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Development of Simple Kinetic Model on Biogas Production from Co-Digestion of Vinasse Waste and Tofu Residue at Variation of C/N Ratio

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ABSTRACT

The Generated Biogas Rate (GBRT) model and the Predicted Maximum Biogas Potential and Yield (PMBPY) model were developed in this work for better understanding of the anaerobic co-digestion of vinasse waste and tofu residue at variation of total carbon/total nitrogen (C/N) ratio which was 3.71, 5.26, 7.30, 32.54, 97.34. Rate constant (k (/day)) and biogas production rate (ū (mL/day)) estimated using GBRT model was 0.071, 0.140, 0.153, 0.150, 0.125 /day and 20.206, 101.393, 111.832, 95.967, 58.616 mL/day respectively for all variables (R^2 of 0.925 – 0.976). The maximum biogas potential (Pm) obtained using PMBPY model for all variables was 335.8317, 737.0868, 760.4523, 608.3871, 523.3872 mL respectively (R^2 = 0.914 – 0.972). The fitting error between measured biogas and predicted biogas through the developed model was 0.20 – 7.03 %. The developed kinetic model can predict biogas potential with prediction efficiency (%) over modified Gompertz model of 91.71 – 98.57%.

Keywords: Biogas production, C/N ratio, Co-digestion, Developed kinetic model, Tofu residue, Vinasse

1. INTRODUCTION

In anaerobic technology, models were developed and used by authors to describe biogas production rate as time function. This model was usually called as kinetic model of biogas production. The kinetic model mostly used was modified Gompertz model. This model gave good fitting correlation between measured and predicted biogas which was R^2 = 0.958 - 0.998 (Syaichurrozi et al., 2013; Budiyono et al., 2014). Furthermore, Budiyono et al. (2014) reported that the maximum biogas yield can be predicted using modified Gompertz model with error 0.76 – 3.14%. However, this model was complex because that had three parameters unknown. The other kinetic models such as Gaussian model, Logistic model, Monod model, Moser model, Hill model, Andrew model and Haldane model also can be used to predict biogas rate. However, the very complex equation and many parameters unknown caused those not easy to be solved (Ghatak and Mahanta, 2014; Yusuf and Benedict, 2014). Hence, those just can be determined using non-linear regression with special software and special computing skill.

For developing country, biogas can be a source of decentralized energy source especially in this era of insecurity and unpredictability in fossil fuel supply (Yusuf et al., 2011). However, the existing models mentioned above were complex and needed special computing skill and specific software. Hence, some authors have modeled simplified kinetic model that was useful for developing country. Derbal et al. (2009) and Mu et al. (2008) modified the Anaerobic Digestion Model No.1 (ADM 1) so that the model had the special features of specific processes based on the anaerobic digestion. However, the model was great complexity, expressed as a nonlinear differential equation system, and contained high number of parameters that must be adjusted so, adjustment of all their parameters will have a high

computational cost. Furthermore, Martinez et al. (2012) made the simplified mathematic-model in their work to cover those problems. The model was simpler, but the model was depended on 17 parameters (three specific rising speeds, three semi saturation constants, two inhibition constants, six constants describing consumption and production of substrates and three initial values of bacterial populations. Moreover, Martinez et al. (2012) reduced the 17 parameters into 6 parameters successfully. However, the number parameters were still high and specific software have to be used in the process of algorithm. Pham et al. (2014) reported the simple exponential equation (correlation between growth rate of anaerobic bacteria and temperature) to predict methane productivity from pig manure and cow manure. This equation was obviously just applicable to specific substrate, because the formula for pig manure was different from for cow manure.

First order kinetic was also used to model biogas generation from anaerobic digesters. This model was simpler than modified Gompertz model, but that was also complex enough. Thus, the authors tried to modify the first order kinetic model to be simpler so that easy to operate. Owamah and Izinyon (2015) found the simpler equation based on first order kinetic. This equation was applied to predict maximum biogas yield from co-digestion of food waste and maize husk at variation of ratio of inoculum to substrate (I/S). The equation did not show the contribution of I/S value in the equation. Also, Owamah and Izinyon (2015) have not discussed the error prediction between measured biogas with predicted biogas yet. Adl et al. (2015) proposed inexpensive procedure to predict methane generation through first order three-stage kinetic model. However, this procedure was needed help Gauss-Newton algorithm of MATLAB software. Yusuf et al. (2011) successfully modified first order kinetic model to observe the rate of substrate biodegradability. This model was applied in co-digestion of horse dung (HD) and cow dung (CD) at variation of HD:CD (% w/w). Yusuf and Ify (2011) showed the simple model developed based on first order kinetic. This model can be used to predict maximum biogas yield from co-digestion cow dung and water hyacinth at variation of waste paper addition. In the co-digestion concept, the comparison between carbon and nitrogen content in the substrate had to note. Thus, the C/N ratio was important parameter. However, in the study of Yusuf et al. (2011) and Yusuf and Ify (2011), they have not discussed the contribution the C/N value in the formula yet.

We concluded that the existing models were not suitable enough for developing countries and did not give clear information yet. Therefore, in this work, we developed the simplified kinetic model, not only inexpensive but also simple in calculation (no need special software). In the formula of model, we showed that the C/N value affected the fitting R^2 value. The developed kinetic model was used to simulate biogas production from vinasse co-digestion waste (VW) and tofu residue (TR) with variation of C/N. In our previous study, co-digestion (VW:TR = 40:60 % v/v) generated biogas was 1.6 time higher than that from tofu residue alone and 11.3 time higher than that from vinasse alone. This mixture was obtained as substrate. Urea addition was done to adjust C/N in the substrate was 3.71; 5.26; 7.30; 32.54; 97.34 (control; no urea addition). The modified Gompertz model was used for validation to the developed kinetic model. The difference between measured biogas and predicted biogas through modified Gompertz and the developed kinetic model was evaluated. There were two the developed kinetic models in this work, the Generated Biogas Rate (GBRT) Model and the Predicted Maximum Biogas Potential and Yield (PMBPY) Model.

