetable, fats and oils, such as cooking oils readily decompose in AD plants. However, mineral oils such as automotive oils and greases, and paraffin cause toxicity problems [2,3,6]. Long-chain fatty acids (LCFA) can also inhibit bacterial growth and slow down biogas yield [7]. An alternative method of improving biogas yields from AD process is co-digestion. Co-digestion leads to stabilization and improved nutrient utilization for variety of substrates composition. Also, it leads to improved biogas yield because of positive synergisms that establish the digestion medium and the supply of missing nutrients [2-3]. Apart from the advantages derived from easier handling of mixed wastes, it can help to establish the required moisture contents of feedstock [8]. Frequent co-digested substrate for anaerobic digestion plant includes the following:

i. Co-digestion of organic wastes with animal manure (e.g., cow dung, poultry drops, pig excrete, etc.) in pre-determined ratio. This improves the C/N ratio, alkalinity and buffering capacity as well as biogas yields [8].

ii. Co-digestion of different organic waste samples: This involves digestion of different substrates with different compositions such as digestion of food remnants, organic matters, agricultural manure, etc. Different researchers had shown that co-digestion of different composition of substrates improve biogas yield [9].

iii. Co-digestion of sewage sludge with animal waste: Co-digestion of sewage sludge with animal manure has been applied in many existing AD plants for starting up digestion process [10]. Patil and Deshmukh [11] showed how sewage sludge together with cattle manure was successfully used to start up a thermophilic (55°C) digestion of biosolids and simulated MSW.

Modeling is widely applied for engineering problems because of the advantages it possesses when it comes to process optimization and control. Most AD models allow for biogas production rate in the process calculation. The first anaerobic digestion model was developed by Andrews (1969) to simulate the AD of waste-activated sludge [12]. Batstone developed the ADM1 model in 2002. The ADM1 model developed by Batstone was a universally applicable model that can be used for different digester temperatures and for a broad variety of input substrates. Although, ADM1 is one of the most detailed AD models available, other models focusing on particular applications were developed that further improved ADM1. In 2007, Jeppson and others modified the ADM1 model and developed two conversion blocks that calculate the ADM1 input variables based on the well-known ASM1parameters. Koch *et al* [13] suggested a standard procedure for model calibration by setting all model parameters to standard ADM1 values and vary the sensitive model parameters until the model performance satisfied the measured values. Benjamin *et al.* [14] modified Batstone ADMI model of 2002. Regardless of the thorough method they used to define the influent, it was an estimated average that was used. Their actual feed composition varied between batches and constantly throughout the day. Their simulated biogas production fits observed data best between days 15 and 60. This was expected because operating conditions during that time is similar to the steady state conditions when many parameters were determined. Koch *et al.* [13] used laboratory generated data to simulate the effluent, although the carbon oxygen demand (COD) was not supported by the lab analysis. However, it was inversely proportional to the feed flow. When the feed rate drops from 30 to 15 L/d on day 6, hydraulic retention time doubles. This implies solids per COD are leaving the reactor at basically the same rate while the amount of liquid leaving is half. In this regard, the simulation shows that the concentration per carbon oxygen demand in the effluent is nearly double [15].

Nevertheless, for better understanding of the effect of operation and process parameters on the anaerobic degradation of complex organic substrates, the anaerobic co-digestion model for complex organic substrates proposed by Esposito *et al.* [12] was used by Flavia Liotta. The model was calibrated with the experimental data of the batch experiments to estimate the kinetic constant of the surface-based disintegration process, Ksbk ($ML^{-2}T^{-1}$). The disintegration kinetic was based on the surface kinetic expression by including $a*$, which characterize the disintegration process.

$$a^* = \frac{A}{M} \quad (1)$$

$$\frac{dc}{dt} = -K_{sbk}\,.\,a^*.\,C \quad (2)$$

However, if all the organic solid particles have the same initial size and cylindrical shape with;

h = 2R; so that they are progressively and uniformly degraded, then $a*$ will be given by the following equations:

$$a^* = \frac{\sum_{i=1}^{n} \quad A_i}{\sum_{i=1}^{n} \quad M_i} = \frac{nA_i}{nM_i} = \frac{3}{\delta R} \quad (3)$$

