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Biodigestion of Mixed Substrates of Cow Manure-Delignified Spent Coffee Ground (DSCG) using Microorganism Enhancer for Biogas Production and Its Kinetic Study

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Environmentally benign energy strategies have been implemented to cope with the rapidly increased global energy needs. Indonesia's coffee consumption has triggered an increase in the generation of spent coffee ground (SCG) that can be used as a biogas raw material. The novelty that we offer in this research effort is to reduce the premature formation of biogas, so that we can extend the biogas production period during the digestion of spent coffee ground by adjusting the right pH and digestion time. This study aimed to produce biogas from an organic substrate mixture containing cow manure and SCG with a 25:1 C/N ratio by employing effective microorganisms-4 (EM-4). The process began with delignification of SCG using sodium hydroxide solution to obtain delignified SCG (DSCG). The biodegradation of the substrate was performed in an anaerobic batch digestion (AD) system at ambient temperature by varying pH (5, 7, and 9) and EM-4 concentration (6%, 9%, and 12%). The biogas product and chemical oxygen demand measurements were carried out every two days for 60 days of digestion. The results showed that the increase in EM-4 concentration induced earlier initial biogas production enhanced the volume, and extended the production time. The pH 7 level and 9% EM-4 loading gave the ideal digestion substrate condition containing cow manure and SCG with a 25:1 C/N ratio to obtain 11.28 mL of biogas/g COD with 100.2% production enhancement. The modified Gompertz equation fitted the experimental data very well as indicated by a high value of the coefficient of determination (R2 > 0.95).

Keywords: delignified spent coffee ground, enhancer, biogas, anaerobic digestion, Gompertz equation.

Introduction

The organic substrate's conversion to biogas in an anaerobic digestion (AD) occurs following four steps, including hydrolysis, acido, aceto, and methanogenesis. Previous studies have revealed that AD effectively treats wastewater with high organic content (Chow et al., 2020; Harris and McCabe, 2020; Zeeman and Lettinga, 1999). The AD process advantages include high biomethane production, inorganic nutrients, and fertilizer with economic and environmental benefits. This process effectively treats industrial and agricultural wastes (Ahamed et al., 2015) to produce biomethane from their organic substances. Furthermore, AD is proven to be suitable with the tropical climate (Hahn and Figueroa, 2015). Various variables influence the AD process, including pH, temperature, solid particle size, volatile fatty acids, organic loading rate, solid retention time, and nutrient concentration. However, the C/N ratio is an important factor (Kondusamy and Kalamdhad, 2014).

Microbe's growth depends on the nitrogen as the primary nutrient and carbon substance ratio (C/N ratio), ranging from 25 to 30 (Gil et al., 2019). The lack of nitrogen limits the microbial population, while the excess of nitrogen leads to increased ammonia formation and organic carbon degradation. Therefore, the value of the C/N ratio determines the AD process performance. The AD process relies on carbon substances as an energy source and nitrogen to control the microorganism's population (Aziz et al., 2019; Gong et al., 2020).

Biogas is an environmentally friendly alternative energy. Generally, biogas production through the AD process utilizes cow manure waste as substrate. The residual slurry of this process can be used as a high-quality organic fertilizer (Luz et al., 2017). The cow manure contains three components, namely hemicellulose, cellulose, and lignin, at 18.6%, 25.2%, and 20.2%, respectively. Additionally, it also contains nitrogen, phosphate, potassium, and calcium oxide at 0.3%, 0.2%, 0.15%, and 0.2%, respectively. This unique composition provides approximately 20–25% C/N ratio (Luz et al., 2018). Therefore, cow manure requires other materials to increase its C/N ratio. Organic substances, such as agricultural, household, cafeterias, and other wastes are the good candidates to increase the C/N ratio of cow manure (Deublein and Steinhauser, 2008).

Indonesia is among the largest global coffee (Coffea sp.) producers, which contributes about 78% of the world's coffee beans production. Its annual production is 644,000 tons. Approximately 59.2% of them are sold to the global market, while 40.8% of them are used to fulfill domestic consumption (Emmanuel et al., 2017). Currently, coffee is an important drink served on various occasions as a part of society's informal, formal, and business communication. As a result, both the increase in coffee production and consumption have led to the abundant generation of solid coffee waste. Previous reports have shown that spent coffee ground (SCG) contains 12.4% of cellulose, 39.1% of hemicellulose, 23.9% of lignocellulose, 2.29% of fat, 17.44% of protein, and 2.1–2.79% of nitrogen providing a16.91 C/N ratio (Suharman and Gafar, 2017; Ballesteros et al., 2014; Caetano et al., 2017). For this reason, it adequately provides nutrients for biogas production.

Effective microorganism-4 (EM-4) has been reported to improve microorganisms' performance in the AD process, characterized as a brownish and sweet-sour liquid with a perfect cocktail of living microorganisms. Herawati and Wibawa (2010) stated that the EM-4 assists biogas-producing microorganisms to increase cellulose, hemicellulose, and lignin degradation. The microorganisms consist of photosynthetic and lactic acid bacteria, actinomycetes, and yeast. Their inoculant consists of 90% of *Lactobacillus sp.* producing lactic acid, which improves lignin and cellulose digestion (Adhilaksma, 2017).

