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Kinetics of carbon dioxide, methane and hydrolysis in co-digestion of food and vegetable wastes

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ABSTRACT: Kinetic models which can express the behaviors of hydrolysis and biogas generation more precisely than the conventional models were developed. The developed models were evaluated based on the experimental data of six batch reactors. Anaerobic digestion test was co-digestion of food and vegetable waste with inoculating horse dung by 15% of the total wet weight, at the temperature of 37°C. For hydrolysis, the modified model was developed from an original first-order kinetic model. The modified first-order kinetic model was proved to be better than the original one with the hydrolysis rate constant in the range of 0.22-0.34/day and hydrolyzable rate of 0.80 to 0.84. Kinetics of carbon dioxide and methane were developed from a current potential model. The comparison between experimental data and modeling values had the high correlation of determination (0.9918-0.9998) and low root mean square errors (0.08-4.51) indicating the feasibility of the developed model. In which, the evolution of methane showed the rate constant in the range of 0.031-0.039/day. The carbon dioxide from fermentation accounted for 12-44% of the total observed carbon dioxide. Thus, separation of fermentation and methanogenesis by various reactors may reduce the price of methane enrichment significantly. There was a lag time between methanogenesis and fermentation in reactors ($\lambda = 7-11$ days). Also, the biogas yield was in the range of 431.6-596.9 Nml/g-VS with the CH₄ concentration of 56.2-67.5%. The best methane yield (393.7 Nml/g-VS) was in a reactor with food waste to the vegetable waste ratio by 1.8:1 (wet basis) and C/N ratio by 25.4.

KEYWORDS: Anaerobic digestion (AD); Carbon dioxide (CO₂); First-order kinetic (FOK); Food waste (FW); Methane (CH₄); Modified first-order kinetic (MFK); Vegetable waste (VW).

INTRODUCTION

Anaerobic digestion (AD) is a series of sequential process including hydrolysis, fermentation, and methanogenesis (Mao *et al.*, 2015). In the hydrolysis, the exo-enzymes (excreted by the fermentative microorganisms) break down high molecular weight constituents (e.g., lipids, carbohydrate, and protein) into smaller soluble organic matter, e.g., amino acid,

fatty acid, and glucose (Gerardi, 2003; Mao *et al.*, 2015). The soluble compounds of the hydrolysis are immediately degraded into organic acids by the fermentative bacteria which include facultative microorganism and obligate anaerobes (Goswami *et al.*, 2016). At the final step, the fermentative products are converted to methane (CH₄) and carbon dioxide (CO₂) by the methanogens. In short, the biogas generation process is a complex metabolism of biodegradable materials depending on the activity of anaerobic microorganisms (Gerardi, 2003; Goswami

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et al., 2016). Therefore, kinetics of biogas production such as the first-order model, Gompertz model, and logistic model has been applied to capture the characteristics of the AD process quickly (Kafle and Chen, 2016; Kumar *et al.*, 2016; Li *et al.*, 2013; Nielfa *et al.*, 2015). However, the lag time parameter in these models was proved as a mere mathematical constant, not like a biological one (Dinh *et al.*, 2018a; Dinh *et al.*, 2018b). Therefore, Dinh *et al.* (2018a) recently proposed a new biogas production kinetic (BPK) model to solve the problem as it is mentioned in Eq. 6. All models mentioned above have the simulation function of the evolution of CH₄ or the overall biogas generation. While the CO₂ generation process is more complex by generated from both hydrolysis/acidogenesis and methanogenesis. Its proportion accounted for 20-50 % of total biogas (Dinh *et al.*, 2018a; Goswami *et al.*, 2016). However, its evolution was not considered as an important role. Thus, a series of valuable information which might relate to making-decision to select treatment technology, cannot be seen in the current models. The lag time (λ) might happen between hydrolysis and methanogenesis (Boulanger *et al.*, 2012; Chen *et al.*, 2015). In this case, the current biogas production kinetics models cannot reflect the sufficient properties of the biogas production curves. The digestion in general significantly depended on the hydrolysis which is the first step of AD process and often expressed by the conventional first-order kinetic (FOK) model (Kafle and Chen, 2016; Vavilin *et al.*, 2008). The FOK model shows that the solid material is exponential decline to zero by the time (totally decaying). Meanwhile, there is always have a certain amount of non-biodegradable fraction in the complex organic materials (Kayhanian, 1995; Vavilin *et al.*, 2008). Therefore, the FOK model should be modified to be suitable for simulating the hydrolysis of co-substrates. The hydrolysis is often considered as the rate-limiting step of the anaerobic digestion process, but some studies reported that the rate constant of hydrolysis was faster than methanogenesis (Goswami *et al.*, 2016; Pile, 2006). Thus, the comparison between