$R = R_0 - K_{sbk}\frac{t}{\delta}$ (4)

where,

C = Concentration of the complex organic substrate in the digester (ML^{-3})

A = Disintegration surface area (L^2)

M = Complex organic substrate mass (M)

A_i = Disintegration surface area of the organic solid particle

M_i = Mass of the organic solid particle

n = Total number of organic solid particles

δ = Complex organic substrate density

R = Organic solid particles radius assumed to be time dependent

R_0 = Initial organic solid particle radius specified as the initial condition for model application.

A stoichiometric model based on Arrhenius equation was used to calculate the organic carbon that can be effectively used for energy production, while K_i depends on characteristics of component i of the waste and on temperature according to Equation (5). The Arrhenius equation is a formula for the temperature dependence of reaction rate [16]. This equation has a vast and important application in determining rate of chemical reactions and for calculation of energy of activation. It can be used to model the temperature variation of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions.

$K_i = K_i exp[-\frac{E}{RT_0}\left(1 - \frac{T_0}{T_w}\right)]$ (5)

$K = Ae^{\frac{-E_a}{RT}}$ (6)

Alternatively, the equation can be expressed as:

$K = Ae^{\frac{-E_a}{K_B T}}$ (7)

The Arrhenius plot is achieved by taking the natural logarithm of Arrhenius' equation yields.

$In(K) = In(A) - \frac{E_a}{R}\frac{1}{1}\frac{1}{T}$ (8)

Rearranging yields;

$In(A) = \frac{E_a}{R}\left(\frac{1}{T}\right) + In(A)$ (9)

This has the same form of equation of a straight line:

$y = mx + c$ (10)

When a reaction has a rate constant that obeys Arrhenius' equation, a plot of ln(K) versus T^{-1} gives a straight line, whose gradient and intercept can be used to determine E_a and A. The activation energy is defined to be (−R) times the slope of a plot of ln (K) againsty (1/T).

where,

K_i = Biodegradation rate constant for the component i

E = Activation energy (in Jmol−1)

T_w = Waste absolute temperature and

T_0 = 308.15 K

k = Rate constant

T = Absolute temperature

a = Constant for each chemical reaction that defines the rate due to frequency of collisions in the correct orientation

E_a = Activation energy for the reaction (in $Jmol^{-1}$)

R = Universal gas constant

A = Pre-expontial factor, a constant for each chemical reaction that defines the rate due to frequency of collisions in the correct orientation

K_B = Boltzmann constant

x = Reciprocal of T.

2. Materials and Methods

2.1 Materials

The materials used in this research work are tabulated as presented in Table 1.

Table 1: List of Materials and their Usage

S/N	List of Materials	Usage
1.	Muffle furnance	The muffle furnace was used to determine the percentage volatile solid of substrate.
2.	Electronic pH meter	The electronic pH meter was used to measure the pH readings.
3.	Weighing balance	It was used for the measurement of substrate and biogas yield.
4.	Anaerobic digestion plant	The fabricated anaerobic digestion plants were used for digestion and co-digestion of substrates.
5.	Nose mask	For protection against poisonous gases, contaminants from collected household wastes.
6.	Feedstock	The feedstock used in this research work include: Pig dung, pineapple peel, poultry dropping, water hyacinth, water melon peel, cassava peel, waste water from slaughter house and ice fish cold room, yam peel, plantain peel, banana peel, sweet potato peel, cocoyam peel, vegetable, fruits, and wastes from food remnant such as fufu, eba, starch, rice, beans, yam, fish, meat and moi moi.
7.	Gesa thermometer	Connected to the anaerobic digestion plant and it was used to monitor the temperature reading of the slurry.
8.	Pressure	For monitoring pressure buildup of generated biogas
9.	Laboratory oven	For determination of percentage total and volatile solid of substrate.
10.	Electronic precision balance	For weighing dry mass and ash content of substrate.
11.	Dish tongs	For removal of the crucible from the laboratory oven and muffle furnance.
12.	Crucible	For heating of the substrate
13.	Hand gloves	For protection
14.	Wash bottles	Used for rinsing
15.	Gas cylinder	Used for biogas storage
16.	Gas hose	For evacuation of biogas

2.2 Methods

The following methods were carried out.

