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ORIGINAL RESEARCH PAPER

A new kinetic model for biogas production from co-digestion by batch mode

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ABSTRACT: Coming out from the growth kinetics, the Gompertz model has been developed and considered as the best one for simulating the biogas production from anaerobic digestion. However, the model has failed to describe the starting point of the process, and no-sense of lag phase constant has been pointed out. Thus, the goal of this study is to develop a new kinetic model of biogas production with meaningful constants that can alternate the Gompertz model. The kinetic constants of the model were determined by applying the least squares fitting method for experimental data. The experimental data were taken from running seven batch reactors of co-digestion of vegetable, sludge and horse manure under 37oC, pH of 6.7, and total solids of 2.5%. The result of the high coefficient of determination (0.9611-0.9906) demonstrated that the new biogas production kinetic model was feasible to simulate the biogas generation process. This finding has opened a new choice that can deal with simulation of the biogas production. Moreover, co-digestion of vegetable, horse manure, and sludge was also evaluated under strong attention. The biogas potential was in the range of 183-648 Nml/g-VS with the best carbon-to-nitrogen ratio of 16. Vegetable waste played a major role in producing the biogas yield while horse manure and sludge contributed to balancing nutrient of the digestion process. Also, the strong correlation between carbon-to-nitrogen ratio and kinetic constants confirmed that the carbon-to-nitrogen ratio was the key factor that influenced biogas generation.

KEYWORDS: *Anaerobic digester; Batch reactor; Co-digestion; Mesophilic digestion, Kinetics.*

INTRODUCTION

The anaerobic digestion (AD) of biodegradable waste materials has attracted remarkable consideration in the scientists-community by bringing two benefits: treating waste and producing energy source (Deng *et al.*, 2014; Mao *et al.*, 2015; Syaichurrozi and Sumardiono, 2013). Under this strong attention, the influences of the physical and chemical conditions (which affect anaerobic biological processes) such as pH, total solids (TS), temperature, etc. have been deeply studied (Deepanraj *et al.*, 2015; Kythreotou *et al.*, 2014; Lay *et al.*, 1996). These influences have been modelled and expressed by many kinds of kinetic models including the growth kinetics, kinetics of biogas production, and kinetics of substrate degradation (Kythreotou *et al.*, 2014; Nopharatana *et al.*, 2007). Among which, the most important model is the kinetics of biogas production. Digestion process relies on the growth of anaerobic bacteria, hence, many studies have used the growth kinetics of bacteria to express the biogas production (Lay *et al.*, 1996; Lo *et al.*, 2010; Schofield *et al.*, 1994; Syaichurrozi and Sumardiono, 2013). Among which, the Gompertz

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(G) model (Eq. 1) has been considered as the best one (Lay *et al.*, 1996; Lo *et al.*, 2010). However, there are some problems in applying G model for the AD of biodegradable waste. In which, the lag phase period (λ) has not been discussed clearly to evaluate its real meaning. The λ-value was often reported to be longer than one day, however, in these reports, the biogas was generated right after starting without any explanation (Deepanraj *et al.*, 2015; Latinwo and Agarry, 2015; Lo *et al.*, 2010; Nopharatana *et al.*, 2007; Syaichurrozi and Sumardiono, 2013). Thus, the λ in the G model cannot reflect the right definition itself. It may be merely a mathematic constant and cannot represent the lag phase period. Also, when t=0 then $G_{(t=0)}$ is always more than zero, which means that this model always fails to describe at the starting time. Waste activated sludge (S) is generated a large amount from the wastewater treatment processing (60-90 g_{solids} per capita a day) and need to be handled before disposal to avert environmental pollution (Appels *et al.*, 2008; Dai *et al.*, 2016). Anaerobic digestion of S is a low-cost solution which has been applied for a long time, but sludge often showed slow biodegradation rate and low biogas yield (Dai *et al.*, 2016; Mao *et al.*, 2015). Therefore, Gomez *et al.* (2006) added vegetable waste (V) to sludge digestion with the aim of increasing the biogas yield. Others reported that co-digestion of sludge and livestock manure improved digestion performance (Li *et al.*, 2011; Marañón *et al.*, 2012). However, co-digestion of sludge, vegetable waste, and horse manure (HM) has not received much consideration. In fact, inhibition of AD may occur because of the nutrient imbalance in the anaerobic digester such as macronutrients are immoderate, or trace elements are inadequate (Zhang *et al.*, 2014). Although co-digestion has attracted many studies recently because of its low-cost and counteracting the inhibition and overcoming the mentioned disadvantages (Mao *et al.*, 2015; Zhang *et al.*, 2014), its effects on the biogas production kinetics model have not gotten much attention. To bridge the gaps above, this study proposes a new kinetic model with meaningful parameters including A, μ_m, and t_o (the time when the gas production rate reaches the maximum value) for simulation of biogas production. For this purpose, co-digestion of vegetable waste, sludge, and horse manure was first performed to have input data to evaluate the model. Furthermore, the role of each raw material was evaluated to satisfy the concern about co-digestion. And the influence of co-digestion on the kinetic model was also investigated. This study was carried out in Okayama University of Japan in 2017.