the rate constants of hydrolysis and methanogenesis should also be verified. The vegetable waste (VW) and food waste (FW) account for a significant amount of municipal solid waste (Kumar *et al.*, 2016; Liu *et al.*, 2009; Nielfa *et al.*, 2015; Pham Phu *et al.*, 2018). In developing countries, landfilling which is popular disposal causes environmental problems such as greenhouse gases emission, odor and leachate pollution (Liu *et al.*, 2009; Mao *et al.*, 2015). Meanwhile, these wastes are evaluated for AD due to their high biodegradability and moisture contents (Lin *et al.*, 2011; Liu *et al.*, 2009). Thus, digestion from FW and VW has been widely studied recently (Mao *et al.*, 2015). However, studying on co-digestion of VW and FW is still limited. Consequently, the current study was conducted to clarify some following issues of the AD; i) developing the kinetics of CO₂ and CH₄ based on a current potential model, ii), modifying the FOK model to be suitable with the hydrolysis of the complex materials, iii) doing co-digestion of FW and VW. This study was carried out at Okayama University of Japan in 2018.

MATERIALS AND METHODS

Materials and inoculum

The VW, FW, and horse dung (HD) were collected at a cafeteria and agriculture field of Okayama University. FW and VW had been reduced into particles (< 3mm), then stored in the temperature of below 4°C. HD was used as the inoculum of the feedstock. Chemical compositions of these materials are shown in Table 1.

Chemical analysis

The method for analyzing total solids (TS), volatile solids (VS), pH, carbon (C), and nitrogen (N) was described in the study of Dinh *et al.* (2018a). Soluble total carbon was determined using a TOC analyzer (TOC-L, Shimadzu, Japan) according to standard methods for the examination of water and wastewater Bridgewater *et al.* (2012). The liquid samples were filtered (three filter levels with the last

Table 1: Properties of the raw materials (number of samples n = 3)

Properties	C (% TS)	N (% TS)	C/N	Total solids (%)	Volatile solids (%TS)
Vegetable waste	36.84±0.87	2.50±0.10	14.76±0.25	13.18±0.36	82.81±1.51
Food waste	41.32±0.18	1.21±0.04	34.13±1.10	29.31±0.28	88.56±1.26
Horse dung	41.45±0.62	1.07±0.03	38.89±0.25	26.59±0.46	83.03±1.02

Table 2: The characteristics of the feedstock

Reactors	R1	R2	R3	R4	R5	R6
VW:FW:HD (wet basis)	10:75:15	30:55:15	55:30:15	75:10:15	10:75:15	55:30:15
C/N	31.0	25.4	20.5	17.6	31.0	20.5
TS (%)	3.00	3.00	3.00	3.00	5.00	5.00
VS (%)	2.62	2.60	2.56	2.52	4.37	4.27
Carbon (%TS)	40.89	39.99	38.87	37.98	40.89	38.87

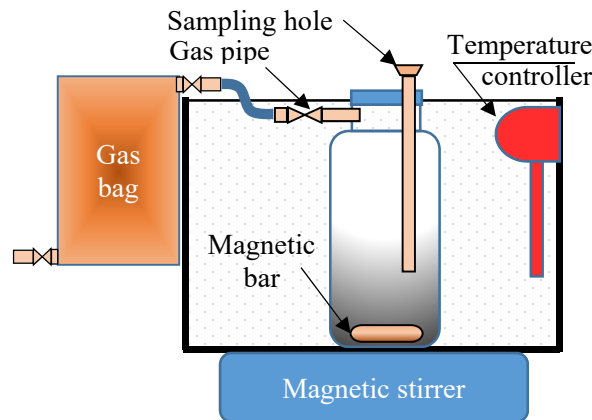


Fig. 1. Diagram of the study experiment

one of 0.45 μm) and diluted before analyzing soluble carbon. The biogas composition was determined by a gas chromatograph (GC 2014, Shimadzu, Japan) equipped with a thermal conductivity detector and a packed column (Shin carbon – ST 50/80 mesh 2 x 2mm x 3mm).

Experimental setup

Table 2 presented the characteristics of feedstocks used in the six batch reactors which are shown in Fig. 1. In which, all reactors were kept in a hot water tank with the temperature controlled by a temperature controller. The substrate inside the reactors was mixed by using a magnetic stirrer. The pH of reactors was manually adjusted to the stable state (6.7-7.2) by daily adding NaOH 10 mol/L solution through a sampling hole. The biogas volume and its concentrations were monitored daily during 72 days of experiments.

The kinetics of hydrolysis

The hydrolysis was characterized by the hydrolysis rate constant (k_h) and expressed by the conventional first-order kinetic model as Eq. 1 (Kafle and Chen, 2016; Vavilin et al., 2008).

$$\frac{dC}{dt} = -k_h \cdot C \tag{1}$$

Where C (g) was mass of current solid state carbon at digestion time t (days). As the mass balance, C was equal to the initial solid-state carbon (C_o) minus the metabolized (gas-state) carbon.