Collection of Feedstock

Non-uniform multiple feedstock typically available in Nigeria that comprises of pig dung, pineapple peel, poultry dropping, cow dung, water hyacinth, water melon peel, cassava peel, waste water from slaughter house and ice fish cold room, yam peel, plantain peel, banana peel, sweet potato peel, cocoyam peel, vegetable, fruits, and wastes from food remnant such as fufu, eba, starch, rice, beans, yam, fish, meat and moi moi were collected from households, farm, and slaughter house in Nigeria and used in this research work.

Experimental Procedure

The anaerobic digestion plant has a total capacity of $0.3m^3$. The digester was initially seeded with mixture of cow dung, pig dung, and poultry dropping. Samples of collected substrate composition were weighed with a weighing balance. The collected feedstock was divided into different mass composition (i.e., S_1= 40 kg, S_2 = 48 kg, S_3 = 60 kg, S_4 = 65, S_5 = 75, S_6 = 87, S_7= 95 kg). The feedstock was ground into fine particles to increase its surface area, and then mixed with waste water collected from slaughter house and ice fish cold room in a ratio of 1:2 as recommended by Ebunilo *et al*. [17]. The percentage total solid and percentage volatile solid of the formed slurry were determined using standard method. The mixture was finally charged into the digester and made air tight. The digester content was stirred several times per day with the aim of mixing the substrates inside the digester for optimum biogas yield. The pressure and temperature readings were monitored and recorded. The pH of the slurry was monitored and recorded during each evacuation using a digital pH meter. Before each evacuation of biogas, the initial mass of the gas cylinder and the final mass after biogas evacuation were recorded. The mass of biogas evacuated was calculated by subtracting the initial mass of the gas cylinder from the final mass of the gas cylinder.

That is:

$M_{GE} = M_2 - M_1$ (11)

where,

M_{GE} = Mass of biogas evacuated

M_2 = Final mass of the gas cylinder

M_1 = Initial mass of the gas cylinder

Modeling of Cumulative Biogas Yield

The cumulative production of biogas with time is described with modified Gompertz equation. It comprehensively represents the basic framework for kinetics of biogas production process simulation. The biogas yield rate kinetics for the description and performance evaluation of anaerobic digestion process was carried out by fitting in the results obtained from the anaerobic co-digestion of feedstock to the modified Gompertz kinetic model. The modified Gompertz kinetic model describes the cumulative biogas yield in anaerobic digestion. It assumes that cumulative biogas yield is a function of the hydraulic retention time. Equation (12) shows modified Gompertz kinetic model. The constants were determined using the non-linear regression approach with the aid of solver function of the MS Excel Toolpak.

$$Y\ (t) = Aexp\left[-exp\left(\frac{\mu e}{A}(\lambda - t) + 1\right)\right] \quad (12)$$

where,

Y = Cumulative of specific biogas production (ml)

A = Biogas production potential (ml)

μ = Maximum biogas production rate (d^{-1})

λ= Lag phase period

t = Cumulative time for biogas production (days)

e = Mathematical constant (2.718282)