MATERIALS AND METHODS

Materials

Vegetable waste (V) and horse manure (HM) were collected at Okayama University. Vegetable with high water content was cut into particles (2-5 mm) with the aim of keeping the samples homogeneous. Sludge was collected from Kobe anaerobic digestion plant. Every material was stored in a refrigerator with the temperature below 4°C (APHA, 2005). Both V and HM were ground by a household grinder for 5 minutes before being used. Three samples of each material were taken soon after being homogenized to determine their characteristics by the analytical methods in the section below. The summarised result is shown in Table 1. In this study, horse manure and sludge also play the role of inoculums.

Methods for chemical analysis

The total solids (TS), volatile solids (VS), and pH of the substrates were measured as being specified by the Standard Methods (APHA, 2005). Briefly, the TS content was calculated after drying the samples at 105 °C for 24 hours to reach the constant weight. The VS was determined after drying the total solids at 550 °C for an hour to reach the constant weight. The pH-value was detected using the LAQUAtwin (Horiba, Japan). Carbon and Nitrogen were analyzed using a CHNS/O analyzer (2400 II, 2005, PerkinElmer, USA). The appearance of CH_4 was confirmed by a gas analyzer (GC 2014, Shimadzu, Japan).

Table 1: Properties of the raw substrates

Properties	C (%)	N (%)	C/N	Total solids (%)	Volatile solids (%TS)
Vegetable waste	39.6 ± 0.27	3.0 ± 0.01	13.2 ± 0.07	10.05 ± 0.26	83.32 ± 1.23
Horse manure	42.8 ± 0.08	1.9 ± 0.01	22.5 ± 0.03	22.0 ± 1.04	83.95 ± 1.15
Sludge	44.5 ± 0.10	1.5 ± 0.01	29.7 ± 0.48	1.56 ± 0.02	96.10 ± 0.17

Experimental setup

By varying ratio of vegetable waste, horse manure, and sludge in the mixture, there were seven reactors (type 500ml) set up with the same TS (2.5%) condition. The characteristics of every reactor (Table2) were calculated based on the ratio of the materials in the mixture and characteristics of these materials in Table 1. The reactors were set in a hot water tank shown in Fig. 1. The initial pH values were controlled at 6.7 by using NaOH 10M. For the first sixteen days, hydrolysis might come soon accompany with unstable biogas generation and produced a large amount of volume. Therefore, biogas was collected day by day. In the following time, gas generation became stable, hence, biogas was collected every four days.

The reactors (01) had a sampling hole (02), a gas pipe (03), and a magnetic bar (05) inside. Taking the sample and adding NaOH solution were performed through the hole (02). Biogas was collected to a gas bag (04) through the gas pipe (03). Every six hours, the substrate inside the reactor was mixed using a magnetic bar (05) and a magnetic stirrer for five minutes. The reactor (01) was taken into a closed water tank (09). The temperature inside the water tank (9) was set at 37°C and ensured the homogeneity by using a temperature controller (06), a sensor (07), a water heater (08), and a circulating pump (10). The ambient temperature was observed every day by a thermometer (11) in order to convert biogas volume to the volume at the standard condition (25 °C; P=1 at).

The Gompertz model

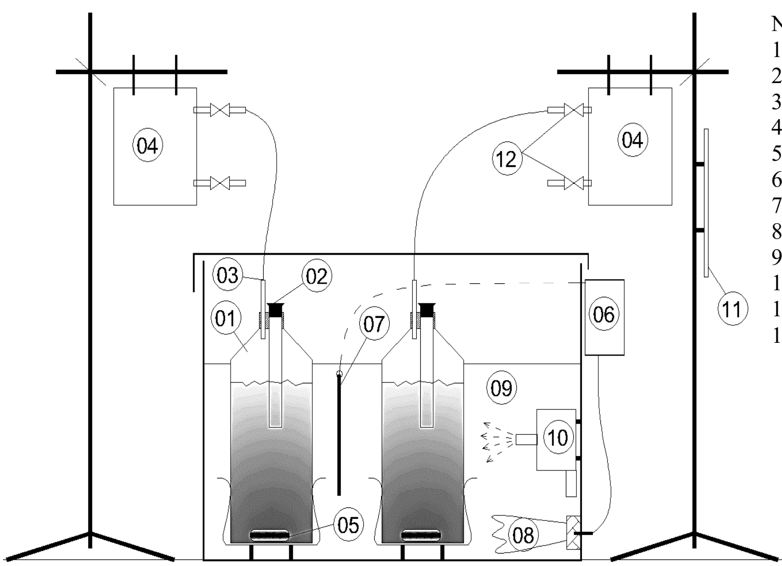
The Gompertz model describes the cumulative biogas production curve in batch digestion assuming that substrate levels limit growth in a logarithmic relationship (Schofield *et al.*, 1994). And the Gompertz model is often shown as the Eq. 1 (Deepanraj *et al.*, 2015; Lo *et al.*, 2010)

$$G_t = A \times Exp\left\{-\exp\left[\frac{\mu_m . Exp(1)}{A}(\lambda - t) + 1\right]\right\} \quad (1)$$