2. METHODS

2.1 Wastewater and inoculum

The wastewater used was vinasse waste obtained from a bioethanol industry. The bioethanol industry located in Solo, Central Java Province, Indonesia, that produced bioethanol from molasses. Whereas, tofu residue was obtained from a tofu industry located in Serang, Banten Province, Indonesia. The rumen fluid was used as inoculum. In this study, rumen fluid that was in fresh condition was obtained from slaughterhouse in Serang, Banten Province, Indonesia.

2.2 Experimental set up

Anaerobic co-digesters were made from polyethylene bottles having 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 (Syaichurrozi et al., 2013; Yusuf et al., 2011; Yusuf and Ify, 2011). In this method, each digester was connected to gas collector that usually was reserved gradual glass cylindrical. The connection was done using connecting tube. Each gas collector was immersed in through of water to ensure complete sealing. Biogas formed in digester was collected by the downward displacement of water.

2.3 Experimental design

Anaerobic digestions of experimental laboratory using 600-mL volumes were operated in batch system. Total volume of VW and TR mixing of 250 mL with volume VW:TR of 40:60 was put into the digester. Rumen fluid as methanogenic bacteria provider that was added into the digester as much as 10% v/v substrate. Furthermore, initial pH for all variables was adjusted 7.0 by using NaOH solution 10 N. Urea synthetic was added into substrate to adjust the C/N ratio of 3.71, 5.26, 7.30, 32.54, 97.34 (no addition). The variables in this work can be seen in Table 1

2.4 Experimental procedures

Fermentation was done until biogas production stop. Each digester was mixed manually for one minute once a day. Biogas formed was measured every once in two

days to know biogas production by using water displacement method. pH of substrate in the digesters was measured by pH meter every once in two days.

2.5 Fitting of experimental data using the 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 (Syaichurrozi et al., 2013; Yusuf et al., 2011). The modified Gompertz equation as follows:

$$Pt = Pm.\exp\left\{-\exp\left[\frac{\mu.e}{Pm}(\lambda - t) + 1\right]\right\} \quad (1)$$

Where:

Pt = the cumulative biogas yield at a digestion time t days (mL)
Pm = the biogas production potential (mL)
μ = the maximum biogas production rate (mL/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 ym, λ and μ was determined using non-linear regression with help of polymath software (Syaichurrozi et al., 2013).

Table 1. Variables in this study

Parameters	Digester				
	D-1	D-2	D-3	D-4	D-5
VW:TR (%) (v/v)	40:60	40:60	40:60	40:60	40:60
Substrate volume (mL)	250	250	250	250	250
Inoculum (rumen fluid)(mL)	25	25	25	25	25
Total Solid (TS) (gram)	12. 63	12. 63	12. 63	12. 63	12. 63
Urea addition (mg)	774	536	378	61	0
Carbon content	1370.87	1370.87	1370.87	1370.87	1370.87
Nitrogen total	369.95	260.67	187.83	42.13	14.08
C/N ratio	3.71	5.26	7.30	32.54	97.34
pH	7.0	7.0	7.0	7.0	7.0

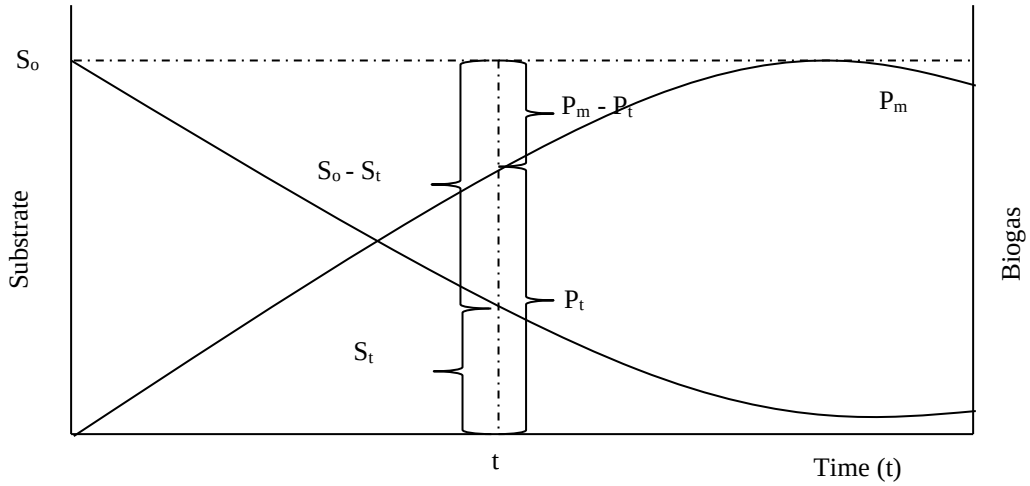

Fig 1. Substrate transformation into biogas during anaerobic degradation

3. DEVELOPMENT OF KINETIC MODELS

3.1 The Generated Biogas Rate (GBRT) Model

In the first order reaction, organic material in the substrates (symbolized S) was converted into biogas (symbolized B) with reaction rate formula, $\bar{u} = -k.S = k.B$, with –k is the biodegradability of organic materials rate constant (1/day) or k is the biogas production rate constant (1/day).