This study assumed that α was the hydrolyzable rate of the substrate, then the initial hydrolyzable carbon and the converted hydrolyzable carbon were ($\alpha \cdot C_o$) and ($C_o - C$), respectively. Therefore, the current hydrolyzable carbon was equal to $[\alpha \cdot C_o - (C_o - C)]$. The Eq. 1 can be re-written as Eq. 2.

$$\frac{d[\alpha \cdot C_o - (C_o - C)]}{dt} = -k_h \cdot [\alpha \cdot C_o - (C_o - C)] \tag{2}$$

The Eq. 2 was a modified version of the FOK model, called MFK model. The k_h and α of the FOK and MFK models were determined using the least squares fitting method.

Determination of Ultimate biodegradable rate

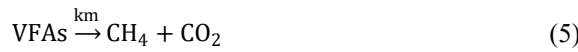
To assess the possibility of being converted into

biogas of the feedstock, the term “biodegradability” or “biodegradable rate” was used (Li *et al.*, 2013; Lin *et al.*, 2011). However, biogas is only the final product among many products produced by the digestion steps. Thus, to avoid misunderstanding, this paper used the term of ultimate biodegradable rate (UBR). The UBR determined the proportion of carbon in the feedstock being converted into biogas (CO₂ and CH₄). Thus, the UBR was calculated by the Eq. 3.

$$\text{UBR (\%)} = \frac{\text{Biogas (Nml)}}{22400 \text{ (Nml/mol)}} \times \frac{12}{C_o} \times 100 \text{ (\%)} \quad (3)$$

Kinetics of carbon dioxide and methane:

The AD process could be briefly described as Eqs. 4 and 5. Where S, solid organic materials; VFAs, volatile fatty acids; k_c, k_m: rate constants.



The first-order model, Gompertz model, and logistic model have been often applied to simulate the kinetics of biogas production (Kafle and Chen, 2016; Kumar *et al.*, 2016; Li *et al.*, 2013; Nielfa *et al.*, 2015). However, the lag time parameter in these models was proved as a mere mathematical constant, not like a biological one (Dinh *et al.*, 2018a; Dinh *et al.*, 2018b). Therefore, Dinh *et al.* (2018a) recently proposed a new biogas production kinetic (BPK) model to solve the problem mentioned above. The BPK model was expressed by Eq. 6.

$$G_t = A \left\{ 1 - \exp \left[(m - 1) \left(\frac{t}{t_o} \right)^{\frac{1}{m}} \right] \right\} \quad (6)$$

Where A, biogas yield potential of the substrates (Nml/g-VS); G_t, accumulative biogas yield at digestion time t (Nml/g-VS); m, an intermediate constant; t_o, the time when the biogas rate reaches maximum (μ_m). In which, μ_m was calculated by Eq. 7.

$$\mu_m = \frac{A}{e \cdot m \cdot t_o} \cdot \exp(m) \cdot (1 - m) \quad (7)$$

Notably, the term of μ_m/A was referred to the

average specific rate of digestion (k) (Schofield *et al.*, 1994). Hence the average rate constant could be written as Eq. 8.

$$k = \frac{1}{e \cdot m \cdot t_o} \cdot \exp(m) \cdot (1 - m) \quad (8)$$

Applying the BPK model for the fermentation and methanogenesis, respectively with a lag time (λ) between these processes, the kinetics of CO₂ and CH₄ could be written as Eq. 9.

$$\begin{cases} \text{CO}_2 = A_{c1} \left\{ 1 - \exp \left[(m_1 - 1) \left(\frac{t}{t_1} \right)^{\frac{1}{m_1}} \right] \right\} \\ + A_{c2} \left\{ 1 - \exp \left[(m_2 - 1) \left(\frac{t - \lambda}{t_{o,m}} \right)^{\frac{1}{m_2}} \right] \right\} & t > \lambda \\ \text{CO}_2 = A_{c1} \left\{ 1 - \exp \left[(m_1 - 1) \left(\frac{t}{t_1} \right)^{\frac{1}{m_1}} \right] \right\} & t \leq \lambda \end{cases} \quad (9)$$

$$\begin{cases} \text{CH}_4 = A_m \left\{ 1 - \exp \left[(m_2 - 1) \left(\frac{t - \lambda}{t_{o,m}} \right)^{\frac{1}{m_2}} \right] \right\} & t > \lambda \\ \text{CH}_4 = 0 & t \leq \lambda \end{cases} \quad (10)$$

Where A_{c1} and A_{c2}, carbon dioxide potential of fermentation and methanogenesis (Nml/g-VS), respectively. A_m, methane potential (Nml/g-VS), m₁ and m₂, intermediate constants of fermentation and methanogenesis, respectively.