3. Results and Discussion

Peak biogas production was obtained for both digesters at pH of 6.85. Figure 1 to Figure 7 show the actual cumulative biogas yield and cumulative biogas yield predicted by modified Gompertz kinetic model. The results show increase in cumulative biogas yield throughout the hydraulic retention time period for the different masses of substrate used. This might be as a result of better acclimatization in the methanogenesis stage resulting from methane forming bacteria activities as they overcome the protective barrier that initially prevented degradation by bacteria for conversion of substrate to biogas [18]. The coefficient of determination (R^2) was high (0.9986, 0.9993, 0.9630, 0.9963, 0.996, 0.998, 0.9985) for different substrate composition (S_1-S_7) used. The high R^2 value demonstrates the appropriateness of the modified Gompertz kinetic model for accurate estimation of anaerobic digestion of the substrate [19]. The constants parameters; biogas production potential (A), lag phase period (λ) and maximum biogas yield rate (μ) were determined using the non-linear regression approach with the aid of the solver function of the MS Excel Toolpak (Table 1). The values of biogas production potential (A) was found to be relatively high while a low lag phase period (λ) was obtained and this was an indication of the presence of essential microbes that enhances anaerobic digestion of the substrates.

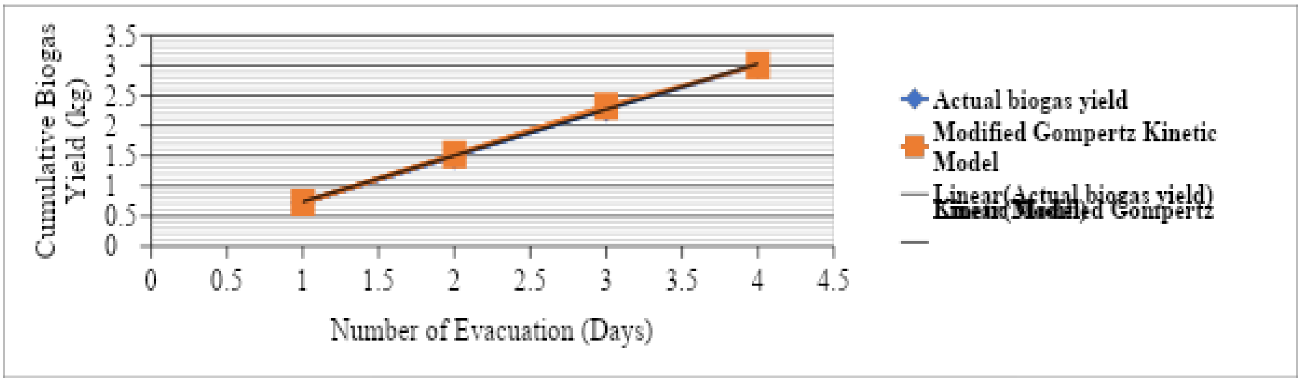

Figure 1: Results of cumulative biogas yield using modified Gompertz kinetic model (S_1=40 kg)

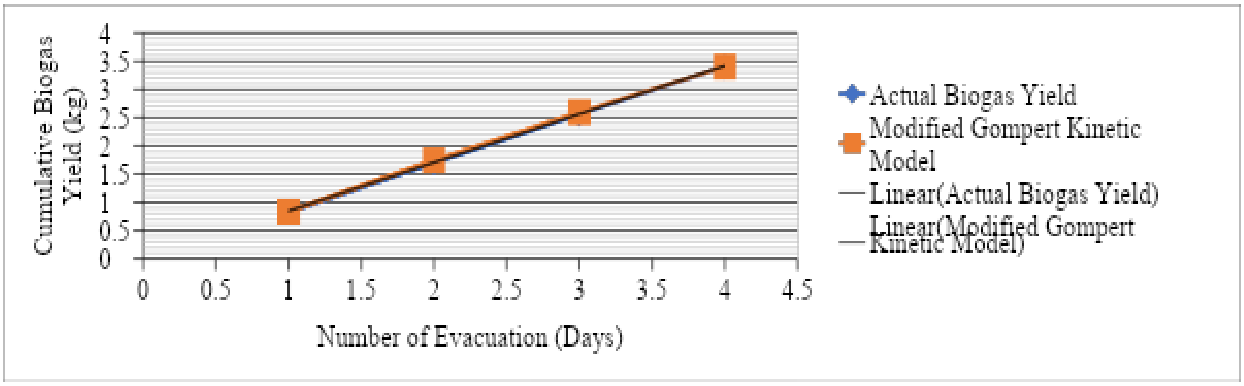

Figure 2: Results of cumulative biogas yield using modified Gompertz kinetic model (S_2=48 kg)