Where, G_t is accumulative biogas yield at digestion time t (Nml/g-VS), A is biogas yield potential of

Table 2: Characteristics of the substrate inside the reactors

Reactor No.	D1	D2	D3	D4	D5	D6	D7
Vegetable (%)	0	50	50	33.3	66.6	16.7	16.7
Horse manure (%)	100	50	0	33.3	16.7	66.6	16.7
Sludge (%)	0	0	50	33.3	16.7	16.7	66.6
C/N	22.5	16.8	18.7	19.8	16.0	21.1	23.9
VS (%)	2.099	2.091	2.243	2.195	2.139	2.147	2.299



Note:
1: Reactor;
2: Sampling hole;
3: Gas pile;
4: Gas bag;
5: Magnetic stirrer;
6: Temperature controller;
7: Temperature sensor;
8: Water Heater;
9: Water tank;
10: Circulating pump;
11: Thermometer.
12: Gas valve

Fig. 1: Diagram of the experiment

the substates (Nml/g-VS), μ_m is maximum biogas production rate (Nml/g-VS), λ is lag phase period or minimum time to produce biogas (day), t is digestion time (day).

Proposal of a new model for biogas production kinetics (BPK)

The most basic equation to describe the substrate degradation is expressed by Eq. 2 (Kafle and Chen, 2016; Linke, 2006).

$$\frac{dM}{dt} = -k \times M \;\rightarrow\; \frac{M}{M_o} = Exp\left(-\int k \times dt\right) \tag{2}$$

Where k is the first-order disintegration rate constant (day^{-1}), M is biodegradable substance concentration (mg/L), M_o is inceptive biodegradable substance concentration (mg/L), t is the digestion time (Kafle and Chen, 2016). It is assumed that inhibition does not occur. Thus, substrate concentration is correlated with the biogas production by Eq. 3 (Kafle and Chen, 2016; Linke, 2006; Yusuf *et al.*, 2011).

$$\frac{(A - G_t)}{A} = \frac{M}{M_o} \tag{3}$$

Replace M/M_o from Eq. 2 to Eq. 3, thereby:

$$G_t = A \times \left[1 - exp\left(-\int k \times dt\right)\right] \tag{4}$$

In fact, k changes considerably over time and depends on many factors. Because of which, recently many authors have tried to develop multi-dimension models of k (Kythreotou *et al.*, 2014; Moestedt *et al.*, 2015; Wu *et al.*, 2006). This study assumes that k varies exponentially over time by the equation: $\int k \times dt = (t/u)^\wedge v$, where v and u are specific constants for the kinetic process. Thus, the Eq. 4 can be rewritten as Eq. 5.

$$G_t = A\left\{1 - \exp\left[-\left(\frac{t}{u}\right)^v\right]\right\} \tag{5}$$

The gas production rate is the first derivative of G_t with respect to t (dG_t/dt). And the gas production rate reaches the maximum value (μ_m) at $t = t_o$, when $d^2Gt/dt^2 = 0$, hence from Eq. 5.

$$0 = \left[\frac{d^2G_t}{dt^2}\right]_{t=t_o} = \frac{A.v}{u^2}.\exp\left[-\left(\frac{t_o}{u}\right)^v\right].\left(\frac{t_o}{u}\right)^{v-1}\left[(v-1) - v\left(\frac{t_o}{u}\right)^v\right] \tag{6}$$

$$\mu_m = \left[\frac{dG_t}{dt}\right]_{t=t_o} = \frac{A.v}{u}.\exp\left[-\left(\frac{t_o}{u}\right)^v\right].\left(\frac{t_o}{u}\right)^{v-1} \tag{7}$$

From Eq. 6:

$$\rightarrow u = t_o.\left(\frac{v}{v-1}\right)^{\frac{1}{v}}, set\ v = \frac{1}{m}, then \quad u = \frac{t_o}{(1-m)^m} \tag{8}$$

Replace u and v from Eq. 8 into Eqs. 7 and 5.

$$\begin{cases} \mu_m = \dfrac{A}{e.m.t_o}.\exp(m).(1-m) & (9) \\ G_t = A\left\{1 - \exp\left[(m-1)\left(\dfrac{t}{t_o}\right)^{\frac{1}{m}}\right]\right\} & (10) \end{cases}$$

The Eq. 9 can be rewritten as:

$$m = f(m) = \frac{A.\exp(m)}{e.\ \mu_m.t_o + A.\exp(m)} \tag{11}$$

Because $0 < f'(m) \leq 1/4 < 1$, the Eq. 11 can be easily solved by the contraction mapping method. Besides, the Eq. 9 can also be treated by using the Maclaurin series of exponential function for an approximate method. Also, when t = 0, G_t also equals to zero.