This study utilized cow manure and DSCG mixture as a substrate and EM-4 to enhance biogas production. Animal manure such as cow is the most popular substrate for full-scale biogas production, despite its low biogas yields. Therefore, this study proposed the co-substrate system to improve biogas production. The experiments were conducted in a batch process, at room temperature and atmospheric pressure, with 60 days of digestion and periodic biogas product measurements. It used initial C/N of 25 and 37,000 mg/L COD ratios. Additionally, the performance of substrate pH and EM-4 addition on the biogas production and COD decline in the AD process was evaluated.

Methods

Materials

The AD experiment utilized naturally fermented cow manure instead of fresh manure called compost fertilizer. It was obtained from an agricultural shop, while the SCG was collected from numerous café shops in Semarang, Central Java. Sodium hydroxide and other chemicals were of analytical grade and were purchased from Merck, Singapore. Meanwhile, the effective microorganism-4 (EM-4) was procured from Indrasari Chemical Store in Semarang.

Substrate preparation

The compost fertilizer was analyzed for its carbon and nitrogen contents before being used as the substrate for the AD experiment to determine the (C/N) ratio. The results indicated that the manure's carbon and nitrogen content were 9.3% and 0.34% (Gil et al., 2019), respectively, providing a 27.35 (C/N) ratio. Prior to the delignification process, the SCG was dried in an oven at 70°C overnight. The dried SCG was delignified using 1.5 N sodium hydroxide solution at 120°C for an hour. The delignified SCG (DSCG) was decanted, the filtrate was removed and was further washed several times with hot water to remove the residual alkali to achieve neutral DSCG material. The DSCG was then dried in an oven at 120°C. The DSCG contained 49.9 % of carbon and 2.70% of nitrogen with a 17.87 (C/N) ratio. Nitrogen is a major limiting nutrient for treating substrates (Kondushamy and Kalamdhad, 2014). Based on the fact that the substrate's ideal carbon to nitrogen ratio for effective digestion is (25–30):1, Candia-Garcia et al. (2017) suggested an 18 to 30 (C/N) ratio for anaerobic digestion. The manure and DSCG (C/N) ratio was adjusted to 25:1 based on optimum anaerobic digestion following a previous study by Herawati and Wibawa (2010). This means that the microorganisms in anaerobic digestion used 25–35 times more carbon than nitrogen.

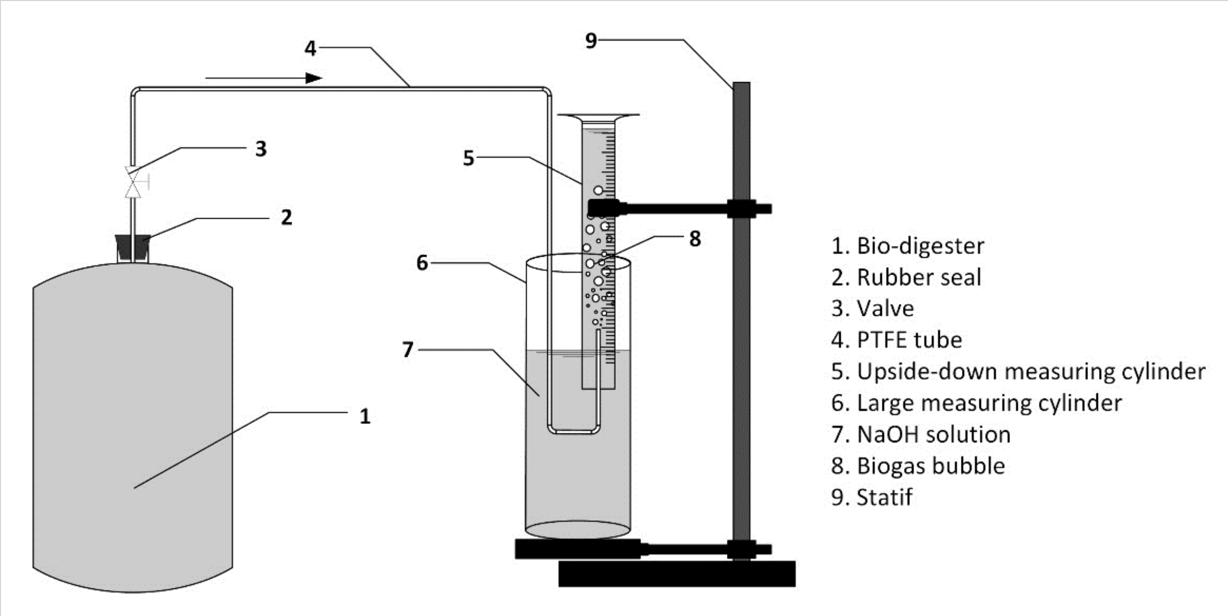
Bio-digestion experiment

The experiments were carried out in a batch biodigester, as shown in *Fig. 1*. The substrate (500 g) was an appropriate pre-determined mixture of cow manure (480.63 g) and DSCG (19.37 g) to obtain a 25 (C/N) ratio. *Table 1* presents the substrate and EM-4 bacteria mixture formula and the amount of water added to achieve 1000 mL mixture volume. The mixture's initial pH value for each variable was adjusted by adding a predetermined volume of buffer solution. The substrate feed was introduced into the biodigester and hermetically closed to allow the achievement of an anaerobic condition. The biogas production volume was recorded every two days during the bio-digestion process, using the water displacement method (Selvankumar et al., 2017). The initial and final (60^{th} day) COD concentrations were analyzed using COD thermoreactor (HANNA HI839800, USA), while the absorbance was measured a spectrophotometer.