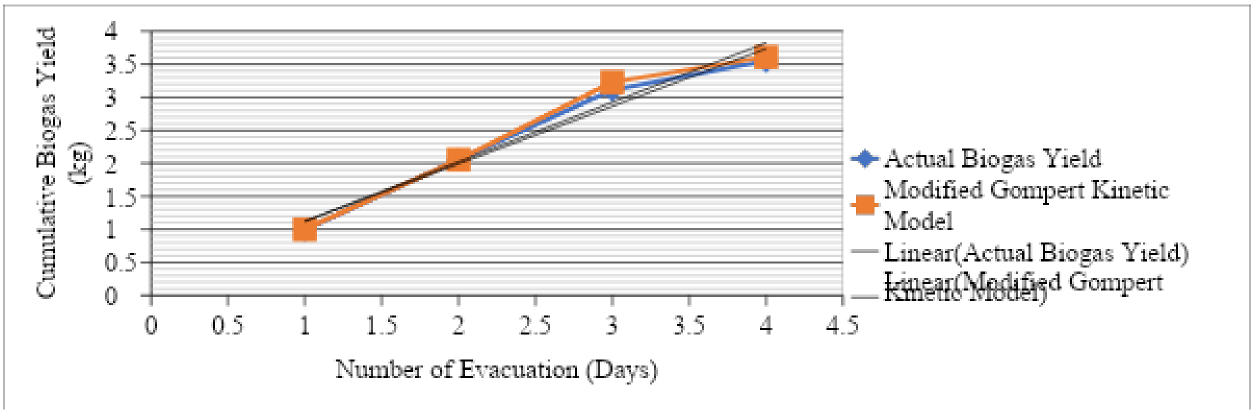

Figure 3: Results of cumulative biogas yield using modified Gompertz kinetic model (S_3= 60 kg)

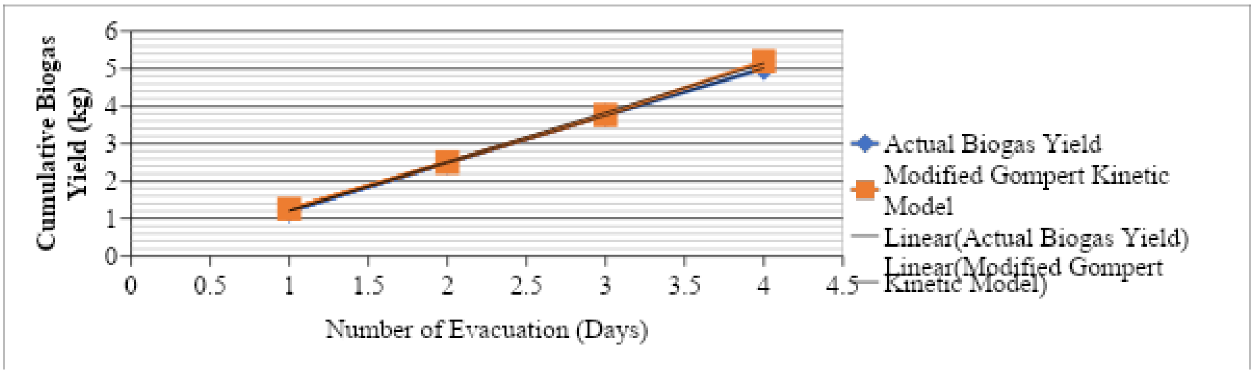

Figure 4: Results of cumulative biogas yield using modified Gompertz kinetic model S_4= 65 kg)

