Research Article
Kinetic Model of Biogas Yield Production from Vinasse at Various Initial pH: Comparison between Modified Gompertz Model and First Order Kinetic Model

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Abstract: Anaerobic treatment using anaerobic digestion can convert organic materials of vinasse into biogas. The purpose of this study was modeling kinetic of biogas production using modified Gompertz model and first order kinetic model at variation of initial pH. Substrates were consisted of two kinds of compositions, which were vinasse+rumen (VR) and vinasse+rumen+urea (VRU). Initial pH in each substrate was 6, 7 and 8. Degradation process was done in 30 days using batch anaerobic digesters at room temperature. Both, at VR and VRU, initial pH of 7 generated the more total biogas than the others two (initial pH of 6 and 8). Biogas formed at substrate of VRU was more than that at substrate of VR. The best condition was substrate of VRU and initial pH of 7. At best condition, kinetic constants of biogas production model using modified Gompertz were ym (biogas production potential) = 6.49 mL/g VS; U (maximum biogas production rate) = 1.24 mL/g VS. day; λ (minimum time to produce biogas) = 1.79 days. Whereas kinetic constants of biogas production model using first order kinetic were ym (biogas production potential) = 6.78 mL/g VS; k (biogas production rate) = 0.176 /day. The difference between the predicted and measured biogas yield (fitting error) was higher with the first-order kinetic model (1.54-7.50%) than with the modified Gompertz model (0.76-3.14%).

Keywords: Biogas, first order kinetic model, initial pH, modified gompertz model, vinasse

INTRODUCTION

Biogas is gas formed from degradation of organic materials under anaerobic condition. The degradation is consisted of four major phases that are hydrolysis, acidogenesis, acetogenesis and methanogenesis (Esposito *et al*., 2011). Many authors have studied the biogas production from organic materials. Budiyono *et al*. (2010) studied the biogas production from cattle manure. Adiga *et al*. (2012) produced biogas from water hyacinth, poltry litter, cow manure and primary sludge. Sumardiono *et al*. (2013) and Budiyono *et al*. (2013) investigated the potential of vinasse as feed stock of biogas under anaerobic condition. Zhu *et al*. (2009) utilized municipal solid waste as feed stock of biogas. Patil *et al*. (2012) studied biogas production from water hyacinth.

Recently, some authors have made prediction of biogas production potential using modified Gompertz model (Budiyono *et al*., 2010; Adiga *et al*., 2012; Patil *et al*., 2012) and first order kinetic model (Raposo *et al*., 2009; Kafle *et al*., 2012). Modified Gompertz model was developed by Zwietering *et al*. (1990) to predict bacterial growth. By assume that biogas production rate had correspondence to methanogenic bacterial growth rate in digester, some authors (Budiyono *et al*., 2010; Adiga *et al*., 2012; Patil *et al*.,

2012) used modified Gompertz model to predict biogas production potential. Besides that, kinetic of biogas production also could be modeled by using first order kinetic (Raposo *et al*., 2009; Kafle *et al*., 2012). Both of them, modified Gompertz model and first order kinetic model, give the different result in predicted biogas production. According to Kafle *et al*. (2012), the prediction of biogas yield using modified Gompertz model (fitting error 0.7-13.7%) was more accurate than first order kinetic (fitting error 9.2-37.1%). In other hand, Raposo *et al*. (2009) reported that first order kinetic could be used to predict biogas yield with good fitting error (10% or less). The different results may be caused by kind of substrates, where Kafle *et al*. (2012) used fish industry waste and Raposo *et al*. (2009) used sunflower oil cake (SuOC).

Based on information above, the accuracy of biogas yield prediction in model is depended on substrates that are used as feedstock. That means, using of modified Gompertz and first order kinetic in making kinetic of biogas yield production must be aware of the substrates used to get the best accurate prediction.

In this study, authors compared kinetic model of biogas production from vinasseobtained using modified Gompertz and using first order kinetic model. Sumardiono *et al*. (2013) investigated the effect of pH control and COD/N ratio to biogas production.

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Budiyono *et al*. (2013) studied the influence of initial pH and pH control to biogas production. However, Sumardiono *et al*. (2013) and Budiyono *et al*. (2013) have not modeled the kinetic of biogas production from vinasse. In addition, the comparison of modified Gompertz and first order kinetic at vinasse as feedstock of biogas has not been reported by other authors yet, whereas this information was important. Thus, this study was necessary to do.

MATERIALS AND METHODS

Wastewater and inoculum: The wastewater used was vinasse obtained from an ethanol industry. The ethanol industry located in Solo, Central Java, Indonesia, that produced ethanol from molasses. Properties of vinasse that was used as biogas feedstock are shown in Table 1.

The rumen fluid was used as inoculum. In this study, rumen fluid in fresh condition was obtained from slaughterhouse in Semarang, Central Java, Indonesia.

Experimental set up: Anaerobic digesters were made from polyethylene bottles which have a volume of 600 mL. The bottles were plugged with rubber plug and were equipped with valve for biogas measurement. Anaerobic digesters were operated in batch system and at room temperature. Biogas formed was measured by liquid displacement method as also has been used by the other authors (Budiyono *et al*., 2010; Yusuf *et al*., 2011; Yusuf and Ify, 2011). The anaerobic digestion of experimental laboratory set up is shown in Fig. 1.