The mathematical analysis

In this study, the material ratios were used to develop a multiple regression model for estimating the biogas potential (Nml/g-VS). Eq. 12 represents the three-variable linear regression equation, where Y is the biogas yield, β_o represents the Y-intercept, X_i is material ratio, and β_i is X_i- regression coefficient; n is the number of observations.

$$Y = \beta_o + \sum_{i=1}^{3} \beta_i.X_i \tag{12}$$

The kinetic constants A, μ_m, and t_o of the model were determined by using the least squares fitting method. Most previous studies used the correlation of determination (r^2) to evaluate the biogas production kinetic models (Latinwo and Agarry, 2015; Lo *et al.*, 2010; Schofield *et al.*, 1994). However, r^2 is only significantly applied to the linear regression models. Thus, the BPK was converted into a linear regression equation (Eq. 13) for assessment.

$$\log\left(ln\frac{A}{A-G_t}\right) = \left[\log(1-m) - \frac{1}{m}.\log(t_o)\right] + \frac{1}{m}.\log(t) \tag{13}$$

In order to evaluate the models, the statistical indicators such as r^2, correlation coefficient (R), and root mean square error (RMSE) relying on Eqs. 14 to 16 were also calculated (Kafle and Chen, 2016). In Eqs. 14-16, z_i and $\bar{z}$ are the actual observed value and its average value, respectively; w_i is the predicted data, and $\bar{w}$ is the average of w_i.

$$R = \frac{\sum_{i=1}^{n}(z_i - \bar{z})(w_i - \bar{w})}{\sqrt{\sum_{i=1}^{n}(z_i - \bar{z})^2 \sum_{i=1}^{n}(w_i - \bar{w})^2}} \quad (14)$$

$$r^2 = R^2 \quad (15)$$

$$\mathrm{RMSE} = \sqrt[2]{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{z_i - w_i}{z_i}\right)^2} \quad (16)$$

RESULTS AND DISCUSSION

Gas production

Results of biogas yield are shown in Fig. 2. Anaerobic digestion process completed within 45 days with biogas potential from 183 Nml/g-VS to 648 Nml/g-VS. The appearance of CH_4 at all reactors (58-76% of biogas by the 16th day) demonstrated the success of anaerobic digestion. Biogas yield from this research could be compared with its value (257-633 ml/g-VS) in the digestion of sludge and food leftovers from the study of Heo *et al.* (2004), or biogas yield (300-600 ml/g-VS) by co-digestion of vegetable and sludge from the study of Gomez *et al.* (2006).

The lowest biogas yield (183 Nml/g-VS) was observed in reactor D7 where substrate contained 66.6% sludge. This result can be explained by the low degradation rate of sludge (Zhang *et al.*, 2014). Moreover, high C/N ratio in sludge (C/N_{sludge}=29.7) may lead to nitrogen deficiency in reactor D7 causing the inhibition of biogas production (Hartmann and Ahring, 2006). The second lowest biogas yield was found in reactor D1 which contained 100% of HM. The reason can be pointed out by the fact that horse manure holds a large amount of cellulose (Hills and Roberts, 1981; Mönch-Tegeder *et al.*, 2013) which has the structural complexity leading to slow biodegradation process (Beardmore *et al.*, 1980). Except for reactor D7, increasing the V ratio in the mixture improved biogas yield. It means that the V was much more effective than HM and S in generating biogas. Moreover, reactor D2 and D3 evenly contained 50% V, however, biogas yield in reactor D2 was higher than reactor D3. Thus, the effectiveness of producing biogas seemed to be V> HM>S. To evaluate the role of every material in the biogas generation, the correlation between biogas yield and each material was considered and shown in Fig. 3. Obviously, the high positive correlation of R_V (0.89) indicated that biogas yield mainly depended on the V ratio. However, V had a low value of C/N (=13.2) while, Wang *et al.* (2014) pointed out that C/N being as low as 15 in the feedstock led to significant ammonia inhibition. Futhermore, Heo *et al.* (2004) revealed that the reduction of biogas potential (633 to 257 ml/g-VS) was caused by reducing C/N (16 to 5.79). Thus, a higher proportion of 66.6% vegetable may lead to inhibition instead of enhancing biogas

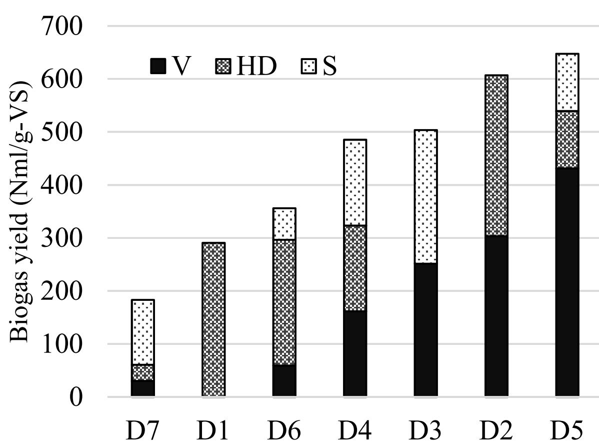


Fig. 2: Biogas yield and substrate compositions in reactors

production. The relationship of the biogas yield with S and HM ratio manure was weak and antagonistic (R_{HM} =-0.32, R_S=-0.40). Thus, HM and S should only keep the role of controlling carbon-to-nitrogen ratio. In fact, Heo *et al.* (2004) showed that a small amount of sludge in the mixture (sludge and food leftovers) was the best. And Kalia and Singh (1998) reported that the lower amount of HM in the mixture (with cattle dung) improved the biogas yield. Moreover, the ratio of sludge in the mixture should be lower than HM because $0 > R_{HM} > R_S > -0.5$, but the difference was not significant. In short, every raw material certainly played a significant role in the digestion process. Vegetable waste played a major role in producing the biogas, and HM and S contributed to the nutrient balance of AD process.

