

# The Determination of Anaerobic Biodegradability and Organic Fractionation of Agricultural Byproducts by Biochemical Methane Potential Assay Using Double First-Order Kinetic Model

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반응속도 모델을 적용한 농업부산물의  
혐기성 유기물분해율과 메탄생산잠재량 분석

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**초 록:** 본 연구는 독일 유기물분해율 표준시험법인 VDI4630 시험을 통해 메탄 생성 및 유기물의 분해율을 조사하였으며 시험을 위해 농업 분야의 11개의 폐기물 바이오매스를 공시재료로 선택하여 시험하였다. 본 연구의 목적은 초기에 빠르게 분해되는 생분해성 유기물과 이후 천천히 지속적으로 분해되는 유기물의 비율을 계산하기 위해 Double first-order kinetics 모델을 이용하여 유기물의 분포를 추정하고자 하였다. 그 결과로 본 연구에 적용된 모든 바이오매스는 초기 단계에서 빠른 분해를 보이다가 이후 분해 속도가 일정 시간 느려지기 시작하여 초기 분해 속도보다 10배 이상 느려지는 결과를 보였다. 이러한 분해율 변화 경향은 바이오매스 분해의 전형적인 형태이며 쉽게 분해되는 인자( $k_1$ )는 채소 작물에서  $0.097\sim 0.152\text{ day}^{-1}$  범위였고, 분해에 저항성을 가지는 인자( $k_2$ )는  $0.002\sim 0.024\text{ day}^{-1}$  사이에 위치하였다. 유기물 분해율이 높을수록  $k_1$  상수 값이 더 크게 나타났으나 ( $0.152, 0.144\text{day}^{-1}$ ) 오이와 파프리카 열매와 같이 표면에 왁스층이 존재하는 부산물은  $k_1$  값이 오히려 줄기보다 낮았고 ( $0.002, 0.005\text{day}^{-1}$ ), 무와 꿀꺽질도  $k_1$  각각  $0.097$ 과  $0.094\text{ day}^{-1}$ 로 낮은 분해율과  $k_1$  값을 보여 유기물의 분해율은 이분해성 유기물 분해 상수인  $k_1$  값에 크게 영향을 미치는 것으로 분석되었다.

**주제어:** 혐기소화, BMP, 농산부산물, Kinetic model

**ABSTRACT:** This study investigated methane productions and a degradation rate of organic matters by German standard method, VDI4630 test. In this study, 11 waste biomasses from agricultural fields were selected for the investigation. The objective of this study was to estimate a distribution of organic matters by using the Double first-order kinetics model in order to calculate the rate of biodegradable organic matters which degrade rapidly in the initial stage and the persistently biodegradable organic matters which degrade slowly later. As a result, all the biomasses applied in this study showed rapid decomposition in the initial stage. Then the decomposition rate began to slow down for a certain period and the rate became 10 times slower than the initial decomposition rate. This trend of decomposition rate changes is typical conditions of biomass decompositions. The easily degradable factors ( $k_1$ ) were ranged between  $0.097\sim 0.152\text{ day}^{-1}$  from vegetable crops and persistent degradable factor ( $k_2$ ) were  $0.002\sim 0.024\text{ day}^{-1}$ . Among these results, greater organic matter decomposition rates from VDI4630 had greater  $k_1$  values ( $0.152, 0.144\text{day}^{-1}$ ) and smaller  $k_1$  values ( $0.002, 0.005\text{day}^{-1}$ ) from cucumbers and paprika. In a meanwhile, radishes and tangerine rinds which had low decomposition rates showed  $0.097$  and  $0.094\text{ day}^{-1}$  of  $k_1$  values and decomposition rates seems to affect  $k_1$  values.

**Keywords:** Anaerobic digestion, Biochemical methane potential, Agricultural biomass, Kinetic model

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## 1. Introduction

Recently, biomass resources of various wastes get more interest because of the exhaustion of fossil fuels and efforts to decrease of CO<sub>2</sub>. The organic biomass, such as food wastes, sewage sludge and swine slurries, are scattered all over Korea and it is urgent to ban dumping of these organic biomasses in ocean. If these waste biomasses are left as they are, it can cause adverse effects on environments. Therefore the waste biomasses require special treatments. Composting and liquid fertilizer of these biomasses are used as treatments of waste biomasses, but these treatments only approach to the disposal concept. The needs for the energy conversion of biomass resources are raised to overcome the disposal concept. Currently, the biogas technology by anaerobic digestion is already widely used around the world among Biomass-to-energy conversion technologies. The anaerobic digestion technologies to produce biogas are determined by properties of biomass materials. The effectiveness of methane production is determined by the ultimate biodegradability which is the degree of material degradation over a period in a reactor. In order to measure methane yields, the test method suggested by Owen et al. (1979) has been used that calculating methane yields for applied substrates using the batch anaerobic reactor. However, calculating potentials of methane yields is affected by diversity of used equipment and environments of methane potential analyses, such as anaerobic microbial inoculum, nutrient balance of medium, pH and a head space in a anaerobic reactor. These influences make difficult for the direct comparison of organic degradation rates and research results of methane yield.<sup>1,9,10)</sup> Because of this difficulty, the standard method to measure methane yield potentials and organic degradation rate has been established and applied world-widely. In addition, various tests to measure ultimate biodegradability of the batch anaerobic reactor, such as serum bottle test, BMP (biochemical methane potential) test, and Cartesian plot test have been applied. But these tests only analyze the ultimate biodegradability