$$V_R\frac{dS}{dt} = Q_i.S_i - Q_o.S_o + V_R.\bar{u}$$

$$V_R\frac{dS}{dt} = Q_i.S_i - Q_o.S_o + V_R(-k.S) \quad (2)$$

In batch system, flow of input (Q_i) = flow of output (Q_o) = 0. Whereas S_i and S_o were influent and effluent organic materials and V_R was volume of reactor, so that the equation (2) can be written as:

$$V_R\frac{dS}{dt} = V_R(-k.S) \quad (3)$$

Both sides of equation (3) were divided by V_R, so equation (3) can be written as:

$$\frac{dS}{dt} = (-k.S)$$

$$\frac{dS}{S} = -k.dt$$

$$\int_{So}^{St}\frac{dS}{S} = -k\int_0^t dt$$

$$\ln(\frac{St}{So}) = -k.t \quad (4)$$

Correlation between substrate biodegradability and biogas yield at any time can be developed assuming all organic materials in the substrate are converted into biogas as shown in Fig 1 (Linke, 2006). From Fig 1, can be deduced that:

$$\frac{So-St}{So} = \frac{Pt}{Pm}$$

$$\frac{So}{St} = \frac{Pm}{Pm-Pt} \quad (5)$$

Substituting equation (4) into (5) to get (6)

$$\ln\left(\frac{Pm-Pt}{Pm}\right) = -k.t \quad (6)$$

Rearrange equation (6)

$$Pt = Pm\,(1-\exp(-k.t)) \quad (7)$$

Linearization of equation (7) by differentiation

$$\frac{dPt}{dt} = 0 - (-k).Pm.\exp(-k.t) \quad (8)$$

$$\frac{dPt}{dt} = k.Pm.\exp(-k.t) \quad (9)$$

Taking natural logarithm on both sides of the equation (9)

$$\ln\left(\frac{dPt}{dt}\right) = \ln(k.Pm.\exp(-k.t)) \quad (10)$$

$$\ln\left(\frac{dPt}{dt}\right) = \ln(k.Pm) - k.t \quad (11)$$

$$\frac{1}{t}\ln\left(\frac{dPt}{dt}\right) = \frac{1}{t}(\ln(k.Pm)) - k \quad (12)$$

From equation (12); Pm, volume of maximum biogas potential (mL); Pt, volume of biogas formed at any time (t); k, rate constant associated with production of biogas (/day). k.Pm is equal with ū value. The ū kinetic is the biogas production rate (mL/day). The equation (12) can be changed into:

$$\frac{1}{t}\ln\left(\frac{dPt}{dt}\right) = \frac{1}{t}(\ln(\bar{u})) - k \quad (13)$$

Equation (13) represented straight line equation y = mx + c, where:

y = $\frac{1}{t}\ln\left(\frac{dPt}{dt}\right)$
m (slope) = ln (ū)
x = $\frac{1}{t}$
c (intercept) = -k, so that –c = k

3.2 The Predicted Maximum Biogas Potential and Yield (PMBPY) Model

The correlation between production rate of biogas and degradation organic material can be written below (equation (14)) (Wang and Wan 2009).

$$\frac{dP}{dt} = -Y_{p/s}\frac{dS}{dt} \quad (14)$$

Rearrange equation (14)

$$\frac{\int_0^{Pt} dP}{\int_0^{t} dt} = -Y_{p/s}\frac{\int_{So}^{St} dS}{\int_0^{t} dt}$$

$$\frac{(Pt-0)}{(t-0)} = -Y_{p/s}\frac{(St-So)}{(t-0)}$$

$$\frac{Pt}{t} = -Y_{p/s}\frac{St-So}{t}$$

$$Pt = -Y_{p/s}\,(St-So)$$

$$Pt = Y_{p/s}\,(So-St) \quad (15)$$

Meanwhile, from equation (5)

$$\frac{So}{St} = \frac{Pm}{Pm-Pt} \quad (5)$$

$$So - St = \frac{Pt}{Pm}So \quad (16)$$

Substituting (15) and (16)

$$Pt = Y_{p/s}\,(\frac{Pt}{Pm}So) \quad (17)$$

$$Pm = Y_{p/s}So \quad (18)$$

Substituting (7) and (18)

$$Y_{p/s}\,(So)\,(1-\exp(-k.t)) = Pt \quad (19)$$

$$\frac{Pt}{So} = Y_{p/s}\,(1-\exp(-k.t)) \quad (20)$$

The power n was applied in the equation (20). The value of n = (1- 1/(C/N))

$$\frac{Pt}{So} = Y_{p/s}\,(1-\exp(-k.t))^n \quad (21)$$

Whereas, maximum biogas potential (Pm) was calculated using equation (18), which was $Pm = Y_{p/s}So$. Equation (21) represented straight line equation y = mx + c, where:

y = $\frac{Pt}{So}$
x = $(1-\exp(-k.t))^n$
m (slope) = $Y_{p/s}$

From equation (21); Pt, volume of biogas formed at any time (t); So, organic materials in the substrates (gram TS); $Y_{p/s}$, product (biogas) yield coefficient; k, rate constant associated with production of biogas (/day); n, the power constant.

4. RESULTS AND DISCUSSION

4.1 Biogas production at variation of C/N ratio

Fermentation during 42 days was done for all digesters. Total biogas volume for digesters of D-1, D-2, D-3, D-4, D-5 were 322, 732, 762, 596, 489 mL respectively (Fig 2). Digester D-5 (C/N = 97.34) that was control variable, no urea addition, generated total biogas in little amount. This was caused by too high of C/N ratio in the substrate. By urea addition, the more urea was added, the less C/N ratio in the system. The less C/N ratio of substrate, the more biogas generated, until C/N ratio of C/N = 7.30 (D-3). Digester D-3 produced the most biogas (762 mL) of all digesters. Moreover of urea addition, which was less than C/N = 7.30, biogas production was decreased. Digester D-1 (C/N = 3.71) and D-2 (C/N = 5.26) was less than D-3 (C/N = 7.30). The C/N ratio of 7.30 was the optimum ratio, that means comparison carbon and nitrogen content of 7.30 was good for bacterial activity to degrade organic materials into biogas.

During fermentation, nitrogen source such as protein and urea was decomposed to be ammonia (NH_3) or ammonium ion (NH_4^+) (Sung and Liu, 2003). Those were utilized by anaerobic bacteria to build cell structures (Angelidaki and Ahring, 1993; Fang et al., 1994). However, ammonia/ammonium ion that was abundant in the system inhibited bacterial growth, and those can be toxic at specific concentration (Deublein and Steinhauser, 2008). Moreover, Syaichurrozi et al. (2013) stated that methanogenic bacteria was the least tolerant and the most easily killed by ammonia inhibition among the four anaerobic bacteria in four step biogas production which were hydrolysis, acidogenesis, acetogenesis, methanogenesis. The carbon content (organic materials) was degraded into VFAs (Volatile Fatty Acids). The VFAs was the intermediate product that was decomposed to be main product which was biogas under anaerobic fermentation. However, the accumulation of that in large amount also poisoned and killed mathanogenic bacteria (Syaichurrozi et al. 2013;Budiyono et al., 2014).