Experimental design: Anaerobic digestion of experimental laboratory using 600-mililiter volumes was operated in batch system. 250-mL substrate was put intodigesters. Rumen fluid as methanogenic bacteria provider that was added into the digesters as much as 10% v/v substrate.

Initial pH was adjusted 6, 7 and 8 by using NaOH solution 10 N.Composition of substrate was divided into two terms, which were Vinase+Rumen (VR) and Vinase+Rumen+Urea (VRU). Urea (46% Nitrogen content) added into substrate was I gram. Degradation process was done in 30 days. The variables in this study can be seen in Table 2.

Experimental procedures: Biogas formed was measured every once in two days to know biogas production with water displacement method (Fig. 1). pH substrates in the digester were measured by pH meter every once in two days to know pH profile daily.

Kinetic model of biogas yield production:
Modified Gompertz model: Biogas production kinetic was modeled through modified Gompertz model (Zwietering *et al*., 1990). Kinetic of biogas production in batch condition was assumed that had correspondence to specific growth rate of methanogenic bacteria in digester (Budiyono *et al*., 2010; Yusuf *et al*.,

Table 1: Vinasse properties

Parameters	Values
COD	299, 250±1.060
Crude carbohydrate	268, 647±0.000
Crude protein	9, 117±0.000
Crude fat	6, 894±0.000
TS	27.865±0.000
VS	284, 659±0.000
pH	3.25±0.212
N	1, 458±0.000

Remarks: COD, chemical oxygen demand (mg/L); TS, total solid (%); VS, volatile solid (mg/L); pH, power of hydrogen; N, nitrogen content (mg/L); crude carbohydrate (mg/L); crude protein (mg/L); crude fat (mg/L)

Table 2: Variable of composition of substrate and initial pH

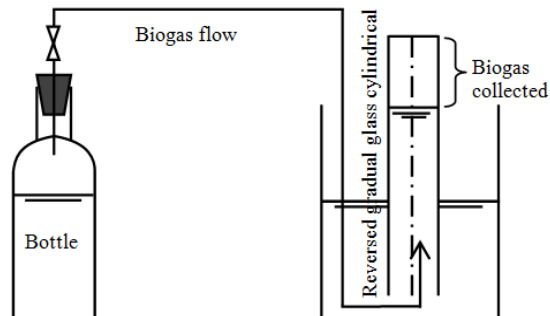| Run	Composition of substrate	Initial pH
1	Vinasse+Rumen	6
2		7
3		8
4	Vinasse+Rumen+Urea	6
5		7
6		8

Fig. 1: The batch anaerobic digestion of experimental laboratory set up

2011; Zhu *et al*., 2009; Patil *et al*., 2012; Adiga *et al*., 2012). The modified Gompertz equation as follows:

$$y(t) = y_m . \exp\left\{-\exp\left[\frac{U.e}{y_m}(\lambda - t) + 1\right]\right\} \qquad (1)$$

where,
$y(t)$ = The cumulative biogas yield at a digestion time t days (mL/g VS)
y_m = The biogas production potential (mL/g VS)
U = The maximum biogas production rate (mL/g VS.day)
λ = Lag phase period or minimum time to produce biogas (days)
t = Cumulative time for biogas production (days)
e = Mathematical constant (2.718282)

Kinetic constant of y_m, λ and U was determined using non-linear regression with help of polymath software (Budiyono *et al*., 2010; Patil *et al*., 2012; Adiga *et al*., 2012).

- **First order kinetic model:** Biogas yield production was modeled using first order kinetic model as also has been used by Kafle *et al*. (2012). The first order kinetic model as follows:

$$y(t) = y_m (1-\exp(-k*t)) \qquad (2)$$

where,

y(t) = The cumulative biogas yield at a digestion time t days (mL/g VS)

y_m = The biogas production potential (mL/g VS)

k = The biogas rate constant (1/day)

e = Mathematical constant (2.718282)

RESULTS AND DISCUSSIONS

Kinetic of biogas yield production using modified Gompertz Model: Cumulative biogas yield production experimental data obtained was used to make kinetic model of biogas production through modified Gompertz model. Kinetic constant of y_m, U and λ was determined by using non-linear regression. Kinetic constants obtained were presented completely in Table 3. By plotting experimental data and simulation of modified Gompertz model was obtained the graph as shown in Fig. 2.

At substrate of VR (Vinasse+Rumen), initial pH of 7 generated the more biogas yield (3.74 mL/g VS) than the other variables, which were initial pH 6 (3.19 mL/g VS) and initial pH 8 (3.43 mL/g VS). Some authors reported that pH condition of neutral produced biogas maximally. According to Metcalf (2003), the best range pH condition to produce biogas was 6.9-7.3. Anderson and Yang (1992) stated that 6.4-7.6 was the optimum range in anaerobic digestion. Budiyono *et al*. (2013) reported that pH neutral (7) was the best pH condition needed anaerobic bacteria to do degradation process and generate biogas. Thus, pH neutral was the optimum condition in biogas production process.