Table 1. *Composition of the EM-4 and mixture of cow manure and DSCG for experiments*

Experiment	EM-4 addition (%)	DSCG and Cow manure		EM-4 volume (mL)	The volume of water (mL)
		Volume (mL)	COD (mg/L)		
Control	-	748	37,000	-	252.0
pH = 5	6	748	37,000	44.9	207.4
	9	748	37,000	67.3	184.7
	12	748	37,000	89.8	162.2
pH = 7	6	748	37,000	44.9	207.4
	9	748	37,000	67.3	184.7
	12	748	37,000	89.8	162.2
pH = 9	6	748	37,000	44.9	207.4
	9	748	37,000	67.3	184.7
	12	748	37,000	89.8	162.2

Fig. 1. *Experiment equipment for biogas production*



Kinetic model

The 60 days' digestion data were used to evaluate the kinetic study, while the modified Gompertz model was employed to evaluate the biogas production (Syaichurrozi et al., 2013). The model was based on the AD process completion, corresponding to the methanogenic bacteria growth rate in the digester. The advantage of the modified Gompertz model is that it can predict the initial biogas formation, maximum rate, and cumulative production. The modified Gompertz equation is as follows:

$$y(t) = A \cdot \exp\left\{-\exp\left[\frac{\mu}{A}(\lambda - t) + 1\right]\right\} \quad (1)$$

Where: $y(t)$ – cumulative of specific biogas production (mL/g COD);

A – biogas production potential (mL/g COD);

μ – maximum biogas production rate (mL/g COD. Day);

λ – lag phase or minimum time for biogas production (days);

t – cumulative time for biogas production (days);

e – a constant (2.718282).

The kinetics constants of A, μ, and λ were determined using nonlinear regression.

Results and Discussion

Biogas formation rate

The results (*Table 2*) showed both the cumulative and enhancement of biogas production at various pH and EM-4 loading. The control experiment was performed without the addition of EM-4 as the anaerobic digestion enhancer. As tabulated in *Table 2*, the addition of EM-4 to the substrate mixture in the digestion chamber enhanced biogas production. The biogas production was enhanced from 7.9% to 26.4%, 56.2% to 100.2%, and 33.9% to 62.5% for initial pH of 5, 7, and 9, respectively. The bio-digestion experiments used three pH values, with all pH conditions significantly achieving the biogas production enhancement than the control experiment. However, bio-digestion at a pH of 7 (neutral condition) showed the highest biogas production enhancement than pH of 5 (acidic) and 9 (alkali). The addition of 9% of EM-4 into the digestion system was found to produce a higher biogas production enhancement than those added with 6% and 12% EM-4. The EM-4 positively enhanced biogas

Table 2. *Results of biogas production and COD removal for various variable experiments*

Experiment	EM-4 addition (%)	Cumulative biogas volume (mL)	Biogas production (%)	COD input (mg/L)	COD output (mg/L)	COD removal	
						kg	%
Control	-	53.4	-	37,000	24,666	12,334	33.34
pH = 5	6	57.6	7.9	37,000	23,666	13,334	36.04
	9	69.5	30.1	37,000	22,400	14,600	39.46
	12	67.5	26.4	37,000	21,333	15,667	42.34
pH = 7	6	83.4	56.2	37,000	16,666	20,334	54.96
	9	106.9	100.2	37,000	15,533	21,467	58.02
	12	98.7	84.8	37,000	17,333	19,667	53.15
pH = 9	6	71.5	33.9	37,000	18,200	18,800	50.81
	9	86.8	62.5	37,000	19,400	17,600	47.57
	12	84.2	57.7	37,000	20,200	16,800	45.41

production because it provides an inoculate mixture of living microorganisms that accelerates anaerobic digestion. Food waste substrates contain higher methane than lignocellulosic biomass, animal manure, and sewage sludge (Mao et al., 2017; Gunes et al., 2019). The EM-4 living microorganisms degrade the cow manure and DSCG substrate. Gong et al. (2020) observed that the generation of biogas from cow manure and soluble fraction of SCG in a batch of an anaerobic digester significantly enhanced biogas production by up to 10% compared to that only using cow manure as a substrate.

The pH of the reactor influences both the AD process and the efficiency of the digestion process. Methanogens perform their roles more effectively between pH ranges of 6.5–8.2, with an optimum pH of 7.0. Although it has been previously reported that the optimum pH ranges for obtaining the highest biogas yield in AD are 6.5–7.5, the pH range is generally wide for biogas production plants, and the optimal value of pH may vary with the type of substrate and digestion process (Han and Figueroa, 2015). Indeed, the pH variation can be due to some influential digestion parameters, such as VFA, bicarbonate concentration, alkalinity of the system, and also by the fraction of CO2 produced during the process.