For all variables, pH substrates were fluctuation (Fig 2). Bacteria degraded carbon into VFAs and nitrogen into ammonia/ammonium. The VFAs caused pH value drop, whereas the ammonia/ammonium caused pH value up. The presence of VFAs and ammonium was simultaneously during fermentation, hence pH substrate

was fluctuation. Biogas production daily was ran out from digester D-1, D-2, D-3, D-4, D-5 at 44-day, 42-day, 42-day, 20-day, 18-day of fermentation time. Anaerobic bacteria can grow until 44-day fermentation (the longest of all variable), but total biogas was the least (322 mL) in digester D-1. At the condition, bacteria did not lack nitrogen so that can live in the substrate for a long time, but high accumulation of ammonium caused bacteria was disturbing. Meanwhile, anaerobic bacteria can just live in 18-20 days in digester D-4 and D-5. Those were caused by VFAs accumulation in the system. The optimum condition was in D-2 and D-3, bacteria grow well and produced biogas in large amount.

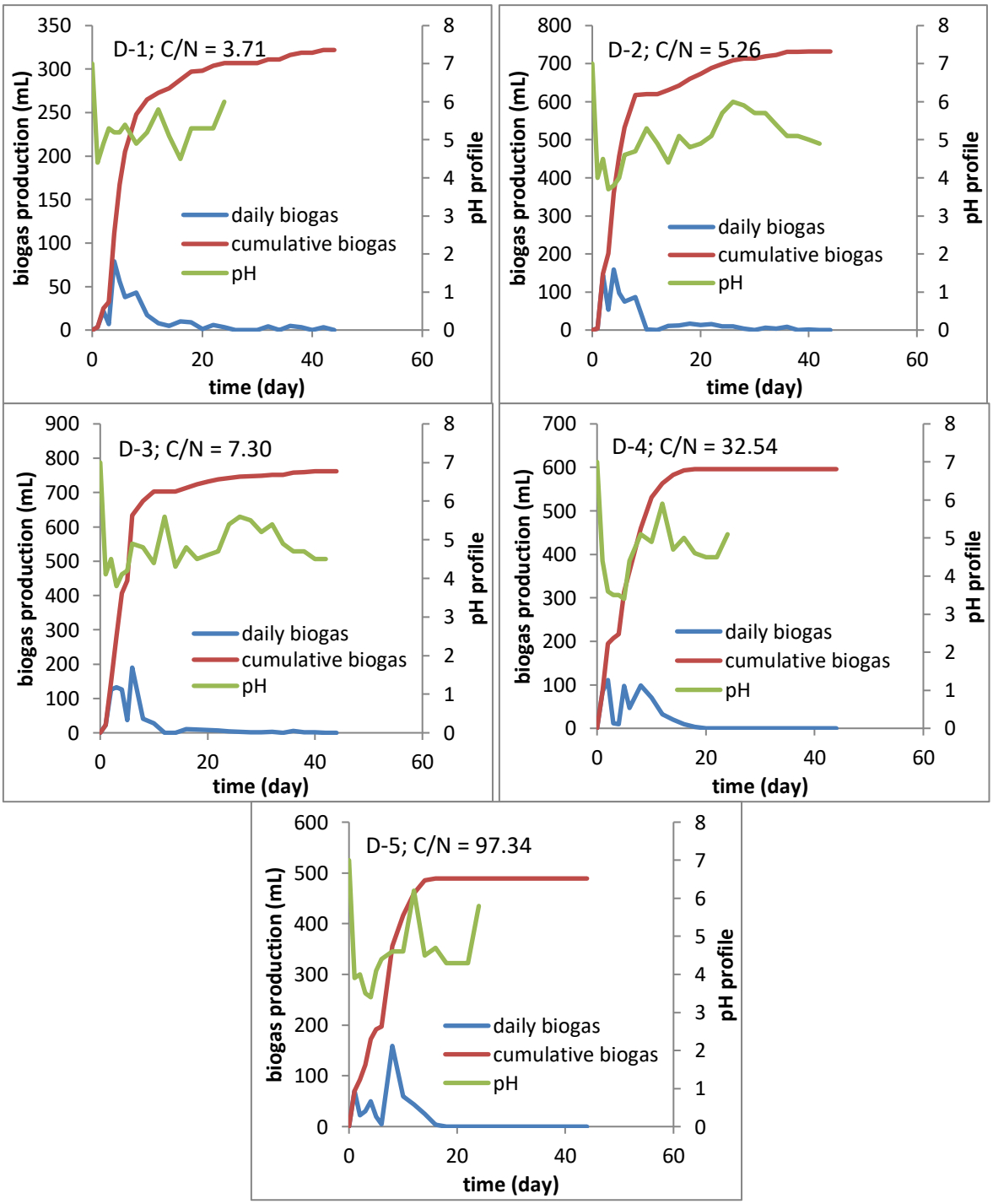

Fig. 2. The effect of C/N ratio to biogas production and pH profile

4.2 Simulation of experimental data using modified Gompertz model

In this section, we predicted biogas production rate using modified Gompertz equation. Polymath software was used to solve non-linear regression of the model. The experimental and simulated data predicted using the model was plot in graph (Fig 3) with goodness fitting of 0.974-0.992. The kinetic parameters founded can be seen in Table 2.