From Fig. 3a, variable with initial pH of 6, 7, 8 had the same pH profile daily, but initial pH of 7 generated the most of total biogas. Based on that, lag period, that time needed bacteria to adapt in substrate, was the main point which was at the first two day.

Decreasing in pH was caused by production of VFAs (Volatile Fatty Acids) during fermentation. Vinasse obtained in this study was produced from ethanol industry that produced ethanol from molasses. In the process of producing ethanol, molasses was hydrolyzed and fermented with help of *Saccaromyces cerevisiae*. Then, ethanol formed was separated from broth using distillation. The bottom product of distillation was called vinasse so that vinasse contained many simple molecular chain compounds (Budiyono *et al*., 2013). These compounds were degraded easily by bacteria so that VFAs was formed in large amount. Accumulation of VFAs caused drop in pH (Fig. 3). Sumardiono *et al*. (2013) reported that during degradation process of vinasse in the anaerobic digesters, pH profile of substrate had decreasing trend from beginning until ending of process. That was caused by high carbohydrate content of vinasse. Substrates that were rich carbohydrate generated VFAs in large amount. Yadvika *et al*. (2004) stated that concentration of VFAs in digester was no more than 2000 mg/L that was good for fermentation process.

During fermentation process, there are two kinds of organic acid in the substrate, which are not dissociated acid and dissociated acid (Deublein and Steinhauser, 2008). The ratio composition of them is depended on pH substrate. The more acid condition of substrate, the more amount of not dissociated acid. In this study, pH substrate was drop (Fig. 3), so the kind of organics acid that was dominant, was not dissociated acid. Presence of not dissociated acid hampered the methanogenic bacterial activity. Not dissociated acid was penetrated into cell and denatured the protein of bacteria (Deublein and Steinhauser, 2008). Whereas, According to Brannen and Davidson (1993), the inhibitory mechanism of bacterial activity by organic acid (acetic acid, propionic acid, butyric acid) was related with acid-base equilibrium. Acid-base equilibrium in cell of bacteria was in neutral condition of pH. Organic acid penetrated into cell, disturbed acid-base equilibrium so that bacterial cell was lysis. Changing in pH could spoil protein, nucleic acid and phospholipid in cell bacteria. At pH condition less than 7, presence of acetic acid of 1000 mg/L could hamper degradation process. Whereas, iso-butyric acid and iso-valeratewere 50 mg/L; propionic acid was 5 mg/L (Deublein and Steinhauser, 2008).

At substrate of VRU (Vinasse+Rumen+Urea), initial pH of 7 also generated the more cumulative biogas yield (6.53 mL/g VS) than the others, which were initial pH of 6 (4.55 mL/g VS) and initial pH of 8 (3.82 mL/g VS). Initial pH of 7 was the optimum initial pH condition at substrate with or without urea addition. Addition of urea did not change the pH profile (Fig. 3b). It showed that VFAs was generated rapidly and in

Table 3: Kinetic constant of modified Gompertz model

Variable		Modified Gompertz model			
		y_m (mL/g VS)	U (mL/g VS. day)	λ (day)	R^2
V+R	Initial pH 6	3.29	0.22	-0.52	0.986
	Initial pH 7	3.68	0.88	1.60	0.996
	Initial pH 8	3.49	0.29	2.24	0.997
V+R+U	Initial pH 6	4.51	0.69	0.45	0.996
	Initial pH 7	6.49	1.24	1.79	0.998
	Initial pH 8	3.71	0.38	2.12	0.985