The mathematical analysis

The kinetic constants of the models were determined by using the least squares fitting method which minimizes the sum of squared residuals (SSR, Eq. 11) (Schofield *et al.*, 1994; Vavilin *et al.*, 2004). Akaike’s Final Prediction Error (FPE) criterion, defined as Eq. 12 provided a measure of model quality based on actual observed data (Vavilin *et al.*, 2004). Thus, the FPE criterion was applied to make a comparison between FOK and MFK models; the better model had, the smaller FPE value.

$$\text{SSR} = \sum_{i=1}^n (z_i - w_i)^2 \quad (11)$$

$$FPE = \frac{1 + p/n}{1 - p/n} \cdot \frac{1}{n} \cdot \sum_{i=1}^n \frac{1}{2} \left(\frac{z_i - w_i}{z_i} \right)^2 \quad (12)$$

Where z_i and w_i were the actual observed value and the predicted data and p was the degree of freedom, n was the number of samples.

The Eqs. 1 and 2 were converted into the linear regression (Eqs. 13 and 14, respectively) for evaluation.

$$\ln\left(\frac{C_o}{C}\right) = k_h \cdot t \quad (13)$$

$$\ln\left(\frac{\alpha \cdot C_o}{\alpha \cdot C_o - (C_o - C)}\right) = k_h \cdot t \quad (14)$$

For the complex models, the evaluation could be taken based on the comparison between observed data and experimental data (Kafle and Chen, 2016).

Hence, the models were assessed the correlation of determination (r^2), and root mean square error (RMSE), relying on Eqs. 15 and 16, respectively.

$$r^2 = \frac{\sum_{i=1}^n (z_i - \bar{z})(w_i - \bar{w})}{\sqrt{\sum_{i=1}^n (z_i - \bar{z})^2 \sum_{i=1}^n (w_i - \bar{w})^2}} \quad (15)$$

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

RESULTS AND DISCUSSION

Kinetics of hydrolysis

The results of the total solid carbon degradation were shown in Fig. 2. Table 3 presented the hydrolysis rate constant (k_h) of all reactors as results of the two models. In which, the FOK model revealed the rate constant in the range of 0.13-0.198/day. Puyuelo *et*

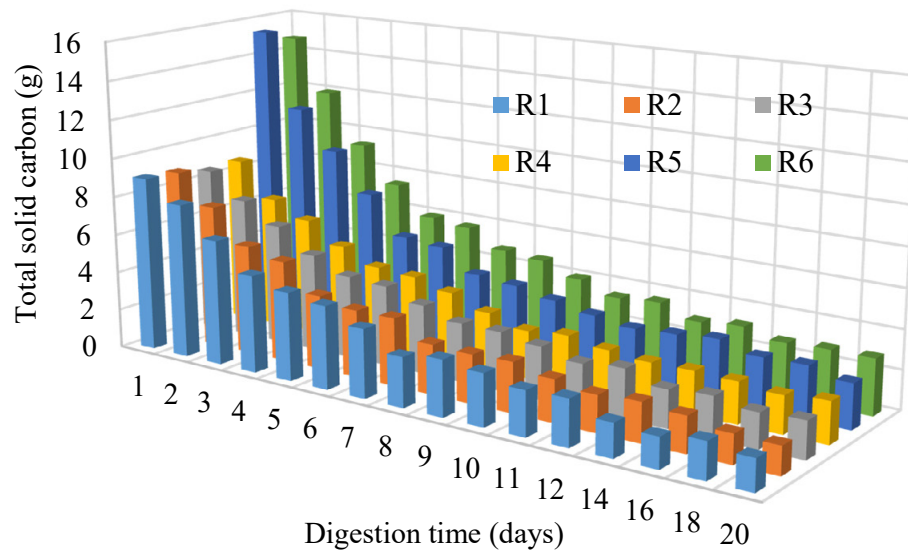


Fig. 2: The decay of total solid carbon during anaerobic digestion

Table 3: The hydrolysis rate constant from first-order and modified first-order kinetic models