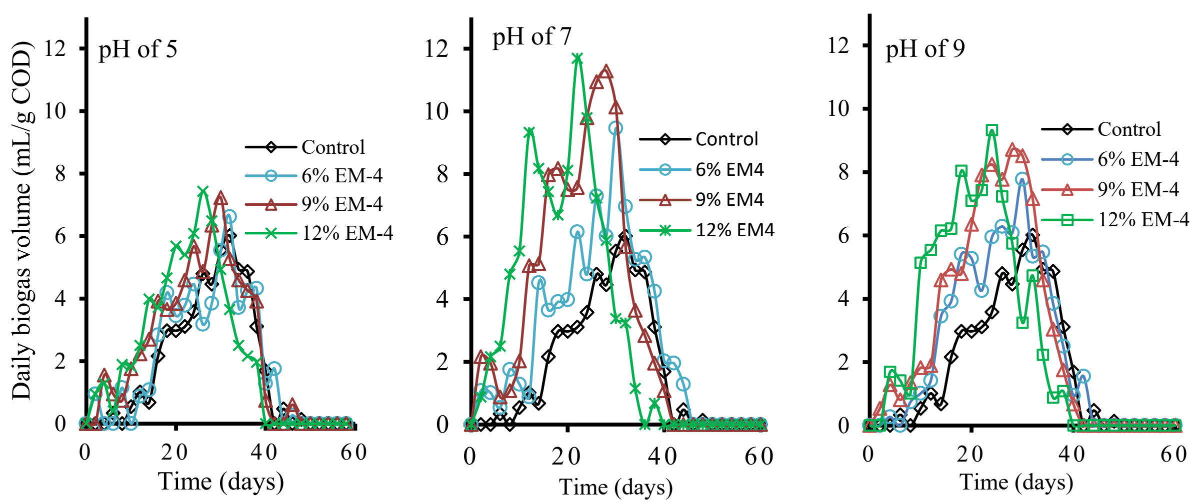
Table 2 also presents that pH is essential in the degradation of organic materials in the AD process. Previous studies reported that the AD performance depended on pH to control the activities of the bacteria group in each stage (Kondusamy and Kalamdhad, 2014; Gunes et al., 2019). Under weakly acidic conditions (pH of 5.5 to 6.5), the bio-digestion process is dominated by hydrolysis and acidogenesis reaction. Some intermediate AD products, such as volatile fatty acids and acetate, were produced in the acidogenesis stage. As a result, the biodigester pH decreased and interfered with the biogas formation. The methanogenesis stage is the most sensitive to pH changes and is usually optimum at neutral conditions (7.0 ± 0.2) (Ali et al., 2019; Han et al., 2015). The AD's performance decreased at alkaline conditions (9) due to the reduction of methanogenesis bacteria, and led to a decline of the biogas formation. An increased COD removal rate was achieved through anaerobic bio-digestion of organic substrate derived from the mixture of cow manure and SCG with addition of EM-4 (Labatut et al., 2011). The trend of COD removal was similar to the biogas production enhancement. The anaerobic bio-digestion with an additional 9% EM-4 at neutral condition (pH of 7) yielded the highest biogas production and COD removal enhancement.

Table 3 and *Fig. 2* (*a, b, c*) demonstrate the biogas production along the experiments (digestion time with various pH and EM-4 addition). All experiment conditions show the typical phase of the bio-digestion

Table 3. *Data of pH and the EM-4 addition on the biogas production*

Experiment	EM-4 addition (%)	First biogas production day (th day)	Highest biogas production		Decrease of biogas production	
			(th day)	Vol (mL/g COD)	(th day)	Vol (mL/g COD)
Control	-	6th	34th	3.72	36th	1.96
pH = 5	6	2nd	32nd	5.27	46th	0.41
	9	2nd	30th	7.23	46th	0.61
	12	2nd	26th	7.43	38th	1.96
pH = 7	6	2nd	30th	9.46	44th	1.28
	9	2nd	28th	11.28	40th	1.08
	12	2nd	22nd	11.69	38th	0.68
pH = 9	6	4th	30th	7.77	42nd	2.03
	9	2nd	28th	9.72	40th	0.68
	12	4th	24th	9.32	38th	1.08

Fig. 2. *Daily biogas production with various EM-4 addition at different pH conditions*



process, including the adaptation, log, stationary, and death. The control experiment of bio-digestion substrate (without EM-4 addition) started to produce biogas on day 6, reaching the highest production on day 34 (3.72 mL/g COD). However, its biogas production leveled off on day 36 (1.96 mL/g COD). Furthermore, the EM-4 addition shortened the initial biogas production period and increased biogas volume compared with the control experiment.

The bio-digestion under weak acidic and neutral conditions (pH 5 and 7) with a 6% to 12% EM-4 addition produced biogas on day 2. Meanwhile, the biogas production under alkali conditions (Budiyono et al., 2010) began on days 2–4, earlier than the control experiment. The DSCG, as the digestion co-substrate consisted of cellulose, hemicellulose, and lignocellulose, improved digestion performance. The delignification process reduced the lignin content that is difficult to degrade. Previous studies have explained that the DSCG maintains the substrate pH in the biodigester, hence, the pH decline was less than without DSCG (Luz et al., 2017; Orfanoudaki et al., 2020). The EM-4 easily utilized the cellulose and hemicellulose in the DSCG to accelerate biogas production.

The control experiment achieved its highest biogas production (3.72 mL/g COD) on day 34. This experiment also had a shorter digestion period than those with 6% to 12% EM-4 addition and 5 to 9 pH, obtaining the highest biogas production. The EM-4 addition extended the biogas production period and increased cumulative volume. A 6% to 12% EM-4 addition reduced the initiation biogas formation period than the control experiment. *Fig. 2* (*b*) shows that the neutral condition (pH of 7) was the ideal digestion performance for the highest biogas production period and accumulative volume than under acidic (pH of 5) and basic (pH of 9). The biogas production completion period was influenced by the EM-4 addition, increasing the bio-digester substrate with a shorter digestion period. The results showed a lower biogas production rate than the bio-digestion using domestic, and restaurant food wastes substrates, classified as high-methane substrates due to high lipids and other nutrient contents (Meng et al., 2015; Feng and Lin, 2017).