Remarks: V, vinasse; R, rumen fluid; U, urea; y_m, biogas production potential; U, maximum biogas production rate; λ, minimum time to produce biogas; R^2, correlation coefficient
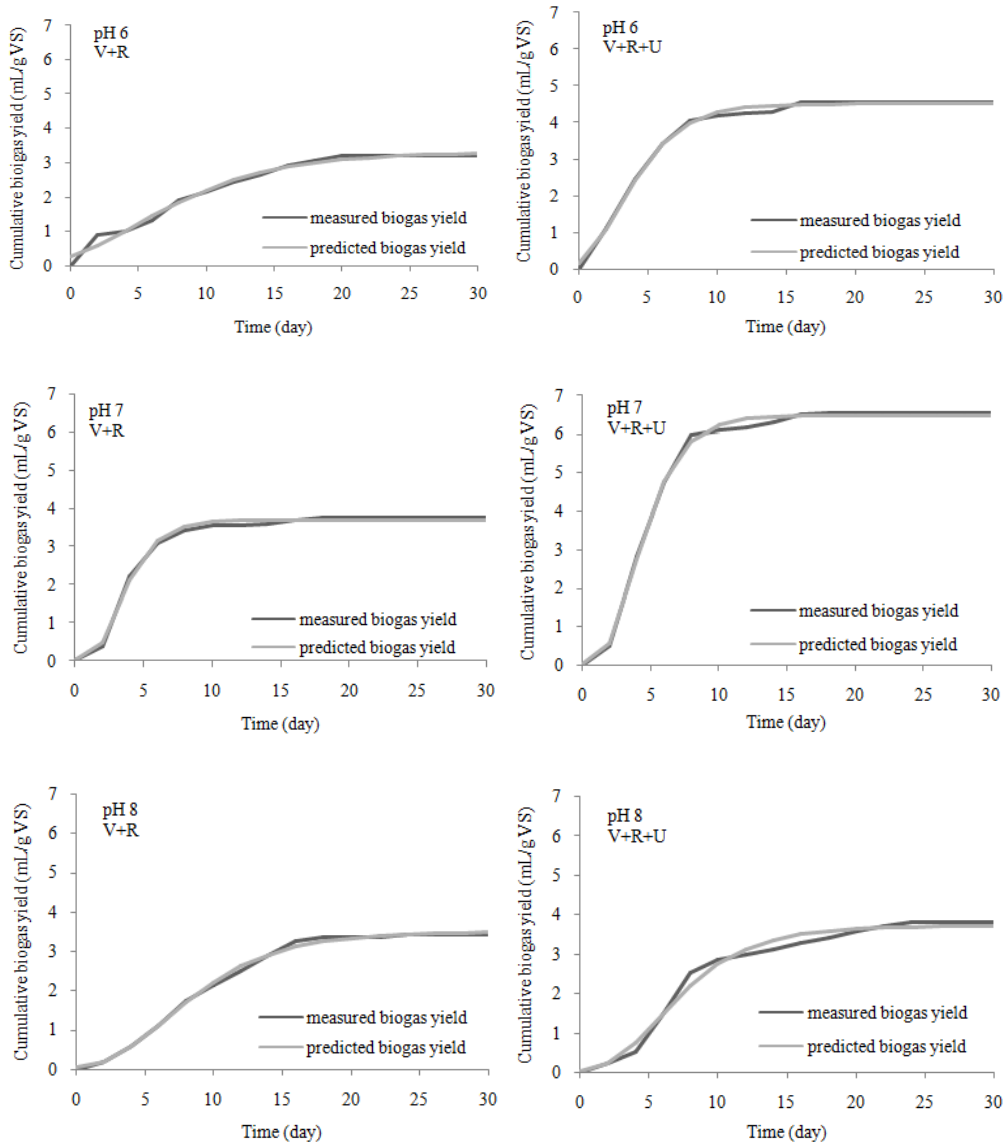
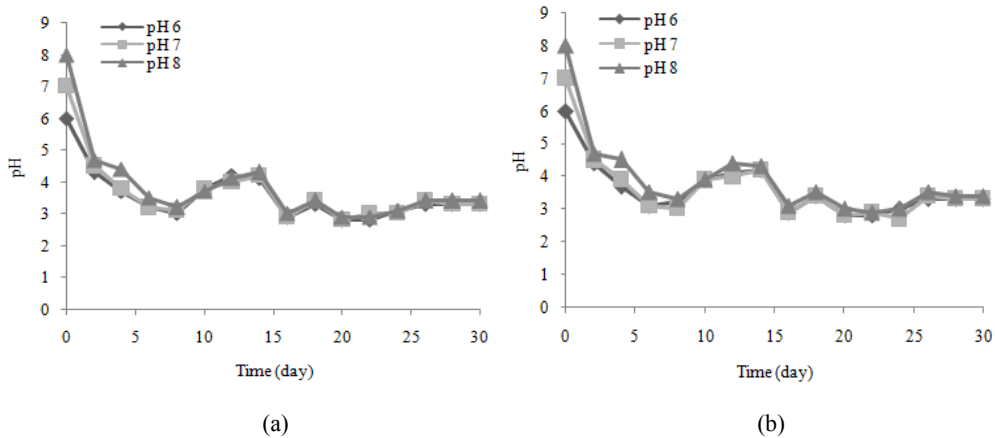Fig. 2: Comparison of experimental data and modified Gompertz model

Fig. 3: pH profile at various initial pH in (a) substrate vinasse+rumen, (b) substrate vinase+rumen+urea

large amount so that bacteria involved biogas production was death. Elbeshbishy and Nakhla (2012) stated that accumulation of VFAs in large concentration was toxic for methanogenic bacteria.

Although urea addition did not change the pH profile daily, it caused total biogas formed more than not urea addition. Vinasse obtained in this study had ratio of COD/N of 1436/7, whereas the optimum range of COD/N was 350/7-1000/7 (Speece, 1996). Hence, addition of 1 gram urea caused the ratio of COD/N in substrate that was in the optimum range.

At initial pH of 6, at substrate of VRU biogas formed had 1.4 times greater than that at substrate of VR. Whereas, at initial pH of 7 and 8 were 1.7 and 1.1 times greater than at VR. Budiyono *et al*. (2013) stated that at urea addition, biogas formed had 52.47% greater than that at not urea addition. Sumardiono *et al*. (2013) reported the same result that COD/N of 400/7-700/7 generated the more total biogas than COD/N of 1436/7 (without urea addition).