Reactors	FOK model			MFK model			
	k_h	r^2	FPE	k_h	α	r^2	FPE
R1	0.14	0.8880	0.037	0.22	0.839	0.9085	0.004
R2	0.16	0.8915	0.052	0.26	0.825	0.9561	0.004
R3	0.14	0.8306	0.044	0.25	0.808	0.8908	0.005
R4	0.12	0.8894	0.026	0.22	0.800	0.9256	0.002
R5	0.20	0.7897	0.095	0.34	0.832	0.9298	0.002
R6	0.17	0.8217	0.067	0.30	0.810	0.9673	0.001

al. (2011), Veeken *et al.* (2000), and Vavilin *et al.* (2004) also used the FOK model to determine k_h of organic waste in the mesophilic condition. As a result of these studies, the k_h of organic waste was 0.06-0.245/day (Veeken *et al.*, 2000), food waste was 0.55/day (Vavilin *et al.*, 2004), and organic municipal solid waste was 0.10/day (Puyuelo *et al.*, 2011). Other studies calculated k_h based on the biogas production (Deepanraj *et al.*, 2015; Kandel *et al.*, 2017; Kumar *et al.*, 2016; Li *et al.*, 2013). As this perspective, hydrolysis must be the slowest step in the three processes of anaerobic digestion. However, microbiology research proved that methanogenesis was much slower (Goswami *et al.*, 2016; Pile, 2006). Therefore, the first-order rate constant in those studies was a general rate constant for all processes rather than only for hydrolysis. The FOK model showed that the solid material was exponential decline to zero of with increase in time (decay totally). However, there is always a certain amount of non-biodegradable fraction in the organic materials (Kayhanian, 1995; Vavilin *et al.*, 2008). Thus, the FOK model could not accurately reflect the degradation process.

Table 3 shows that the k_h of the MFK model was 53-94% higher than that of the FOK model, there was a significant relationship between k_h from two models ($r^2=0.8378$; p -value<0.05). With the coefficient of hydrolyzable rate (α), the MFK model was more flexible (degree of freedom = 2) than the FOK model. Moreover, determining the hydrolyzable fraction of the organic substrates was difficult

(Kayhanian, 1995). Hence, use of the MFK model was more reasonable. Furthermore, the higher values of r -squared and the lower values of FPE criterion demonstrated that MFK model was better than the FOK model. The hydrolysis was reported as the rate-limiting step in the AD process (Neves *et al.*, 2006; Veeken *et al.*, 2000). However, this study showed that the rate constant of hydrolysis was substantially higher than methanogenesis. Neves *et al.* (2006) even reported a negative relationship between k_h and methane yield when investigated co-digestion of coffee waste and sewage sludge. Meanwhile, use of the mechanical pre-treatment methods could increase significantly α -values (Vavilin *et al.*, 2008). Therefore, the suggestion of the rate-limiting step in the AD process must be considered in the properties of the raw materials and pre-treatment methods used. The hydrolyzable rate (α) accounted for 80-84%, in another word the non-hydrolyzable percentage was 16-20 % of total carbon. By using the least squared fitting method, the hydrolyzable ratios of the raw materials were 0.88 for FW, 0.74 for VW, and 0.61 for HD. This result explained why Dinh *et al.* (2018b) and Kafle and Chen, (2016) observed the low biogas yield from HD digestion.

Biogas generation and ultimate biodegradable rate

The experimental results are shown in Fig. 3. The biogas yield was in the range of 431.6-596.9 Nml/g-VS with the methane content varied from 56.2 to 67.5% biogas. In which, the highest methane yield (393.7 Nml/g-VS) was obtained in reactor R2

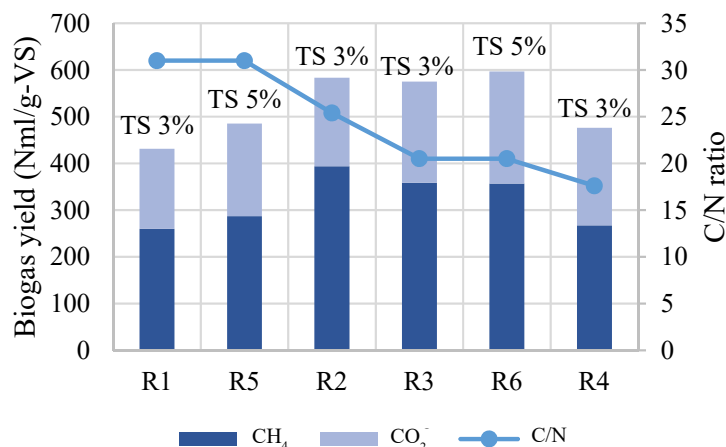


Fig. 3: Biogas yield and biogas composition from experiments

with C/N ratio by 25.4 and a ratio of FW to VW by 18:10 based on the wet weight. Shen *et al.* (2013) reported the same methane yield (198-546 ml-CH₄/g-VS) through the experiment of co-digestion by using similar materials including VW and FW in the mesophilic condition. In the experiment with the same ratio of FW and the green waste, the methane yield was obtained by a lower value (185 ml/g-VS) (Liu *et al.*, 2009). Meanwhile, Lin *et al.* (2011) adjusted the mixture of FW and VW with the optimal ratio by 3:1 (VS basis) and methane yield by 490 ml/g-VS in case of investigation the effects of mixture ratio revealed on the co-digestion by continuous stirred tank reactor. By the same C/N ratios, this study showed that the methane yield in the condition of TS 5% was better than such of TS 3%. Itodo and

Awulu, (1999) revealed that the biogas potential decreased in the increase of solid content from 5% to 20% by the digestion of poultry, cattle, and piggery waste slurries. Abbassi-Guendouz *et al.* (2012) also reported that a decrease of the maximum methane rate occurred when the solid content increase in the range of 10-35%. Therefore, TS 5% seemed to be a critical point in anaerobic digestion of biodegradable waste.