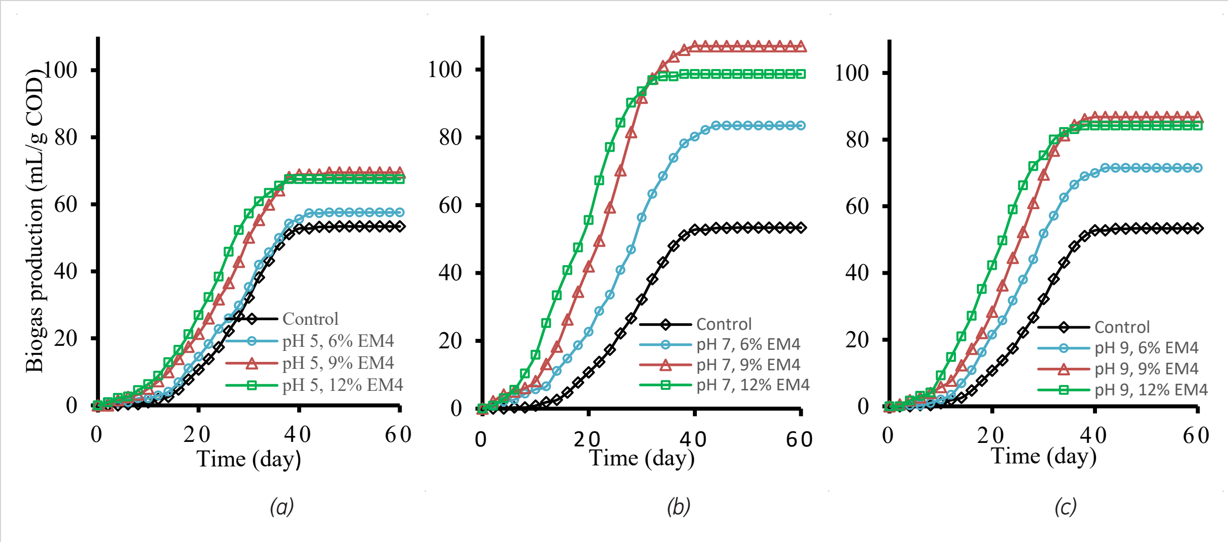
The pH is essential in the AD process because it influences the solubilization of substrates (Dai et al., 2016), suitable for microbes (Neshat et al., 2017), and causes simultaneous enzymatic reactions (Xu et al., 2018). The first step of the anaerobic process involves acidic pH conditions at pH of 5.5–6.5 through a short period (hydraulic retention time of 2–3 days) of acid fermentation (Megawati, 2014). The pH of 5 conditions had acid compounds, requiring a longer biogas production time. In contrast, a higher pH conditions (neutral and basic) increased biogas production and shortened the bio-digestion time. Surprisingly, the neutral conditions (7) showed better digestion performance for the highest biogas production and accumulative volume than other conditions.

The biogas production depends on the AD complete process because it produces CH4 and CO2. Methane is produced in the 6.8–7.2 pH range (Ajay et al., 2021; Allah et al., 2021). Efficient methane production depends on the reactor's stability, with pH as the crucial factor (Ali et al., 2019), and is sensitive to pH changes (Ajay et al., 2021). Anaerobic digestion involves the degradation of organic substances through microorganisms, especially anaerobic microorganisms. Furthermore, it is sensitive to pH value variations. In AD, acidification and methanogenesis depend on a specific pH optimum to degrade organic substances. The acidification pH optimum ranges within 5.5–6.5 and 7.8–8.2 for methanogenesis. The pH level indicates the biogas production quality (Jafar and Awad, 2021). Karamichailidou et al. (2022) have stated that pH is essential in AD, where methanogenic bacteria perform better at a pH of 5.5 to 8.5, and the acidogenic bacteria produce high organic acids and lower the pH value below 5.0 at an optimum pH range of 6.5–8.0, lethal to methanogens bacteria. In contrast, pH values above 8 are highly toxic for most anaerobic organisms, inhibiting their biological functions. Higher methanogen bacteria increase pH values and inhibit acidogenesis (Lohani and Havukainen, 2018). Some studies have investigated the pH effects on AD to produce biogas and found that pH for anaerobic digestion ranged from 6.8 to 8.5 (Glivin et al., 2022), while the pH optimum of methanogens bacteria for chicken manure degradation ranged between 6.5 and 7.2 (Hakimi et al., 2021), 6.8–7.4 (Allah et al., 2021), 6.8–7.2 (Domrongpokkaphan et al., 2021), and 6.5–7.3 (Ajay et al., 2021). Additionally, others have described the ideal pH for methanogenesis as 7, while the hydrolysis and acidogenesis ranged within 5.5–6.5, and the correct pH range was 6.8–7.2 (Buragohain et al., 2021).