of organic matters. When organic matters are degraded in the early stages, they are degraded rapidly. After a period of time, the degradation rate shows a gentle quadratic curve and this phenomenon is identical to the general microorganism exponential growth. Based on this result, it is a reasonable speculation that the general composition of organic matters are made of easily biodegradable, persistently biodegradable and non-biodegradable organic matters. However, there has been no evaluation method for the multiple decay rate of the organic matters except the graphical statistic analysis by Kang and Tritt (1991) in Korea. Therefore this study investigated methane productions and a degradation rate of organic matters by German standard method, VDI4630 (2006) test. In this study, 11 waste biomasses from agricultural fields were selected for the investigation. The objective of this study was to estimate a distribution of organic matters by using the double first-order kinetics model in order to calculate the rate of biodegradable organic matters which degrade rapidly in the initial stage and the persistently biodegradable organic matters which degrade slowly later.

## 2. Materials and Methods

### 2.1. Substrate

In this study, cucumbers, tomatoes and paprika were sampled from greenhouses located in Anseong, Gyeonggi Province. Cucumbers (cultivation area 9,900 m<sup>2</sup>), tomatoes (cultivation area 16,500 m<sup>2</sup>) and paprika (cultivation area 8,250 m<sup>2</sup>) were cultivated in green houses. The samples of agricultural biomasses were taken during August to October, 2010 from each green house. On the other hand, adlays were selected as a testing material from upland cultivation. Adlays are cultivated in a small area, but they have a great amount of biomass and discarded all residues after a threshing. Because of these adlay properties, adlays were selected as a testing material. In addition, samples were taken from a kimchi process

plant and a juice process plant where agricultural by-products are produced. Total of 11 samples with different characteristics were selected from the plants.

## 2.2. Anaerobic digestion

In this study, The inoculum used in the BMP assay was an anaerobic digestates application taken from biogas plant located in Anseong (South Korea). The anaerobic digestates application was passed through a 2 mm sieve and then incubated at 38°C constant temperature incubator to remove easily biodegradable organic matters and residuary gas were thoroughly. The applied substrate was adjusted a content of volatile solids in S/I ratio to 0.5. The application was prepared as three replicates to an anaerobic reactor. The batch anaerobic reactor used 160 mL serum bottle to measure BMP. The head space of the reactor was filled with N<sub>2</sub> gas to get rid of air and the enclosed reactor was incubated at mesophilic conditions (38°C). The reactor was shaken to stir once a day at the 38°C constant temperature incubator for 90 days. In addition, three replicates of inoculums only filled only methane gas were prepared with the same condition as other reactors.

## 2.3. Analytical procedures

Total gas production was measured daily by displacement of an acidified brine solution in burette and recording the volume of displaced solution after correcting to the standard atmospheric pressure (Williams, 1996; Beuvink, 1992). The analysis of gas components was done by gas chromatography installed with a thermal conductivity detector (TCD) (Clarus 680, PerkinElmer, USA). A column was a HayesepQ packed column (3 mm × 3 m, 80~100 mesh size). High purity argon (Ar) gas passed through the column with an operational condition of flow 30mL min<sup>-1</sup>, 150°C of an injector temperature, 90°C of a column oven and 150°C of a detector temperature.<sup>11)</sup> The Standard methods<sup>2)</sup> was used to measure total solid (TS), volatile solid (VS), chemical oxygen remand

(COD), NH<sub>4</sub><sup>+</sup>-N and total nitrogen (TN). Each measurement was repeated three times for the analyses. Biogas produced from the BMP test was applied to create a cumulative methane production curve after adjusting temperature and water content by Eq. 1 and converted to dry gas at 0°C and 1 air pressure (101.325 kPa). In (Eq. 1), each symbol represents as follow: V dry gas represents dry gas volume, V wet gas at T°C represents wet gas volume at an operational temperature in a reactor, T represents an operational temperature in a reactor, P represents a pressure when measuring gas volume and P<sub>T</sub> represents a saturation vapor pressure (mmHg) at T°C. In this study, P was considered as 760 mmHg and P<sub>T</sub> was a saturation vapor pressure at 38°C.

$$V_{dry\ gas} = V_{wet\ gas\ at\ T^{\circ}C} \times \frac{273}{(273 + T)} \times \frac{(P - P_T)}{760} \quad (\text{Eq. 1})$$