From Table 3, both of VR and VRU, initial pH of 7 had the highest kinetic value of ym of all variables, which was 3.68 and 6.49 mL/g VS, respectively. That means initial pH of 7 generated maximum predicted biogas in large amount compared to initial pH of 6 and 8. pH condition of neutral (7) was the best condition for bacterial activity. Although initial pH of 6, 7 and 8 had the same pH profile, initial pH of 7 generated the most total biogas in prediction (ym). That was caused by first six days of fermentation time. In the first six days, initial pH of 7 produced the more total biogas than the others two. Kinetic constant of ym at urea addition (VRU) was highest than that at not urea addition (VR). VR and VRU at initial pH of 7 had value of ym of 3.68 and 6.49 mL/g VS respectively. Ratio of COD/N was one of the important parameters in anaerobic technology. Substrate of VR (without urea addition) had COD/N ratio of 1436/7, whereas substrate of VRU (with urea addition) had COD/N ratio ~600/7. According to Speece (1996), the optimum range of COD/N ratio was 350/7-1000/7 so that substrate of VRU generated the more total biogas than substrate of VR.

Budiyono *et al*. (2010) reported that usually the more value of ym, the more value of U. From Table 3, for all variables, the value of ym, the more value of U obtained. Kinetic constant of U is maximum biogas production rate, so that the more biogas production rate, the more total biogas formed. At substrate of VR, initial pH of 7 had the highest value of U, which was 0.88 mL/g VS. day. That phenomenon showed that initial pH of 7 caused bacteria easily to produce biogas rapidly. At substrate of VRU, initial pH of 7 also had the highest value of U, which was 1.24 mL/g VS. day. Bacteria needed nitrogen to build cell, so presence nitrogen source in appropriate amount in substrate was the important. With urea addition (VRU), bacteria utilized nitrogen source from urea, so that bacterial activity to produce biogas was not disturbed. That caused kinetic of biogas production rate (U) in high value.

Table 4: Kinetic constant of first order kinetic model

Variable		First order kinetic model		
		ym (mL/g VS)	k (1/day)	R^2
V+R	Initial pH 6	3.52	0.099	0.983
	Initial pH 7	3.82	0.210	0.948
	Initial pH 8	4.16	0.073	0.961
V+R+U	Initial pH 6	4.63	0.206	0.986
	Initial pH 7	6.78	0.176	0.945
	Initial pH 8	4.31	0.087	0.956

Remarks: V, vinasse; R, rumen fluid; U, urea; ym, biogas production potential; k, biogas rate constant; R^2, correlation coefficient

Variable that had little value of kinetic constant of λ needed just little time to produce biogas. The value of λ indicated the time that was required for bacteria to adapt (Zwietering *et al*., 1990). Initial pH of 7 had the value of λ of 1.6 days at substrate VR. This value was less than initial pH of 8 (2.24 days). That means bacteria was easily to adapt at pH of 7 than at pH of 8, so that biogas was formed in short time. At substrate VRU, initial pH of 7 (1.79) also had the less than initial pH of 8 (2.12). Both at substrate VR and VRU, initial pH of 7 caused lag time of bacteria in short time. However, initial pH of 6 had the less value of λ than initial pH of 7. That might be caused by microorganism (*Saccaromyces cerevisiae*) that might be presented in vinasse. In ethanol industry, this microorganism actively converts glucose into ethanol and CO_2 at pH of 5. Between pH of 6 and 7, *S. cerevisiae* might more actively at pH of 6 than pH of 7. Based on that, initial pH of 6 was faster to produce biogas firstly than initial pH of 7, because *S. cerevisiae* actively generated ethanol (liquid) and CO_2 (gas). Biogas formed from initial pH of 6 might be dominated by carbon dioxide (CO_2). However, in the 4th and 6th day of fermentation, initial pH of 6 generated biogas that was less than initial pH of 7. *S. cerevisiae* might be involved in the system just at first time fermentation.

Kinetic of biogas yield production using first order kinetic model: Kinetic model of biogas production was simulated through first order kinetic model. Kinetic constant of ym and k was determined by using non-linear regression. Kinetic constants obtained were presented completely in Table 4. By plotting experimental data and kinetic model was obtained the graph as shown in Fig. 4.

Kafle *et al*. (2012) reported that the term k was a measure of the rate of biogas production with time. The more positive the value of k, the faster the rate of biogas production. At substrate of VR, the value of k for the initial pH of 6, 7 and 8 was 0.099; 0,210; 0.073/day, respectively. pH condition of 7 (neutral) was caused bacteria easy to adapt and produce biogas rapidly. That was proven by value of k at initial pH of 7 that was the highest of all variables.