Cumulative biogas production

Fig. 3 shows that all the EM-4 addition percentages produced similar trends for the cumulative biogas production at each interval. A 6% EM-4 addition at a pH 5 obtained a higher cumulative biogas volume than the control experiment. In contrast, the EM-4 addition of 9% and 12% produced higher cumulative biogas volume than the control experiment, which were 67.5 mL/g and 69.5 mL/g COD, respectively. The EM-4 addition shortened the initial biogas formation, reducing the lag time (λ) of Gompertz's kinetic model. Additionally, it proliferated various useful microorganisms

Fig. 3. *Profile of cumulative biogas production of (a) pH of 5, (b) pH of 7, and (c) pH of 9*



in the bio-digestion system, which play an important role in accelerating biogas production. A higher EM-4 addition percentage value reduced the biogas formation period due to increased microorganisms in the anaerobic digester. *Fig. 3* (*b*) indicated a higher cumulative biogas production volume difference between the control experiment and with EM-4 addition under neutral conditions (pH of 7). Increased EM-4 addition shortened the biogas production period (the EM-4 addition of 12%). However, the highest cumulative biogas volume was obtained using a 9% EM-4 addition at bio-digestion.

Higher EM-4 addition increased microorganisms in the bio-digestion system and effectively degraded the substrate to achieve the stationary phase faster (Budiyono et al., 2010). The death phase at a 12% EM-4 addition had an earlier completion than the 6% and 9%. The EM-4 with several living microorganisms indicated the system's improvement. This is due to better EM-4 bacteria performance in the organic matter decay process, accelerating the biogas formation (Luz et al., 2018). A higher substrate degradation rate caused a quicker substrate depletion to fasten the death phase. The bio-digestion experiment with a 9% EM-4 addition produced the highest biogas volume than others due to the microorganism growth's substrate supply and demand balance.