The result of the ultimate biodegradability in the reactors was in the range of 49 -69% initial solid carbon (Fig. 4). This clarifies that UBR had a strong relationship with yield biogas ($r^2 = 0.8726$, $p < 0.05$). Therefore, the higher the UBR, the higher the biogas yield was observed. Relating to the feedstock used in this study, Puyuelo *et al.* (2011), Li *et al.* (2013)

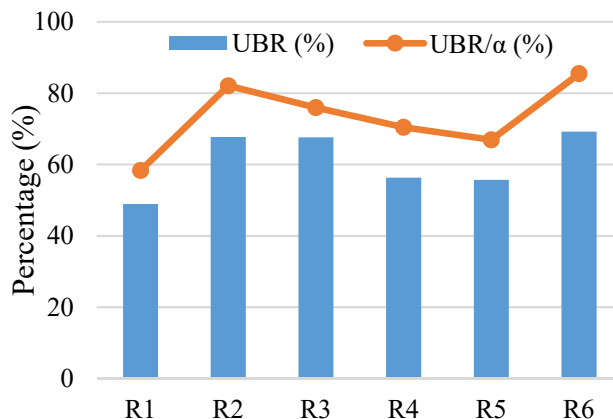


Fig. 4: Biogas yield and biogas composition from experiments

Table 4. Characteristics of methane and carbon dioxide kinetics

Characteristics	R1	R2	R3	R4	R5	R6	
Methane	A _m	257.2	395.9	358.7	268.0	292.5	361.1
	μ _m	10.0	13.2	13.0	9.8	9.3	11.5
	t _{0,m}	27.1	25.7	26.5	26.5	23.6	24.7
	λ	9.5	7.7	6.9	7.0	11.1	9.3
	k _m	0.039	0.033	0.036	0.037	0.032	0.032
	RMSE	0.23	0.20	0.08	0.12	4.51	0.61
	r ²	0.9998	0.9997	0.9997	0.9996	0.9992	0.9995
Carbon dioxide	A _{C1}	60.1	89.7	95.9	59.8	47.8	47.3
	μ _{C1}	10.9	33.1	45.7	42.2	10.9	8.3
	A _{C2}	111.5	100.9	122.6	151.1	156.5	193.5
	μ _{C2}	4.3	3.4	4.4	5.5	5.0	6.1
	t _{0,C1}	3.4	4.5	4.5	3.7	3.7	4.8
	k _{C1}	0.18	0.37	0.48	0.71	0.23	0.18
	RMSE	0.95	0.06	0.19	0.10	0.32	0.45
	r ²	0.9918	0.9969	0.9964	0.9968	0.9970	0.9938