By manipulating the linear regression modelling, the biogas yield (Nml/g-VS) can be predicted from substrate component by Eq. $Y = 27.6 + 9.1131*V(\%) + 2.6798*HM(\%)$ (17). The coefficient of determination r^2 was 0.956, and the coefficients were $p(\beta_1) = 0.000914$ and $p(\beta_2) = 0.019166$. This result demonstrated that the estimated values well reflected the experimental data. From the linear relationship in Eq. 17 above, the ternary graph was used to render a visual representation of biogas yield based on the proportion of the raw materials (Fig. 4).

Related to digestion of V, HM, and S, some results of biogas yield under different experimental conditions can be seen in Table 3. This study showed HM digestion (in reactor D1) having the biogas yield of 290.7 Nml/g-VS under the batch test, mesophilic temperature, and neutral pH. Kusch *et al.* (2008) performed HM digestion in the same conditions and showed that biogas potential could be compared to which of this study (170- Nml-CH_4/g-VS, methane content 51.1-53.5%). Kafle and Chen (2016) obtained the lower biogas yield (222 ml/g-VS) despite the fact that HM characteristics and temperature condition were the same as which in this study because they

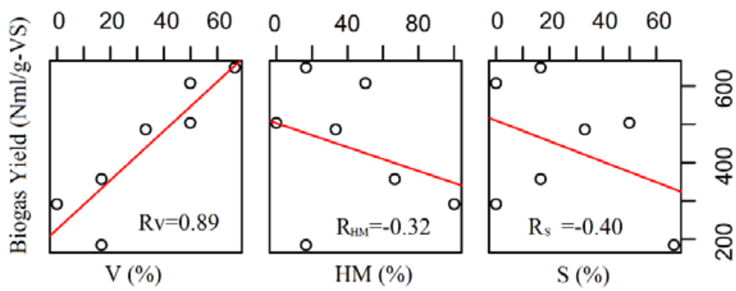


Fig. 3: Correlation coefficients of biogas yield with ratios of every material

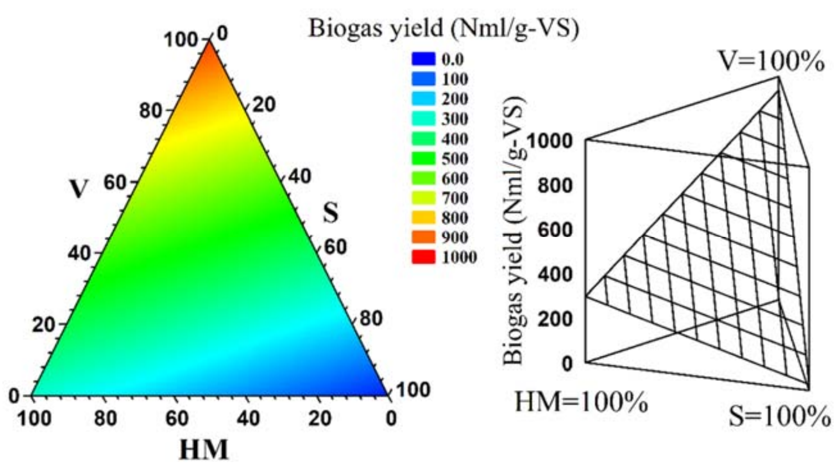


Fig. 4: The estimated biogas yield from substrate components

experimented with pH condition of 8.2 which is not favourable for methanogenesis (Zhang *et al.*, 2014). Kalia and Singh (1998) even received lower biogas potential although doing co-digestion of HM with another material because of experimenting with the lower temperature condition (25°C). Overall, horse manure presented a low biogas yield despite the digestion under different conditions. There have been many papers do compare the digestion of S and V (Appels *et al.*, 2008; Bouallagui *et al.*, 2009). Thus, this research did not do a further assessment.

Simulation of biogas generation by BPK model

The kinetic constants are completely presented in Table 4, while Fig. 5 shows the result of plotting data from the experiments and BPK model. The result of high correlation coefficients (R = 0.9983-0.9997) indicated a very strong linear relationship between experimental values and modelling data. In other words, there was a potential signal of using BPK model to fit the biogas accumulation curve. Furthermore, the high coefficients of determinations (r^2 = 0.9611-0.9906) of the relationship between log(t) and log(ln(A/(A-Gt)) demonstrated feasibility in simulating the gas generation process by BPK model.