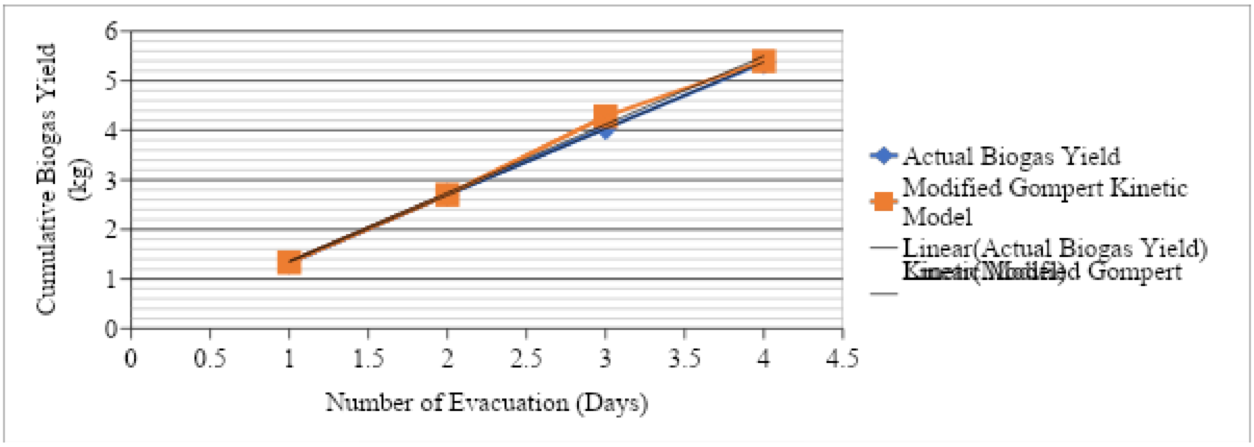

Figure 5: Results of cumulative biogas yield using modified Gompertz kinetic model (S_5= 75 kg)

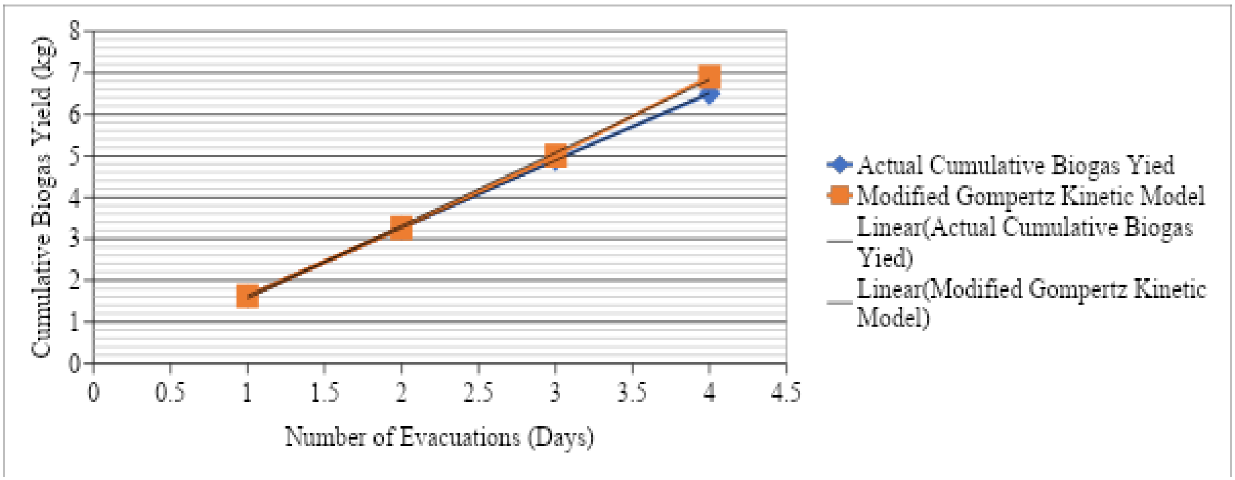

Figure 6: Results of cumulative biogas yield using modified Gompertz kinetic model (S_6= 87 kg)