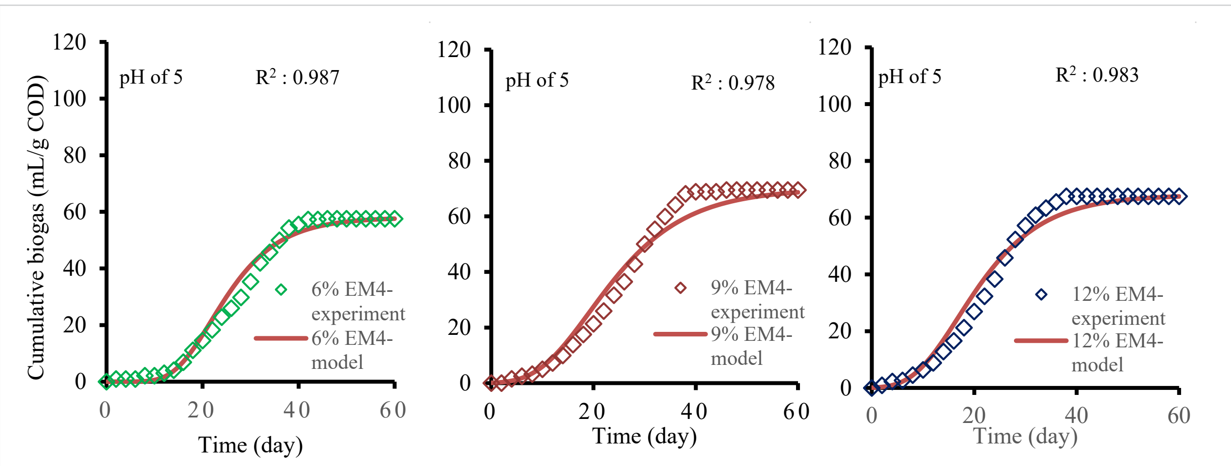
Kinetic model of biogas production

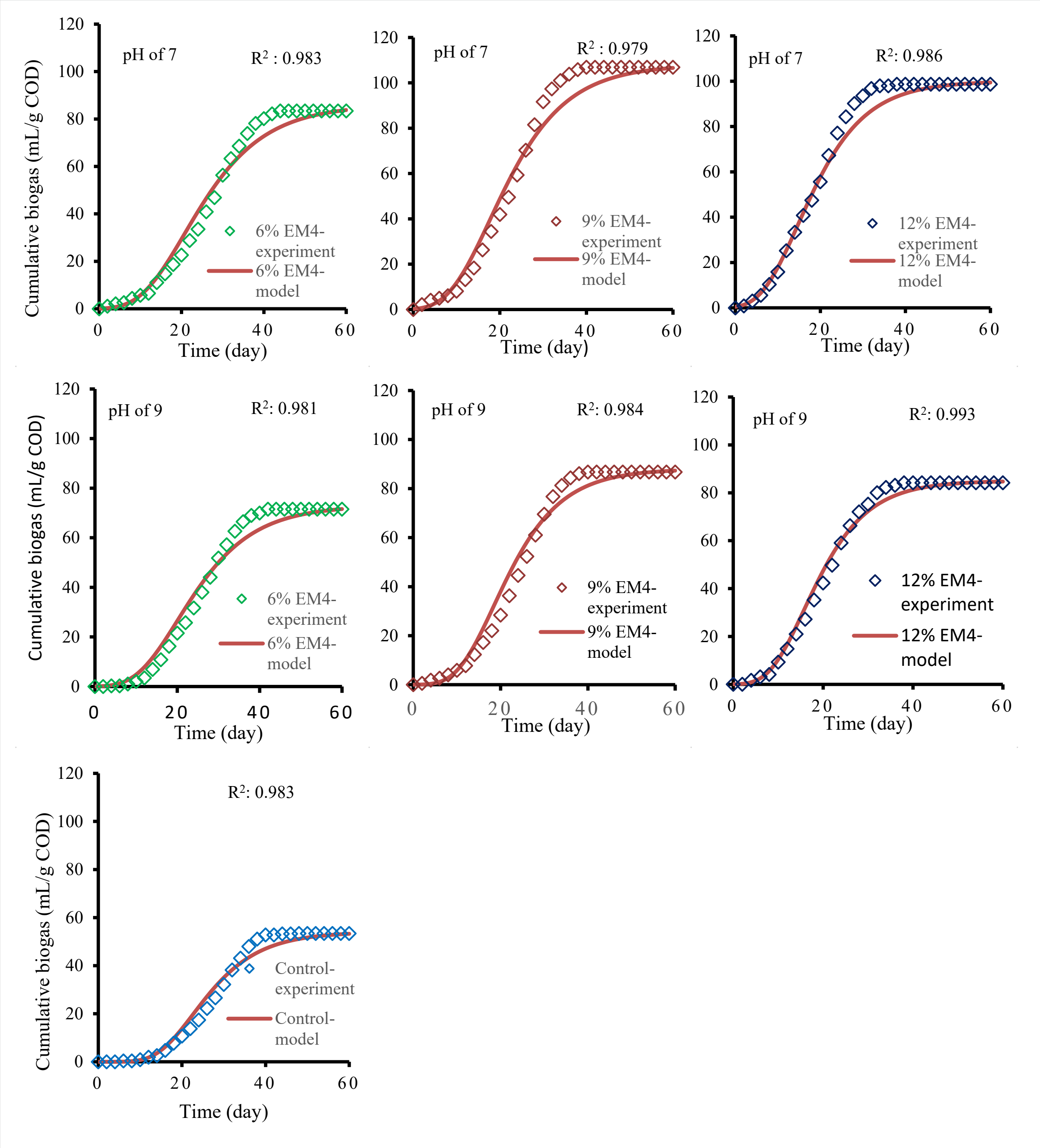
Kinetic modeling optimized the biogas production and predicted the anaerobic bioreactor performance. The modified Gompertz model was introduced to the data shown in *Fig. 3* (Budiyono et al., 2010). This model explains the bacteria growth as the time function. It contains three parameters of A, λ, and μ as a nonlinear model to predict microorganism's growth requiring a longer adaptation period to the substrate at a frequent exponential form. The term λ indicates the lag phase period or the minimum time to produce biogas, and a smaller λ value is better because the system requires a shorter production period. In contrast, a higher λ value indicated slow microorganism's substrate adaptation. The λ value describes the substrate's soluble organic materials in the liquid phase, consumed faster by microorganisms in the anaerobic process (Li et al., 2018). The A parameter described the maximum biogas production, with a higher A value indicating better system performance to produce biogas. The μ value showed the rate of maximum biogas production indicated by the curve's slope to achieve maximum biogas. *Table 4* shows the kinetic model constants from the modified Gompertz equation for all variable experiments. The nonlinear regression provided the constant parameters of A, μ, and λ. *Fig. 4* shows the cumulative biogas production comparisons from experiments and simulation.

Table 4. *Kinetic constant data of Gompertz equation of biogas production*

Variable	EM-4 addition	A mL/g COD	μ mL/g COD.day	λ (days)	R^2	Author
Control	-	54	2.28	14	0.983	This study
pH = 5	6%	58	2.75	14	0.987	
	9%	70	2.50	9	0.978	
	12%	68	2.80	8	0.983	
pH = 7	6%	86	2.94	10	0.983	
	9%	108	4.07	8	0.979	
	12%	100	4.20	6	0.986	
pH = 9	6%	73	2.65	10	0.981	
	9%	88	3.80	10	0.984	
	12%	85	4.01	8	0.993	
Food waste		60.03–65.22 mL CH_4/g VS	0.22–1.38 mL CH_4/g VS. d	0.09–0.49	0.925–0.990	(Li et al., 2018)
Salvinia molesta and rice straw		54.65–60.05 mL biogas/g TS	2.06–2.62 mL biogas/g TS. d	3.75–4.54	0.985–0.991	(Syaichurrozi et al., 2018)
Cattle manure		418.260 mL CH4/g VS	9.490 mL CH_4/g VS. d	4.460	-	(Budiyono et al., 2010)
Municipal solid waste		522 mL CH4/g VS	97 mL CH_4/g VS. d	1.2	0.983	(Zhu et al., 2009)
Water Hyacinth		449.4 mL CH4/g VS	27.9 mL CH_4/g VS. d	6.625	0.981	(Patil e al., 2012)
Poultry litter		390.4 mL biogas/g TS	16.5 mL CH_4/g VS. d	8.749	0.999	(Adiga et al., 2012)

Fig. 4. *Cumulative biogas production at the various conditions of experiments*





The determination coefficient values were high, ranging from 0.978 to 0.993 (*Table 4*). These values showed the suitability of the modified Gompertz model to describe the mixed substrate's AD containing cow manure and DSCG. All graphs indicated a determination coefficient above 0.95. The value of R^2 indicated the data's significance to the model, showing more consistent data with the modified Gompertz model.

The test validity showed the data from the experiments compared to the model (*Fig. 4*). *Table 4* shows the model's constants.