Biogas was generated straight away at the beginning time in all reactors, and this process ended up within 45 days. There was not much difference in the biogas potential (A) between experimental values and model data (<1.6%). The maximum biogas production rate

Table 3: Biogas yield from digestion of vegetable, horse manure, and sludge

No.	Materials	Notifications	Biogas (ml/g-VS)	References
1	V, HM, and S	Batch reactor; operating conditions: T=37°C, pH=7, TS=2.5%; C/N=16-23.9.	257-633	This study
2	100 %HM	Batch reactor; operating conditions: T = 36.5°C; pH = 8.2; TS = 24.5%; VS = 18.6%; C/N = 23.	222	Kafle and Chen (2016)
3	S and V	Continuous sterred tank reactor; mesophilic conditions:		
		22% S + 78%V (TS = 6%; VS = 13.4-19.8g/l).	300-600	Gomez *et al.* (2006)
		100% S (TS = 6%; VS = 17.5-20.3 g/l).	200-500	
4	25%S+75% biowaste	Continuous sterred tank reactor; Operating conditions: T = 35°C; TS = 5.8-6.73%; C/N = 6.07-6.27;		
		Hydraulic retention time = 50 days.	720	Liu *et al.* (2012)
		Hydraulic retention time = 33days.	660	
		Hydraulic retention time = 25days.	730	
5	S+Food Waste (FW)	Continuous sterred tank reactor, T = 35°C; HRT = 13 days; TS = 2.07-2.46%;		
		FW:S = 1:9; C/N = 6.16.	257	
		FW:S = 3:7; C/N = 7.17.	332	Heo *et al.* (2004)
		FW:S = 5:5; C/N = 8.38.	503	
		FW:S = 7:3; C/N = 10.8.	558	
		FW:S = 9:1; C/N = 14.1.	633	
6	HM and Cattle Dung	Batch reactor; T = 25±1 °C; TS = 22.6%; C/N = 32.2.	219	Kalia and Singh (1998)
7	V and S	Batch reactor, T = 35 °C; TS = 2.7-2.9%;		
		30%V + 70% water; C/N = 34.2	310	Bouallagui *et al.* (2009)
		30%V+70%S; C/N = 24.76	490	

Table 4: Characteristics of gas production kinetics

No.	BPK Model			Experimental data			R	RMSE
	A *Nml/g-VS*	μ_m *Nml/g-VS*	t_o *day*	A *Nml/g-VS*	μ_m *Nml/g-VS*	t_o *day*		
D1	290.5	34.7	7.7	290.7	23.3	8	0.9997	0.08
D2	610	45.3	9.3	607.2	36.2	10	0.9992	0.16
D3	500	36.9	9.7	503.7	31.7	11	0.9988	0.19
D4	482.2	47	12.9	485.9	32.3	13	0.9998	0.21
D5	644.9	51	13.3	647.5	35.4	13	0.9998	0.17
D6	350.4	26.7	11.4	356.1	20.2	12	0.9983	0.47
D7	180.3	16.5	15.0	183.1	12.1	15	0.9993	0.25

(μ_m) from the experiment was lower than its value in the model, and there was a strong correlation between them ($r^2 = 0.9121$). In contrast, t_o-value from the experiment was almost higher than its value in modelling. And the relationship between them was also significant ($r^2 = 0.963$). For modelling, the higher the A-value was, the higher the μ_m-value was. There was a significant relationship between A and μ_m ($r^2 =$ 0.8162). Simulation of gas generation was the best in reactor D2 ($r^2 = 0.9906$) and the worst in reactor D7 ($r^2 = 0.9611$). The result of the lowest r^2-value indicated that reactor D7 had the highest roughness of the biogas production rate. Moreover, reactor D7 (66.6% of sludge) exhibited the longest time to reach the maximum biogas rate, but it got the lowest values of the biogas yield and biogas production rate. Therefore, that was able to be a sign of the inhibition that happened in reactor D7 caused by high C/N ratio of the sludge (29.7). The influence of C/N ratio on digestion is presented in the section below. This result also reflected the same conclusion as which of Zhang *et al.* (2014) and Zhang *et al.* (2011) that S exhibited a slow rate of biodegradation. Reactor D5 exhibited the highest biogas yield (644.9 Nml/g-VS) as well as biogas production rate (51.0 Nml/g-VS) and also had a long t_o (13.3 days). The shortest t_o-value was obtained in reactor D1 (100%HM) where the reaction ended soonest on the 25th day. This result was similar to the result of the report of Kafle and Chen (2016) who also did HM digestion under the same conditions as in this study.

Influence of carbon-to-nitrogen on the kinetic model

The biogas yield and stability of AD reactor are first affected by the nutritional quality of the substrates, which is often evaluated by the C/N ratio (Ostrem, 2004; Zhang *et al.*, 2013). On the one hand, too high value of C/N ratio suggests that feedstock is insufficient in nitrogen (Hartmann and Ahring, 2006; Mao *et al.*, 2015). Meanwhile, nitrogen is essential for building up microorganism body. On the other hand, the fact that the carbon-to-nitrogen ratio of the feedstock is too low indicates a high level of ammonia formation from the decomposition of the substrate, which is harmful to the anaerobic microorganism (Hartmann and Ahring, 2006; Mao *et al.*, 2015). Thus, the influence of carbon-to-nitrogen on the kinetic model was also investigated in this study and is shown in Fig. 6.