From Table 2, the λ value of D-5 (no-addition urea) was the highest. Zwietering et al. (1990) reported that value of λ indicated the time that was required for

bacteria to adapt. Based on that, bacteria needed a long time to adapt in the substrate that contained C/N ratio of 97.34 (D-5). With urea addition (D-1 – D-4), the kinetic parameter of λ was less (0.02 – 0.99 days) than without urea addition (1.11 days). It proved that nitrogen source was important for bacteria to build cell. Budiyono et al. (2014) stated that bacteria needed nitrogen to build cell structures, so availability of nitrogen in appropriate amount caused good growth of bacteria in digester. If bacteria were not lack of nutrient, degradation activity was done well. Meanwhile, the kinetic parameter of μ describes the maximum biogas production rate. The highest of μ value was digester D-3 (140.23 mL/day). The μ value had linear correlation with Pm value. The more the μ value, the more the Pm value. The Pm value was biogas production potential which was describe how much the biogas was resulted in prediction.The optimum ratio of C/N = 7.30 (D-3) had the least of λ, the most of μ and Pm.

The modified Gompertz model was suitable to predict biogas potential with the good fitting correlation (R^2 more than 0.90). For scientific people, this model was easy to be used, but for the people in the developing country, that was still difficult. The specific software and special computation skill had to be mastered to found the three parameters unknown. In this study, we tried to find the simple equation with easy using, no-special software and low cost experiment. Those will be discussed in the next section.

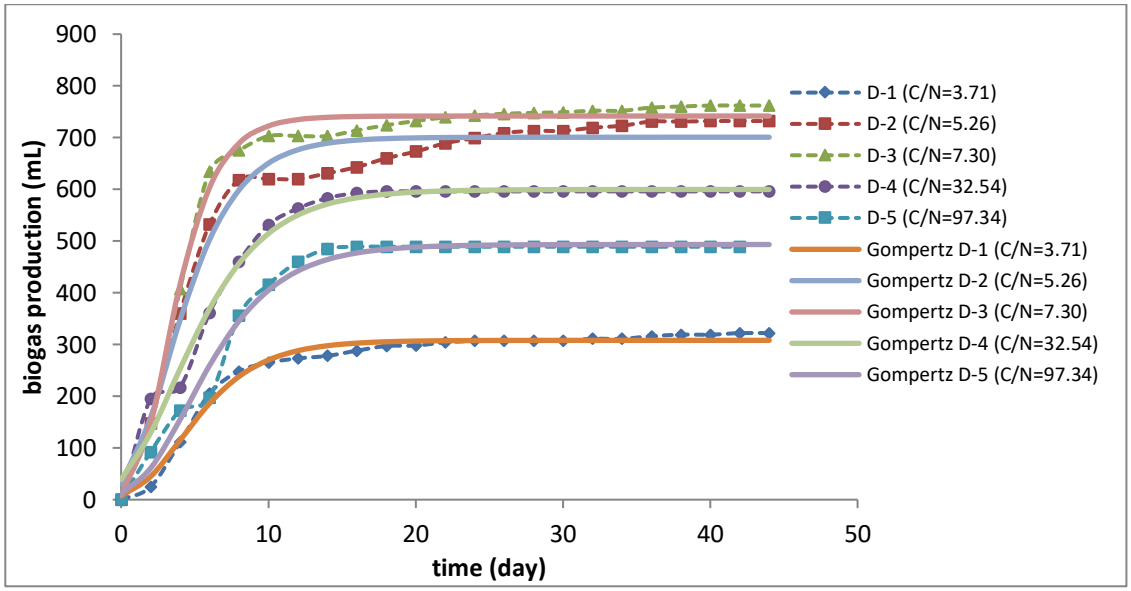

Fig 3. Comparison of experimental data and modified Gompertz model

Table 2. Kinetic parameters in modified Gompertz model

Digester	C/N	Pm (mL)	μ (mL/day)	λ (days)	R^2
D-1	3.71	307.98	38.01	0.98	0.986
D-2	5.26	700.66	96.29	0.38	0.974
D-3	7.30	741.66	140.23	0.99	0.992
D-4	32.54	599.66	63.52	0.02	0.986
D-5	97.34	493.33	53.48	1.11	0.986

4.3 Application of the Generated Biogas Rate (GBRT) Model for estimation of k and ū

This model developed to find the kinetic constant (k). The equation of the model was described in equation (13). By plotting $\frac{1}{t}\ln\left(\frac{dPt}{dt}\right)$ against $\frac{1}{t}$ in Cartesian diagram as linear line (y = mx + c), we found slope (m = ln ū) and intercept (-c = k) (Fig 4). The results of the kinetic parameters from this model were shown in Table 3. This developed model had the good fitting correlation which was 0.925 – 0.976. That means this model was suitable to be used in k value prediction.

The value of k can be negative (-) or positive (+), that was depended on point of view, whether the substrate (organic materials) or product (biogas) (Budiyono et al., 2014). Kinetic constant of (-k) means that the value of k was rate constant associated with degradation of the organic materials (Yusuf et al., 2011; Budiyono et al., 2013). Whereas, kinetic constant of (k) means that the value of k was rate constant associated with biogas generation (Yusuf and Ify, 2011). Thus, the more positive the kinetic of k, the faster the biogas production rate (Budiyono et al., 2014; Kafle et al., 2012). The rate constant of all digesters can be seen in Table 3. Digester D-3 had the highest k value (0.053/day). Kafle et al. (2012) reported that the term k was measuring the biogas production with time. Based on that, biogas was generated in highest rate in the condition of D-3. The rate of biogas production rate was corresponded with the rate of bacterial growth in the substrate. So, the condition of D-3 was the best for bacteria to grow. Whereas, k value of D-1 was the least. Anaerobic bacteria was not tolerance with the condition in digester D-1, so that the bacteria cannot thrive and finally death. That caused the biogas production rate was slow (0.071/day).