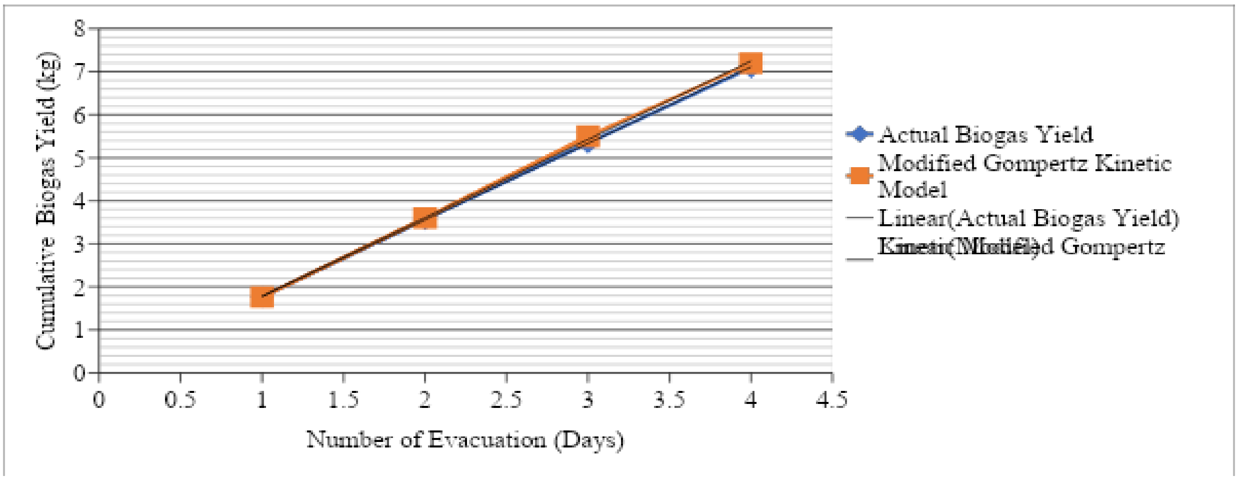

Figure 7: Results of cumulative biogas yield using modified Gompertz kinetic model (S_7= 95 kg)

Table 1: Results of modified Gompertz kinetic model constants parameters

Substrate	Modified Gompertz Kinetic Model			
	A (kg)	**μ**	**λ (d)**	**R^2**
S_1	3.105	0.2903	1.01	0.9986
S_2	3.502	0.3109	1.03	0.9993
S_3	3.560	0.3105	1.04	0.9630
S_4	5.102	0.3210	1.02	0.9963
S_5	5.391	0.3203	1.01	0.9960
S_6	6.528	0.3260	1.01	0.9980
S_7	7.201	0.3587	1.02	0.9985

Table 2 shows the summary of the results obtained with percentage total solid and volatile solid, mesophilic temperature range, pH, hydraulic retention time, and pressure build up as a result of biogas yield. The outcome of the results obtained show that the experiment was conducted using optimum operation and process conditions that favour optimum biogas yield [4, 8, 20].

Table 2: Summary of results of process/operation parameters used

S/N	Parameter	Unit	Results obtained
1	Percentage total solid	%	10.16
2	Percentage volatile solid	%	91.10%
3	Mesophilic temperature range	^oC	37.00
4	pH	m	6.9-7.4
5	Pressure	bar	0.57-1.55
6	Hydraulic retention time	days	37

4. Conclusion

The results of cumulative biogas yield shown that predicted data by modified Gompertz kinetic model were close to the actual data obtain from the performance test evaluation. The coefficient of determination (R^2) was high for modified Gompertz kinetic model (0.9986, 0.9993, 0.9630, 0.9963, 0.996, 0.998, and 0.9985) for each substrate composition (S_1, S_2, S_3, S_4, S_5, S_6, and S_7) used. The modified Gompertz equation well explains cumulative biogas yield as a function of hydraulic retention time.

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