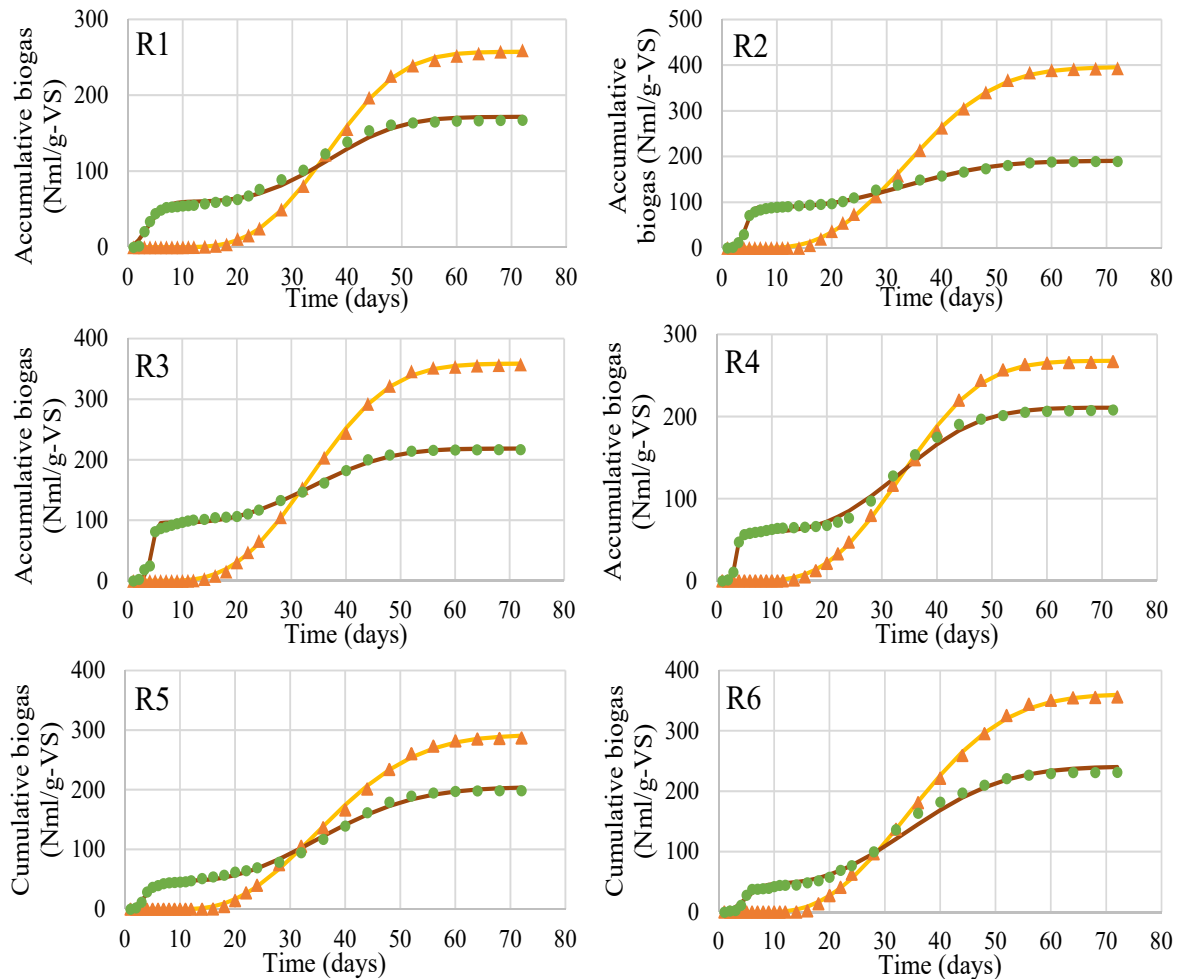


Fig 5: Cumulative carbon dioxide and methane from experiments and modelling
 (Δ Experimental CH₄; ○ Experimental CO₂; — Modeling CH₄; — Modeling CO₂)

Kayhanian (1995) and Lin *et al.* (2011) reported that the biodegradable rate was 44.1 - 50.3% for MSW, 74.8% for kitchen waste, 82.8% for FW, and 59.3 - 71.8% for VW, respectively. Moreover, Fig. 4 revealed that there was a significant amount of carbon hydrolyzed but not converted to biogas (UBR = 58-86% α). It may be explained by the exhaustion of acetic acid and hydrogen which were necessary for creating biogas. Also, some intermediate products could not be transferred to biogas (Gerardi, 2003).

Kinetics of carbon dioxide and methane

The accumulative amount of methane and carbon

dioxide were shown in Fig. 5. Meanwhile, Table 4 described the characteristics of methane and carbon dioxide kinetics. The results demonstrated the feasibility of applying the BPK model to develop the kinetic models of CH₄ and CO₂ due to the high correlation of determination ($r^2 = 0.9918-0.9998$) and the low RMSE (0.06-4.51). The RMSE varied widely among the reactors could be explained by the different growth conditions in these reactors including C/N ratio and total solids content. Carbon dioxide came soon at starting time in all experimental reactors and got the maximum rate after 3-5 days because of the strong and resilient

characteristics of fermentative microorganisms (Gerardi, 2003; Zhang *et al.*, 2009). The rate constant of carbon dioxide formation (k_{c1}) was in the range of 0.18-0.71/day and its relationship with VW/FW ratio was a significant synergetic effect ($p < 0.05$, $r^2 = 0.727$), meant that produced CO_2 in the hydrolysis of vegetable waste was faster than food waste. Moestedt *et al.* (2015) reported the rate constant of carbon dioxide formation was in the range of 0.48-1.2/day from the investigation of CO_2 generation in the hydrolysis of FW, slaughterhouse, and glycerin under mesophilic condition. However, the comparison of the rate constant of carbon dioxide formation (k_{c1}) to the hydrolysis rate constant (k_h) was unreasonable (Gerardi, 2003). Moreover, carbon dioxide from hydrolysis accounted for 12-44% of total CO_2 production. Thus, if hydrolysis is performed in another reactor, then the price of CH_4 enrichment can be reduced significantly.