Whereas at substrate of VRU, the value of k for initial pH of 6, 7 and 8 was 0.206; 0.176; 0.087/day, respectively. Among of them, initial pH of 6 had the higher value of k than initial pH of 7, but initial pH of 6 had the less value of ym than initial pH of 7 (Table 4).
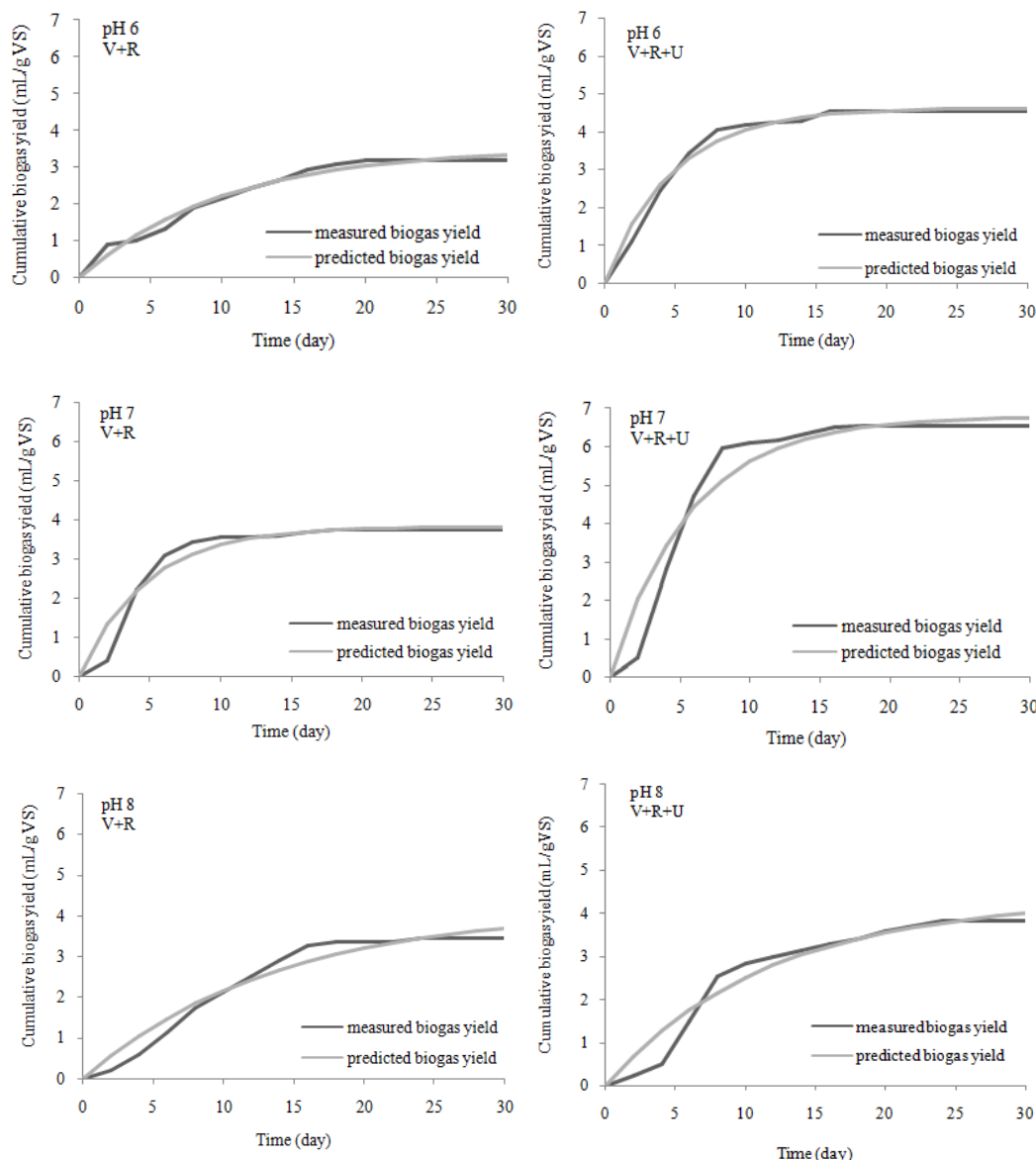
Fig. 4: Comparison of experimental data and first order kinetic model

Yavuz (2007) reported that vinasse contained simple organic compounds (acetic acid, lactic acid and glycerol), so that bacteria could degrade them easily into biogas. Biogas was produced in large amount at beginning fermentation, then decreased. In variable of initial pH of 6, the process of decreasing of biogas production took the shortest time of all variable so that biogas production rate was high although biogas formed was little. Initial pH of 6, 7 and 8 had predicted biogas potential of 4.63; 6.78; 4.31 mL/g VS, respectively. Initial pH of 7 was the best initial pH condition because it had the highest value of ym.

The results of k value in this study (0.087-0.210/day) was higher than the results of Kafle *et al*. (2012) which was 0.017-0.040/day. The difference of the results might be caused by substrates that were used

as feedstock. Kafle *et al*. (2012) used Fish Waste (FW) that contained very high fats. In the hydrolysis phase, fats were converted into Long Chain Fatty Acids (LCFAs) during anaerobic treatment. A large amount of LCFAs in the system had the inhibitory effect to bacterial activity, so that biogas production rate constant at study of Kafle *et al*. (2012) was slower than that at this study.

The value of (k) can be negative (-) or positive (+), that was depended on point of view, whether the substrate or product. Kinetic constant of (-k) means that the value of k is rate constant associated with degradation of the material organic. Whereas, kinetic constant of (k) means that the value of k is rate constant associated with biogas production, so the more negative the value of (-k), the faster the rate of degradation of