Carbon-to-nitrogen ratio of the substrates (16-23.9) had a strong linear relationship with A ($r^2 = 0.9841$) and µm ($r^2 = 0.8027$). Obviously, when living conditions of microorganisms (pH, TS, and temperature) were fixed, the biogas production was mainly affected by the C/N ratio. And this finding can shorten the numbers of parameters in the biogas production kinetic model. This study showed that low carbon-to-nitrogen ratio was more appropriate for the AD, and the best value

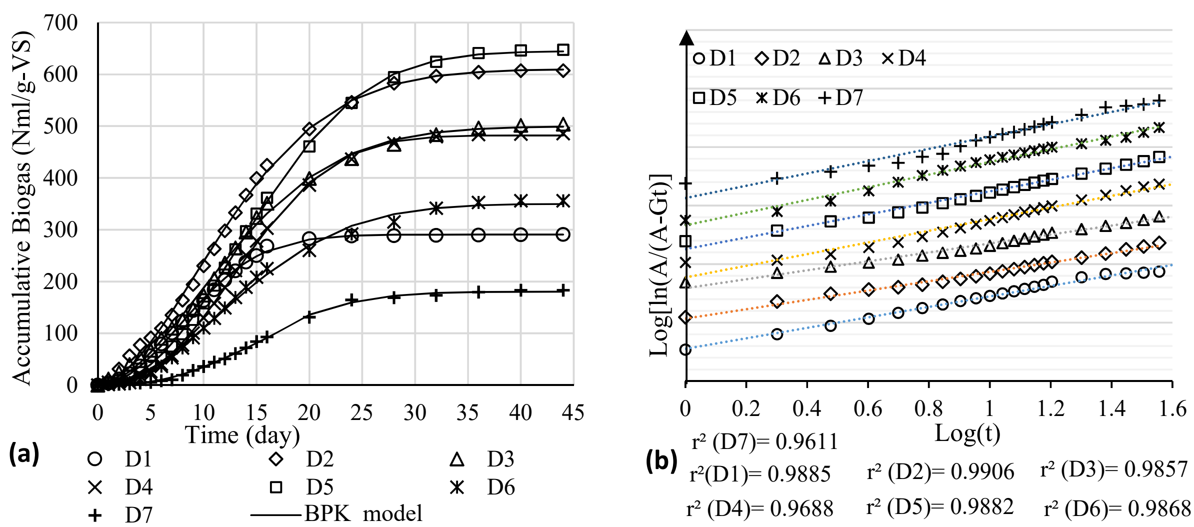


Fig. 5: a) Accumulative gas production from experiments and BPK model;
b) Relationship between log(ln(A/(A-G_t)) and log(t)