The methanogen showed the rate constant - k_m in the range of 0.031-0.039/ day. Kandel *et al.* (2017), Nielfa *et al.* (2015), and Kumar *et al.* (2016) also investigated the k_m in the mesophilic condition by batch test, among which FW (0.12-0.18/day), fruit/vegetable (0.39/day), and grass (0.053/day) are relevant to compare to the raw materials in this study. However, these authors calculated k_m by using the first-order model which is assumed that biogas rate will increase exponentially to the maximum with an increase in time (Nielfa *et al.*, 2015). Meanwhile, the biogas production rate in the batch mode rises exponentially with an increase in time, and after reaching the maximum point, it will decrease to zero with an increase in time. Therefore, the use of the first-order model to evaluate the batch process is not suitable. From Table 4, $A_m/(A_m+A_{c2}) = 0.64-0.80$, hence, methane in the methanogenesis was accounted for 64-80% of biogas. There was a significant lag time between methanogenesis and fermentation in all reactors ($\lambda=7-11$ days). This phenomenon also was reported by Boulanger *et al.* (2012), Chen *et al.* (2015), and Lay *et al.* (1996). Among which, Boulanger *et al.* (2012) demonstrated that there was a strong relationship between latency λ and the inoculum to substrate ratio. Chen *et al.* (2015) showed that the lag time depended on alkalinity sources which were added to control pH value. Lay *et al.* (1996) found the significant correlation between moisture content and λ .

CONCLUSIONS

In the hydrolysis, the FOK model showed the hydrolytic rate constant (k_h) in the range of 0.12-0.20/day. Meanwhile, the MFK model was developed from the FOK model, exhibited the higher k_h values (0.22-0.34/ day), also revealed the hydrolyzable rate in the range of 0.80-0.84. The results of the higher values of r-squared and the lower values of the FPE criterion demonstrated that the MFK model was better than the FOK model. Kinetic model of CO_2 and CH_4 was developed successfully. The relationship between the experimental data and modeling values showed the high correlation of determination ($r^2 = 0.9918-0.9998$) and the low root mean square errors (RMSE = 0.08-4.51) indicating that the feasibility of using the biogas production kinetic model to simulate the evolution of CO_2 and CH_4 . This model did not only solve the academic gap in biogas production kinetics but also provided some interesting information on the biogas generation process. In which, the methane rate constant (k_m) which ranged from 0.031 to 0.039/day, lower several times than k_h . Thus, methanogenesis was the rate-limiting step in anaerobic digestion in this experiment. Furthermore, fermentation produced only CO_2 by 12-44% of the total CO_2 product. Thus, separation of fermentation and methanogenesis can reduce the price of methane enrichment significantly. There was a lag time between methanogenesis and hydrolysis in all reactors ($\lambda=7-11$ days). The ultimate biodegradable rate -UBR was in the range of 49 -69%. In which, there was a substantial amount of carbon was hydrolyzed but could not be converted to biogas (UBR = 60-90% α). The co-digestion of the FW and VW resulted in the biogas yield in the range of 431.6-596.9 Nml/g-VS with the methane concentration of 56.2-67.5%. The best methane yield (393.7 Nml/g-VS) was in reactor R2 with FW/VW ratio by 1.8:1 (wet basis) and C/N ratio by 25.4. Kinetics of CO_2 and CH_4 in this study initiated a new approach in making advantage comparison between applying a one-stage digestion system and two-stage digestion system without doing the two-stage digestion experiment.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

ABBREVIATIONS

A	Biogas yield potential (Nml/g-VS)
A_{C1}	Carbon yield potential in the fermentation (Nml/g-VS)
A_{C2}	Carbon yield potential in the methanogenesis (Nml/g-VS)
A_m	Methane yield potential in the methanogenesis (Nml/g-VS)
AD	Anaerobic digestion
BPK	Biogas production kinetic
C	Current solid-stage carbon (g)
CH_4	Methane
CO_2	Carbon dioxide
C_0	Initial solid-stage carbon (g)
FOK	First-order kinetic
FPE	Akaike's final prediction error
FW	Food waste
G_t	Accumulative biogas production (Nml/g-VS)
HD	Horse dung
k_{C1}	Carbon dioxide rate constant from fermentation
k_h	Hydrolytic rate constant
k_m	Methane rate constant
$m, m1, m2$	Intermediate constant
MFK	Modified first-order kinetic
r^2	Coefficient of determination
$RMSE$	Root mean squared error
SSR	Sum of squared residuals
t	Time (day)
t_o	Time when the biogas rate reaches maximum (days)
TS	Total solids (%)
UBR	Ultimate biodegradable rate (%)
VS	Volatile solids (%)
VW	Vegetable waste
α	Hydrolyzable rate (%)

 λ

Lag time (day)

 μ

Maximum biogas rate (Nml/g-VS/day)

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