Table 5: Results from using modified Gompertz and first-order kinetic model

	Vinasse+Rumen			Vinasse+Rumen+Urea		
	6	7	8	6	7	8
Modified Gompertz Model						
λ (days)	-0.52	1.60	2.24	0.45	1.79	2.12
U (mL/g VS)	0.22	0.88	0.29	0.69	1.24	0.38
R^2	0.986	0.996	0.997	0.996	0.998	0.985
Measured biogas yield (mL/g VS)-30 days	3.19	3.74	3.43	4.55	6.53	3.82
Predicted biogas yield (mL/g VS)-30 days	3.26	3.68	3.47	4.51	6.48	3.70
Difference between measured and predicted biogas yield (%)	2.19	1.60	1.17	0.88	0.76	3.14
First-Order Kinetic Model						
k (1/day)	0.099	0.210	0.073	0.206	0.176	0.087
R^2	0.983	0.948	0.961	0.986	0.945	0.956
Measured biogas yield (mL/g VS)-30 days	3.19	3.74	3.43	4.55	6.53	3.82
Predicted biogas yield (mL/g VS)-30 days	3.34	3.81	3.69	4.62	6.75	3.99
Difference between measured and predicted biogas yield (%)	4.70	1.87	7.5	1.54	3.40	4.45

Remarks: U, maximum biogas production rate; λ, minimum time to produce biogas; -k, the biodegradability organic materials rate constant; R^2, correlation coefficient

Table 6: Comparison between this result and other results in modified and first order kinetic model to predict biogas yield

	Difference between measured and predicted biogas (%)		
Substrate	Modified gompertz	First order kinetic	Authors
Brewery grain waste	3.2	19.5	Kafle *et al.* (2012)
Bread waste	1.6	9.2	Kafle *et al.* (2012)
Pacific saury fish waste	0.7	13.6	Kafle *et al.* (2012)
Mackerel fish waste	6.1	29.8	Kafle *et al.* (2012)
Cuttle fish waste	13.7	37.1	Kafle *et al.* (2012)
Sunflower oil cake	-	≤10	Raposo *et al.* (2009)
Vinasse	0.76-3.14	1.54-7.5	This study

material organic (Yusuf *et al.*, 2011). Based on that, the range of degradation of material organic in this study was (-0.087/day)-(-0.210/day).

Comparison the modified Gompertz model and first order kinetic model: In this study, authors compered the predicted biogas yield obtained from modified Gompertz and first order kinetic model to measured biogas yield. The comparison of that can be seen in Table 5.

From Table 5, the difference between the predicted and measured biogas yield was higher with the first order kinetic model (1.54-4.70%) than with the modified Gompertz model (0.76-3.14). Thus, the modified Gompertz model was found to have better fit for substrate from vinasse. Fitting error of equal or less than 10% was good fitting between measured and predicted biogas yield (Raposo *et al.*, 2009). In this study, first order kinetic model had fitting error just 1.54-4.70%, so first order kinetic model could be used to make and predict biogas production from vinasse. Kafle *et al.* (2012) reported that not all biogas production could be modeled using first order kinetic model, that was depended on substrates used.

The comparison of this study and other studies can be seen in Table 6. Fish waste/FW (pacific saury, mackerel, cuttle fish waste) contained high protein and fat. Brewery Grain Waste (BGW) and Bread Waste (BW) contained high Nitrogen Free Extract (NFE) and low protein and fat (Kafle *et al.*, 2012). Substrates that contained high fat content generated LCFAs in large amount. Accumulation LCFAs too much inhibited the bacterial growth, so that bacteria needed a long time to adapt (lag phase). Biogas production from fish waste needed lag time (λ) of 17.2-24.2 days (Kafle *et al.*, 2012).Whereas, biogas production from BGW and BW needed lag time of 18.2 and 9.1 days, respectively (Kafle *et al.*, 2012). In this study, authors used vinasse that contained high carbohydrate and low fat (Table 1). Yavuz (2007) reported that vinasse contained the simple organic compounds. This content caused biogas production from vinasse needed a short time of lag phase (1.60-2.24 days). In anaerobic treatment, the degradation of carbohydrates could be very rapid (just few days) but proteins and fats needed several weeks (VDI 4630, 2006). Raposo *et al.* (2009) reported that sunflower oil cake (SuOC) contained low fat, so that lag phase required to produce biogas was short.

According to Kafle *et al.* (2012) and Raposo *et al.* (2009), the first order kinetic model gave the satisfactory result with error of 10% or less only if the lag period needed was very short (few days). Carucci *et al.* (2005) reported that substrates contained high carbohydrate took shorter lag time to produce biogas than substrates contained high protein and fat. The lag period in this study was shorter than that in study of Kafle *et al.* (2012) and Raposo *et al.* (2009), so that fitting error at first order kinetic was little (1.54-7.5%). That means modeling kinetic of biogas production from vinasse using first order kinetic model was allowed because the fitting error of that was less than 10%. Whereas, modified Gompertz model gave the satisfactory result in predicting biogas production for all variables.

CONCLUSION

At substrate of Vinase+Rumen and Vinasse+Rumen+Urea, initial pH of 7 generated the more total biogas than the others two (initial pH of 6 and 8), which were 3.74 and 6.53 mL/g VS. Urea addition of 1 g caused COD/N of substrate in optimum range so biogas was generated in large amount at all initial pH (6, 7, 8). Kinetic of biogas production using modified Gompertz model, kinetic constants at initial pH of 7 were ym = 3.68 mL/g VS; U = 0.88 mL/g VS.day; λ = 1.6 days for substrate of Vinasse+Rumen and ym = 6.49 mL/g VS; U = 1.24 mL/g VS.day; λ = 1.79 days for substrate of Vinasse+Rumen+Urea. Kinetic of biogas production using first order kinetic model, kinetic constants at initial pH of 7 were ym = 3.82 mL/g VS; k = 0.21/day for substrate of Vinasse+Rumenand ym = 6.78 mL/g VS; k = 0.176 /dayfor substrate of Vinasse+Rumen+ Urea. The difference between the predicted and measured biogas yield in modified Gompertz model and first order kinetic model was 0.76-3.14% and 1.54-7.50%, respectively.