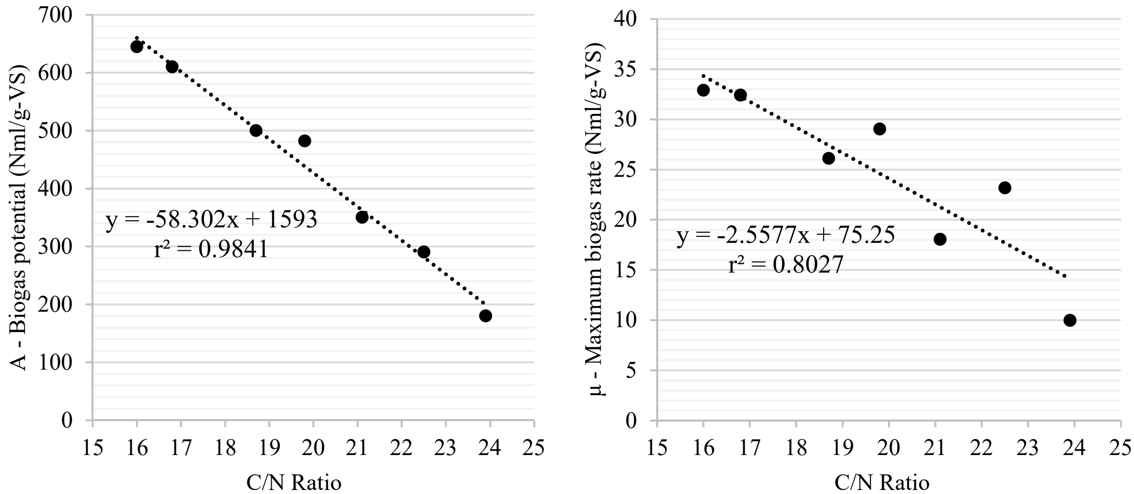


Fig. 6: Impact of carbon-to-nitrogen ratio on the kinetic constants A and μ_m

was 16. With the similar experimental conditions in this study, Zhang *et al.* (2013) reported that C/N of 16 was the best ratio when performing co-digestion of food leftovers and cattle manure. While doing experiments under different pH conditions, Dai *et al.* (2016) found that the optimal C/N ratio was 17 with pH 12 for co-digestion of grass and sludge. Moreover, as a supplement to this study, Heo *et al.* (2004) who performed digestion of food leftovers and sludge, reported that the increase of biogas yield (257-633 ml/g-VS) was the result of increasing C/N ratio (from 5.79 to 16). Therefore, C/N ratio around 16 seemed to be the optimal threshold value for biogas yield purpose. In contrast, despite the batch experiments under the mesophilic condition, Wu *et al.* (2010) reported that the relationship between biogas potential and C/N ratio (within 16-25) was roughly a positive linear regression (r^2 = 0.9988). Meanwhile, Mao *et al.* (2015) reviewed many papers and recommended that the C/N ratio should be within the range of 20-30 with an optimal ratio of 25. Moreover, Dai *et al.* (2016) found that the optimal C/N ratio relied on the pH values when he performed co-digestion of grass and sludge. Wang *et al.* (2014) pointed out that ammonia inhibition of anaerobic digestion was significant to C/N ratio of 15 at 35°C and at a C/N ratio of 20 at 55°C. Therefore, C/N ratio is one of the key factors influence on the AD, and optimal C/N ratio depends on other environmental factors. However, the optimal carbon-to-nitrogen ratio range has often been between 15 and 30.

CONCLUSION

Co-digestion of HM, V, and S by the batch reactors was done successfully with biogas yield of 183-648 Nml/g-VS. In which, the highest biogas yield was in the mixture of 66.6% V, 16.7% S, and 16.7% HM with C/N ratio of 16. The ratio of V in the mixture presented a strong positive effect on the biogas yield. However, too high ratio of V may lead to inhibition instead of increasing biogas potential due to the superabundance of nitrogen. Ignoring the effect of inhibition, the biogas yield (Nml/g-VS) could be estimated from substrate components by equation G=27.6 + 9.1131*V(%) + 2.6798*HM(%) (r^2 = 0.956; p-value = 0.00193). Obviously, S and HM showed much lower biogas potential than V did. Also, the biogas yield was not significant relation with S and HM. Thus, a high proportion of S and HM in the mixture was not encouraged. In short, V played a major role in producing the biogas yield. HM and S played the role of additive materials for nutrient balance purpose. Furthermore, this study showed the feasibility in applying anaerobic digestion for treating S and V (which accounted for a large amount of municipal solid waste) to reduce the environmental burdens. Especially, S and V can be digested directly without any classification step which is the barriers to the biological treatment methods. A new BPK model with the meaningful parameters including A, μ_m, and t_o was developed successfully. Especially, BPK model reflected the right value at the starting point where Gompertz model always failed. The use of BPK model for simulating the accumulative gas production having got the high coefficient of correlation (r^2 = 0.9611-0.9906) demonstrated that BPK model was highly feasible. Especially, the use of the BPK model allows quickly identifying the characteristics (of the complicated biogas generation process) which are related to the calculations of the design and the efficiency of the anaerobic digestion plant. The C/N ratio was regarded as a key influent factor on biogas generation. In which, biogas production potential A (Nml/g-VS) could be estimated from C/N ratio by equation A = 1593-58.302*C/N (r^2 = 0.9841; p-value = 10^{-5}); and the maximum biogas production rate μ_m (Nml/g-VS) could be predicted from equation μ_m = 75.25-2.5577*C/N (r^2 = 0.8027; p-value = 0.006). However, biogas generation also relies on other growth conditions. Thus, the influence of temperature and pH on the kinetic model should also be investigated.

Scale up: BPK model is as a beginning step of our research. The authors would like to evaluate BPK model from the digestion of the different materials under different conditions of pH, TS, and temperature. The authors would also like to compare BPK with much more other models besides Gompertz model. Furthermore, we would like to develop BPK model for evaluating the CH_4 and CO_2 generation processes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

ABBREVIATIONS

A	Biogas production potential (Nml/g-VS)
AD	Anaerobic digestion
BPK	Biogas production kinetics
C	Carbon
C/N	Carbon-to-nitrogen
FW	Food waste
G	Gompertz model
G_t	Accumulatie gas production (Nml/g-VS)
HM	Horse manure
k	First-order substrate utilization rate constant (day^{-1})
M	Biodegradable substrate concentration (mg/L)
M_o	Inceptive biodegradable substance concentration (mg/L)
N	Nitrogen
$p(\beta_i)$	Coefficient of β_i
R	Correlation coefficient
r^2	Correlation of determination
RMSE	Root mean square error
S	Sludge
t	Cumulative time for biogas production (day)
T	Temperature (°C)
t_o	The time when the gas production rate reaches the maximum value (day)
TS	Total solids (%)
u, v, m	Intermediate constants for the kinetic model
V	Vegetable waste
VS	Volatile solids (%)
w_i	Predicted value
X_i	Material ratio (%)
Y	The biogas yield (Nml/g-VS)
z_i	Actual observed value
β_i	X_i- regression coefficient
β_o	Y-intercept
λ	Lag phase period or minimum time to produce biogas (day)
μ_m	Maximum biogas production rate (Nml/g-VS)
$\bar{z}$	Average value of zi
$\bar{w}$	Average value of wi

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