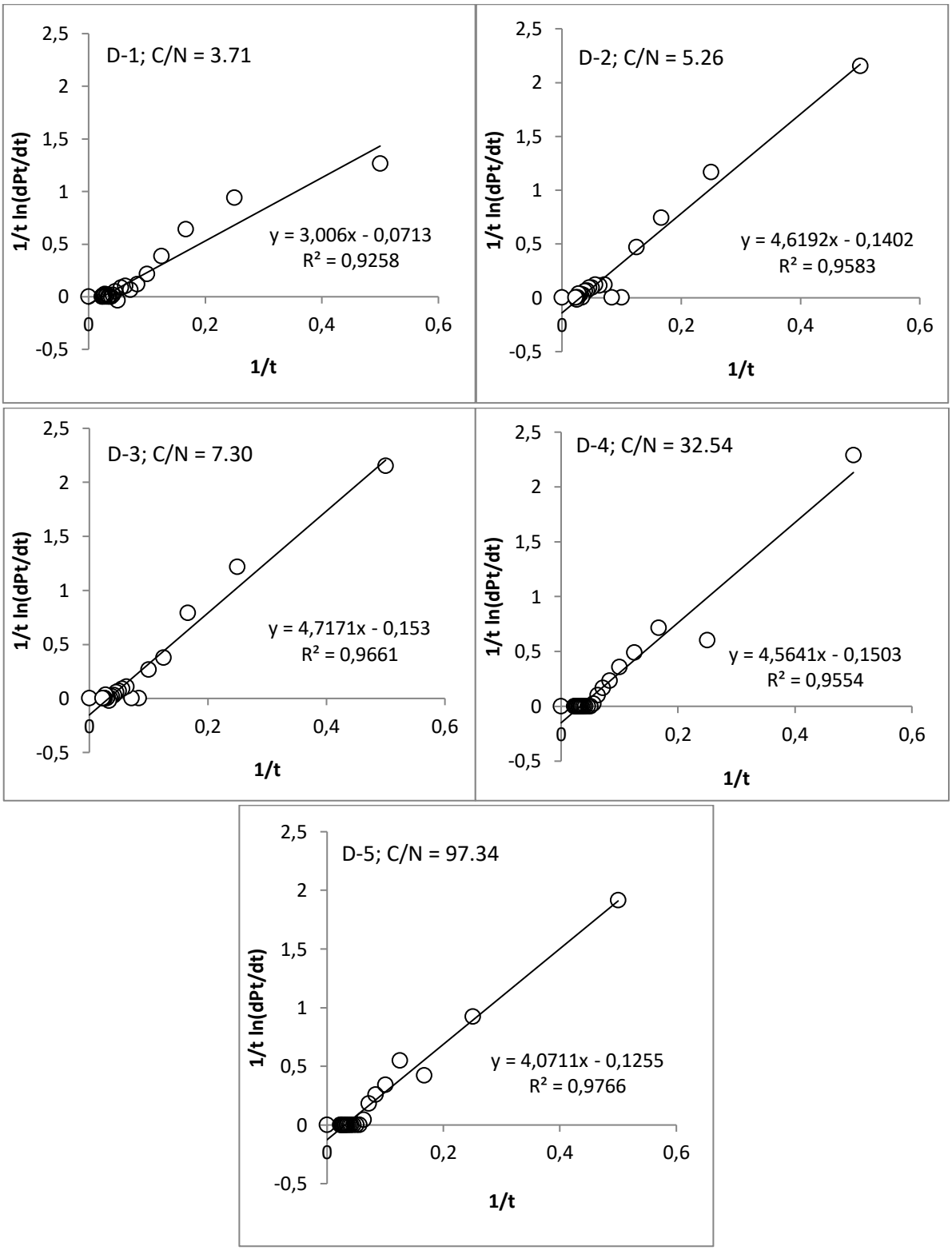

Fig. 4. Plot of 1/t (ln(Pt/dt)) against 1/t

The ū value was also found through this developed kinetic. The ū value described the biogas production rate. From Table 3, the higher the k value, the more the ū value obtained. This kinetic value of ū also showed the stability status. The more the ū value, the more stable digester would be. Digester D-3 was the most stable of all variables. Biogas generated in high rate from digester D-3, which that was caused by comfortable condition of C/N = 7.30 for anaerobic bacteria. The least stable was digester D-1 (C/N = 3.71). Abundant nitrogen in system was very toxic for bacteria, so inhibition factor was very high. Hence, we also stated that the less the ū value, the more inhibition factor.

Table 3. Kinetic parameters in GBRT model

Digester	C/N	ln ū	ū (mL/day)	k (/day)	R^2
D-1	3.71	3.006	20.206	0.071	0.925
D-2	5.26	4.619	101.393	0.140	0.958
D-3	7.30	4.717	111.832	0.153	0.966
D-4	32.54	4.564	95.967	0.150	0.955
D-5	97.34	4.071	58.616	0.125	0.976

4.4 Application of the Predicted Maximum Biogas Potential and Yield (PMBPY) Model for estimation of $Y_{p/s}$ and Pm

This developed model was used to find maximum biogas potential (Pm). By plotting $\frac{Pt}{So}$ against to $(1-\exp(-k.t))$ in cartesian diagram as linear line (y = mx + c), we found slope ($m = Y_{p/s}$). In this study, we tried to find the contribution of C/N ratio to the equation (20). Thus, we added the power of n into equation (20) and we found equation (21). The n parameter was equal with (1-1/(C/N)). In this work, we compared the two equation (20 and 21) to know the effect of n parameter. Hence, The plotting $\frac{Pt}{So}$ against to $(1-\exp(-k.t))^n$ was also conducted. The comparison plotting between equation of (20) and (21) was graphed in Fig 5. The power of n was caused R^2 to be better than that at equation without n parameter. The R^2 by using equation (20) was 0.866 – 0.971, whereas that by using equation (21) was 0.914 – 0.972. The effect of n power was increasing R^2 from 0.866 to 0.914 in D-1, 0.959 to 0.970 in D-2, 0.934 to 0.946 in D-3, 0.971 to 0.972 in D-4, 0.949 to 0.950 in D-5. The conclusion showed that the equation (21) was better than equation (20).