The control condition was the base to evaluate the added enhancer. Various enhancer additions (6% to 12%) at pH 5 and the λ, A, and μ values indicated that the enhancer had positive effects on the biogas product. Increased enhancer percentage increases the maximum biogas product (54 mL/g COD for control and 58 mL/g to 70 mL/g COD for experiments) and the biogas formation rate (2.28 mL/g COD. day for control to 2.75 mL/g to 2.80 mL/g COD.day for experiments), decreasing the lag time (14 days for control and 14 to 8 days for experiments). The biogas formation was caused by the complete anaerobic degradation of the organic substances, producing CH_4 and CO_2. The enhancer improved the microorganisms' activity to improve the biogas formation, with higher enhancer addition positively improving the biogas production. Therefore, the highest biogas produced was achieved at the 9% enhancer (70 mL/g COD), with the biogas formation rate at 12% of the enhancer (2.80 mL/g COD. day), and greater addition lowered the lag time.

The A value of the modified Gompertz equation at pH of 7 was 86 mL/g to 108 mL/g COD, μ had 2.94 mL/g to 4.20 mL/g COD, and λ had 10 to 6 days. The enhancer addition at 6% to 9% increased the value of A and μ constants but reduced at the 12% addition. Not all higher enhancer additions increased biogas production, indicating that at the 12% enhancer addition, the Gompertzs' constant value was opposite for A and μ, and only the λ constant linear value with greater enhancer reduced the lag time. Therefore, greater enhancer addition only accelerated the lag time to produce biogas, not the rate and maximum biogas production.

A pH of 9 and enhancer addition of 6% to 12% had a similar biogas production pattern to the pH of 7. There was increased maximum biogas production at 9% of the enhancer (88 mL/g COD) and μ constant value (2.65 mL/g to 4.01 mL/g COD. Day), while λ constant reduced (10 to 8 days) with an increased enhancer addition. The enhancer addition improved with the control condition, but increased pH indicated nonlinear Gompertzs' parameter correlation.

The results showed that similar enhancer additions (6% to 12%) and increased pH (5 to 9) improved the A constant value enhanced at 9% and pH of 5, 7, and 9, with the highest value at pH 7 of 108 mL/g COD. In contrast, the parameters of μ and λ correlated with the enhancer addition. Increased the amount of enhancers indicate the improve value of μ and shortened value of λ , respectively.

The maximum biogas production rate of the modified Gompertz equation (μ) value was related to the maximum biogas production rate. The control condition showed the slowest biogas production rate, with the lowest μ value (2.28 mL/g COD/day) than the other experimental conditions. *Table 4* and *Fig. 4* show that the highest μ value was obtained at a neutral condition (pH of 7) and a 12% enhancer addition, suggesting quicker biogas production. The A and μ values were better than the food waste, Salvinia molesta, and rice straw (Lia et al., 2018; Syaichurrozi et al., 2018), but the value of λ was longer (based on Volatile Solid, VS). Furthermore, the values of μ were 2.5 mL/g to 4.2 mL/g COD. day, lower than in previous studies (*Table 4*) using cattle manure, municipal solid waste, water hyacinth, and poultry litter as substrates (Zhu et al., 2009; Patil et al., 2012; Adiga et al., 2012; Li et al., 2018).

The AD exhibited a shorter biogas formation period, and the enhancer addition effectively reduced the λ value (*Table 4*) and improved biogas production. Neutral conditions (7) with a 12% enhancer addition showed the lowest λ value (6 days). Increased EM-4 addition benefited the system by increasing the microorganisms to accelerate the organic material degradation to form biogas. However, the lag time (λ) values were higher than in the previous studies (*Table 4*), indicating a slower mixed substrate (cow manure, DSCG, and enhancer) degradation. The longer degradation time was due to the high lignin content of the SCG (Budiyono et al., 2010).

The utilization of DSCG as the raw material for biogas production in a batch anaerobic reactor offers many advantages and can be promisingly implemented due to the following reasons: it is coherent with the united nation's sustainable development goals (SDGs) program; it can be used as an alternative fuel to fuel oil and coal for the electricity generation; it helps to solve the environment issue; it can save household operational costs as a substitute to firewood, fuel, oil, and gas that are relatively more expensive than biogas; the solid residue obtained from the biogas digesters can be used as a high-quality organic fertilizers; and lastly, it can significantly contribute to reducing greenhouse gas emissions due to lack of fuel consumption of oil and wood.

Conclusion

The result showed that the (C/N) ratio upon the completion of the delignification (DSCG) was 17.87. The C/N ratio value indicated that DSCG combined solid waste with a high (C/N) ratio to generate alternative energy. This study used a (C/N) ratio of 25, a pH of 5–9, and an additional enhancer of EM-4 (6–12%). Basically, the biogas in the AD process was strongly affected by the pH because its production was at the final stage of AD degradation. Experimental observation revealed that the mixed substrate of DSCG and cow manure produced higher cumulative biogas (108 mL biogas/g COD) at a pH of 7 and a 9% enhancer addition. The modified Gompertz model plot resulted in a greater determination coefficient (R2) for all data, which were above 0.95. The highest cumulative biogas produced at pH of 7 and the enhancer of 9% estimated by the Gompertz model resulted in some optimized adjustable digestion parameters, such as cumulative biogas (108 mL biogas/g COD), rate of production (4.02 mL biogas/g COD.day), and lag phase period or minimum production time (8 days).

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