REFERENCES

Adiga, S., R. Ramya, B.B. Shankar, J.H. Patil and C.R. Geetha, 2012. Kinetics of anaerobic digestion of water hyacinth, poultry litter, cow manure and primary sludge: A comparative study. Proceeding of the 2nd International Conference on Biotechnology and Environment Management, 14: 73-78.

Anderson, G.K. and G. Yang, 1992. Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration. Water Environ. Res., 64: 53-59.

Brannen, A.L. and P.M. Davidson, 1993. Antimicrobial in Foods. 2nd Edn., Marcel Dekker, New York.

Budiyono, I.N., J. Widiasa and S. Sunarso, 2010. The kinetic of biogas production rate from cattle manure in batch mode. Int. J. Chem. Biol. Eng., 3(1): 39-44.

Budiyono, I.N., I. Syaichurrozi and S. Sumardiono, 2013. Biogas production from bioethanol waste: The effect of pH and urea addition to biogas production rate. Waste Technol., 1(1): 1-5.

Carucci, G., F. Carrasco, K. Trifoni, M. Majone and M. Beccari, 2005. Anaerobic digestion of food industry wastes: effect of codigestion on methane yield. J. Environ. Eng., 131(7): 1037-1045.

Deublein, D. and A. Steinhauser, 2008. Biogas from Waste and Renewable Resources. Wiley-VCH Verlag, Weinheim.

Elbeshbishy, E. and G. Nakhla, 2012. Batch anaerobic co-digestion of proteins and carbohydrates. Bioresour. Technol., 116: 170-178.

Esposito, G., L. Frunzo, A. Panico and F. Pirozzi, 2011. Modelling the effect of the OLR and OFMSW particle size on the performances of an anaerobic co-digestion reactor. J. Process. Biochem., 46: 557-565.

Kafle, G.K., S.H. Kim and K.I. Sung, 2012. Ensiling of fish industry waste for biogas production: A lab scale evaluation of Biochemical Methane Potential (BMP) and kinetics. Bioresour. Technol., 127: 326-336.

Metcalf, E., 2003. Wastewater Engineering: Treatment, Disposal and Reuse. 4th Edn., McGraw-Hill, Singapore.

Patil, J.H., M.A. Raj, P.L. Muralidhara, S.M. Desai and G.K.M. Raju, 2012. Kinetics of anaerobic digestion of water hyacinth using poultry litter as inoculum. Int. J. Environ. Sci. Dev., 3(2): 94-98.

Raposo, F., R. Borja, M.A. Martín, A. Martín, M.A. De la Rubia and B. Rincón, 2009. Influence of inoculum-substrate ratio on the anaerobic digestion of sunflower oil cake in batch mode: Process stability and kinetic evaluation. Chem. Eng. J., 149: 70-77.

Speece, R.E., 1996. Anaerobic Technology for Industrial Wastewaters. Archae Press, USA.

Sumardiono, S., I. Syaichurrozi, Budiyono and S.B. Sasongko, 2013. The effect of COD/N ratios and pH control to biogas production from vinasse. Int. J. Biochem. Res. Rev., 3(4): 401-413.

VDI 4630, 2006. Fermentation of Organic Materials: Characterization of the Substrate, Sampling, Collection of Material Data, Fermentation Tests. In: Verein Deutscher Ingenieure (Ed.), VDI-Handbuch Energietechnik, Beuth Verlag GmbH, 10772 Berlin, Germany.

Yadvika, S., T.R. Sreekrishnan, S. Kohli and V. Ratna, 2004. Enhancement of biogas production from solid substrates using different techniques: A review. Bioresour. Technol., 95: 1-10.

Yavuz, Y., 2007. EC and EF processes for the treatment of alcohol distillery wastewater. Sep. Purif. Technol., 53: 135-140.

Yusuf, M.O.L., A. Debora and D.E. Ogheneruona, 2011. Ambient temperature kinetic assessment of biogas production from co-digestion of horse and cow dung. Res. Agr. Eng., 57(3): 97-104.

Yusuf, M.O.L. and N.L. Ify, 2011. The effect of waste paper on the kinetics of biogas yield from the co-digestion of cow dung and water hyacinth. Biomass Bioenerg., 35: 1345-1351.

Zhu, B., P. Gikas, R. Zhang, J. Lord, B. Jenkins and X. Li, 2009. Characteristics and biogas production potential of municipal solid wastes pretreated with a rotary drum reactor. Bioresour. Technol., 100: 1122-1129.

Zwietering, M.H., I. Jongenburger, F.M. Rombouts and K. van'tRiet, 1990. Modelling the bacterial growth curve. Appl. Environ. Microb., 56(6): 1875-1881.