Because of the equation (21) was better than equation (20), we chose equation (21) to predict maximum biogas potential (Pm). The kinetic parameters in this developed model were shown in Table 4. The product yield coefficient parameter ($Y_{p/s}$) for D-3 was the highest (60.21 mL/g TS). The value of $Y_{p/s}$ was equal corresponding with ū value obtained from GBRT model. The more kinetic of ū obtained using GBRT model, the more $Y_{p/s}$ predicted using PMBPY model. The Pm was obtained through equation (18) which was $Y_{p/s}$. So. The So was organic materials in the substrates (gram TS). Hence, the Pm found for D-1, D-2, D-3, D-4, D-5 was 335.8317, 737.0868, 760.4523, 608.3871, 523.3872 mL. From Table 3 and Table 4, there were good relation between k value obtained through GBRT model and Pm obtained through PMBPY model. The more the k value, the more biogas was produced. Mähnert and Linke (2009) also stated that in degradation of organic materials into biogas, the more the k value, the more maximal biogas potential predicted.

Table 4. Kinetic parameters in PMBPY model

Digester	C/N	So (g TS)	n	$Y_{p/s}$ (mL/g TS)	Pm (mL) $Pm = Y_{p/s}So$	R^2
D-1	3.71	12.63	0.7305	26.59	335.8317	0.914
D-2	5.26	12.63	0.8099	58.36	737.0868	0.970
D-3	7.30	12.63	0.8630	60.21	760.4523	0.946
D-4	32.54	12.63	0.9693	48.17	608.3871	0.972
D-5	97.34	12.63	0.9897	41.44	523.3872	0.950

Table 5. Comparison between measured maximum biogas and predicted maximum biogas by using modified Gompertz model and the developed kinetic model in this study

Digester	C/N	Measured biogas (mL)	Modified Gompertz model		Developed kinetic model in this study		Prediction efficiency (%) the developed model over modified Gompertz model results
			Pm (mL), predicted biogas	Difference between measured and predicted biogas (%)	Pm (mL), predicted biogas	Difference between measured and predicted biogas (%)	
D-1	3.71	322	307.98	4.35	335.8317	4.29	91.71
D-2	5.26	732	700.66	4.28	737.0868	0.69	95.06
D-3	7.30	762	741.66	2.67	760.4523	0.20	97.53
D-4	32.54	596	599.66	0.61	608.3871	2.08	98.57
D-5	97.34	489	493.33	0.89	523.3872	7.03	94.26

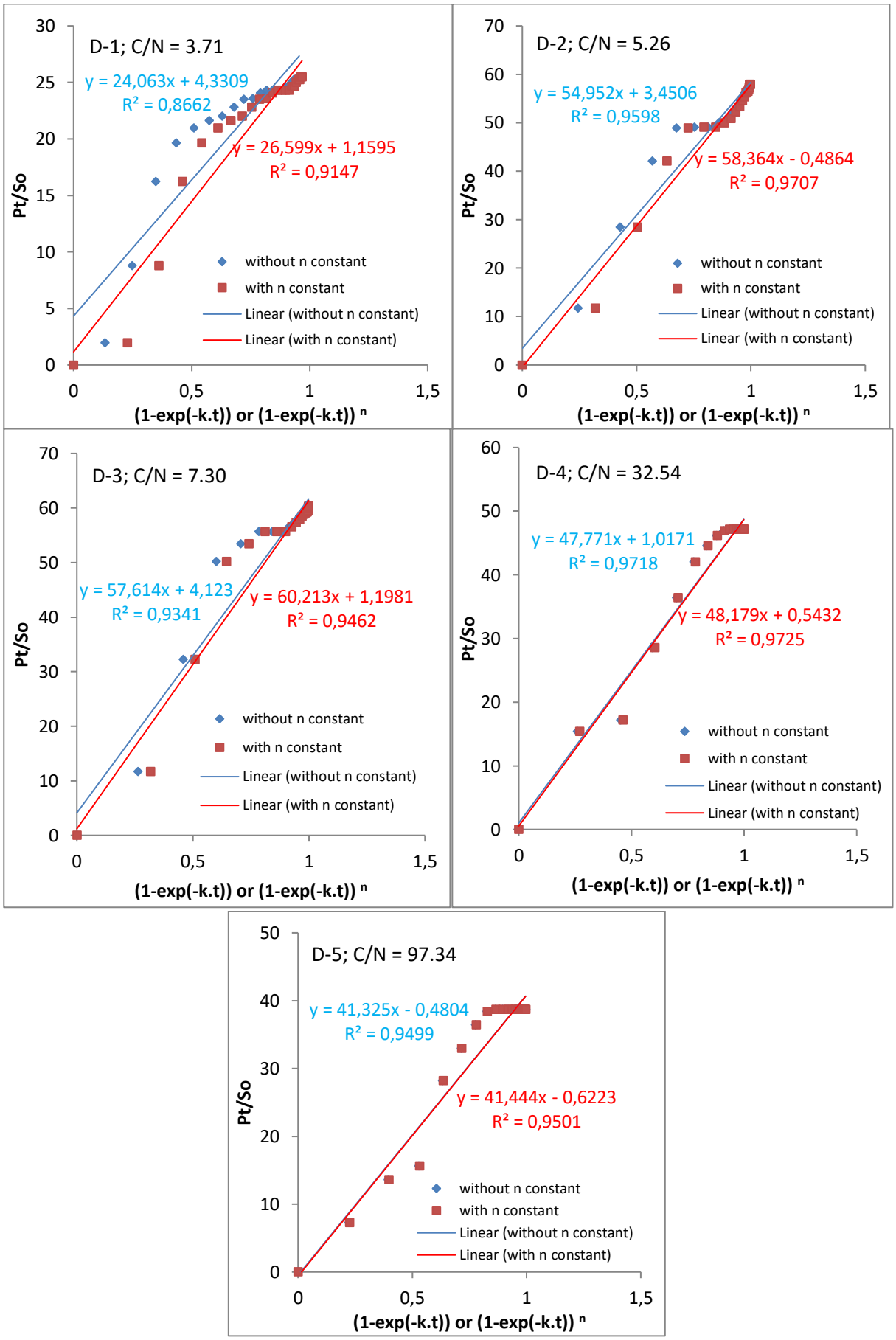

Fig 5. Comparison plotting 1-exp(-k.t)) and (1-exp(-k.t))^n against Pt/So

4.5 Comparison the prediction between the developed kinetic and modified Gompertz model

For validation of the this developed kinetic model, we compared predicted total biogas (Pm) obtained using the developed model and using modified Gompertz model to measured total biogas. The results of comparison can be seen in Table 5. The fitting error between measured total and predicted maximum biogas potential through modified Gompertz model was 0.61 – 4.35 %. Whereas the fitting error of that through the developed model was 0.20 – 7.03 %. The fitting error that was less than 10% was allowable to be used in modeling. Thus, this developed model can be used by developing country. Also, the fitting error of this model was almost same with that of the modified Gompertz.

Furthermore, we calculated the prediction efficiency (%) of this developed model over modified Gompertz model results. The results showed that the prediction efficiency was 91.71 – 98.57 %. This value was very good. That means this developed kinetic model can predict Pm with the result of 91.71 – 98.57 % comparing with modified Gompertz.

4.6 Application of kinetic model in reactor design

The developed kinetic was successfully found . This kinetic gave the good prediction and easy to be used by developing country. In this section, we used this kinetic to predict batch reactor to treat co-digestion vinasse and tofu residue. Yusuf and Ify (2011) stated that a ratio of 1:3 was used to establish a relationship between the volume of the gas chamber (which is proportional to the volume of biogas produced) and the volume of the reactor.

$$V_{gc} = \frac{1}{3} V_R \quad (22)$$

$$3\ V_{gc} = V_R \quad (23)$$

$$V_{gc} = Pt \quad (24)$$

$$V_{gc} = Y_{p/s}.\ So\ (1 - \exp(-k.t))^n \quad (25)$$

$$V_{gc} = Pm\ (1 - \exp(-k.t))^n \quad (26)$$

$$V_R = 3\ (Pm\ (1 - \exp(-k.t))^n) \quad (27)$$

In this work, the volume substrate obtained was 250 mL. So the reactor volume needed to store the biogas from 250 mL-substrate volume was shown in equation (28)

$$V_R = 3\ (Pm\ (1 - \exp(-k.t))^n\ mL\ /250\ mL\ substrate \quad (28)$$

The plotting of 3 $(Pm\ (1 - \exp(-k.t))^n$ against to V_R was graphed in Fig 6. The Fig 6 was described correlation between retention time (day) with reactor volume (V_R). The V_R needed was depended on retention time of organic materials in the reactor. For example, retention of 20 days, the V_R for variable D-3 was 2188.74 (~ 2189) mL/250 mL substrate. For degradation of 10 L substrate, the V_R needed was 10 L × 2189 mL/250 mL = 87560 mL or 87.56 L (~88 L).

Moreover, this developed model also can be used to design volume of semi-continuous reactor. At first, we calculated the Hydraulic Retention Time Critical ($HRT_{critical}$), that was the minimum HRT was chosen with assuming that at the HRT, the organic content was washout. The formula to calculate the $HRT_{critical}$ was $HRT_{critical} = \frac{1}{k}$. The value of k obtained through GBRT model. The $HRT_{critical}$ for variable of D-1, D-2, D-3, D-4, D-5 was 14.08 (~15), 7.14 (~8), 6.54 (~7), 6.67 (~7), 8.00 (~8) days respectively. Hence, the value of V_R for all variables can be found by using Fig 6, which was 718.82 (~719), 1510.60 (~1511), 1588.33 (~1589), 1202.28 (~1203), 997.22 (~998) mL/250 mL substrate.

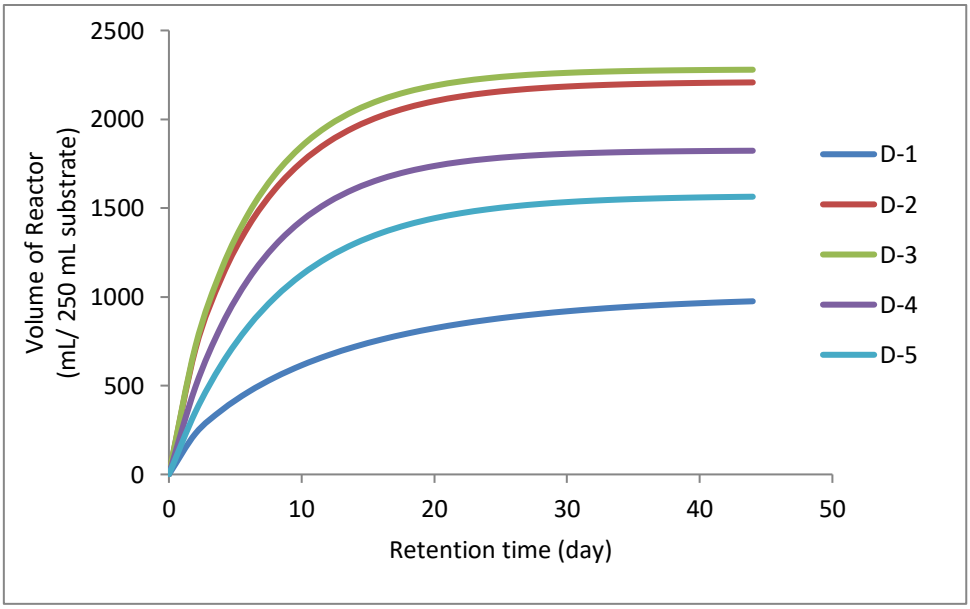

Fig 6. The volume reactor at various of retention time

5. CONCLUSION

The GBRT model was suitable to find the rate constant (k) and biogas production rate (ū) with goodness fitting R^2 of 0.925 – 0.976. The PMBPY model was used to predict maximum biogas production potential (Pm) with R^2 of 0.914 – 0.972. The fitting error between measured and predicted biogas using modified Gompertz model was 0.61 – 4.35 %, whereas the fitting error using the developed model was 0.20 – 7.03 %. The best C/N ratio was 7.30 (D-3) which had kinetic constant from the developed kinetic model of k, ū, $Y_{p/s}$, Pm as 0.153 /day, 111.832 mL/day, 60.21 mL/g TS, 760.4523 mL respectively.

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