An ultimate methane potential (B<sub>0</sub>) of a substrate from the BMP test was calculated by a modified gompertz model (Eq. 2). In the modified gompertz model, M (mL) represents a cumulative methane production, P (mL) represents a maximum methane production, R<sub>m</sub> (mL day<sup>-1</sup>) means a methane production rate, λ (day) means a lag phase time, t (day) means and e is exp (1).

$$M = P \times \exp \left[ - \exp \frac{R_m}{P} (\lambda - t) e + 1 \right] \quad (\text{Eq. 2})$$

A cumulative methane production curve from the BMP test makes possible to identify methane production characteristics by different incubator periods. If there are changes in a growth lag time by anaerobic digestion materials or a reaction rate to anaerobes, characteristics of anaerobic fermentations also change. Therefore various functional formulas have been developed using generalize various characteristics of anaerobic fermentations to estimate a maximum methane production. Among the fomulas, a modified gompertz model and an exponential model are

most widely used models to estimate maximum methane productions. The exponential model is good at characterizing an exponential phase growth of anaerobes, but it has difficulty in analyzing characteristics of growths and reaction rates from microbes with a long growth phase. On the other hand, the gompertz model has a merit of analyzing anaerobes a lag growth phase, an exponential growth phase, and a stationary growth phase. Therefore this research applied the modified gompertz to analyze characteristics of anaerobic fermentations.

#### 2.4 Anaerobic biodegradability

In this study, German VDI4630 was applied to an anaerobic decomposition rate of organic matters. The calculation of decomposition rate of organic matters using VDI4630 is shown in Eq. 3. VDI4630 is widely used to calculate an anaerobic decomposition rate of organic matters in German as a way of using ASTM in the USA.

$$AB_{i, VDI4630} = \frac{V_{i, biogas} \times C_{i, CH_4 + CO_2}}{m_{substrate} \times (VS_{substrate} + VFA_{substrate}) \times 0.93} \times 100 (\%) \quad (\text{Eq. 3})$$

where  $AB_{i, VDI4630}$  (%) is VS decomposition rate at an  $i$ -th day,  $V_{i, biogas}$  (mL) is dry biogas production at an  $i$ -th day,  $C_{i, CH_4 + CO_2}$  (g mL<sup>-1</sup>) is a mass fraction of methane and carbon dioxide in biogas at an  $i$ -th day,  $m_{substrate}$  (g) is mass of a substrate,  $VS_{substrate}$  (g g<sup>-1</sup>) is VS concentration of a substrate,  $VFA_{substrate}$  (g g<sup>-1</sup>) is volatile fatty acid (VFA) concentration of a substrate, and a biogas conversion factor is 0.93. In microbe reactions of actual anaerobic digestion tests, 5~10% of applied organic matters are used to multiply anaerobic microbe biomasses. For this reason, a biogas conversion factor was determined to lower of 7% than a calculated value.

Concentrations of methane and carbon dioxide to calculate  $C_{i, CH_4 + CO_2}$  were adjusted by Eq. 4 in the VDI4630 decomposition formula. This adjustment assumed that main components of biogas were methane and carbon dioxide. Based this assumption, a total amount of biogas

was turned into only methane and carbon dioxide by this equation.

$$C_{i, CH_4(CO_2)-corr} = C_{i, CH_4(CO_2)} \times \frac{100}{C_{i, CH_4} + C_{i, CO_2}} \quad (\text{Eq. 4})$$

where  $C_{i, CH_4(CO_2)-corr}$  (% v v<sup>-1</sup>) is a compensation concentration of components in biogas,  $C_{i, CH_4(CO_2)}$  (% v v<sup>-1</sup>) is a measured concentration of carbon dioxide or methane at  $i$ -th day,  $C_{i, CH_4}$  (% v v<sup>-1</sup>) is a measured concentration of methane at  $i$ -th day,  $C_{i, CO_2}$  (% v v<sup>-1</sup>) is a measured concentration of carbon dioxide at  $i$ -th day.

#### 2.5 Double first-order kinetics model

The BMP test analyzes qualitatively toxicity and inhibition of anaerobic microbes from applied materials using a batch anaerobic reactor and quantitatively ultimate methane potentials ( $B_u$ ). Estimating methane production potentials is based on decomposition reactions of anaerobic microbes. Therefore measurement accuracy of methane production potentials and degree of precision are affected by organic matter components and various factors that influence anaerobic digestion of microbes. In addition, a decomposition rate also differs by these factors.

Therefore, after calculating a decomposition rate from the previous BMP test, persistent biodegradable organic matters ( $VS_p$ ) and degradable organic matters ( $VS_e$ ) were calculated to estimate organic matter components by different reaction rates. In this study,  $VS_p$  and  $VS_e$  were calculated as follows.

A total volatile solid ( $VS_T$ ) in a biomass consists of degradable components ( $VS_B$ ) and non-biodegradable components ( $VS_{NB}$ ) in a anaerobic digestion (Eq. 5).

$$VS_T = VS_B + VS_{NB} \quad (\text{Eq. 5})$$

Where,  $VS_T$  (g) is a content of total volatile solids,  $VS_B$  (g) is a content of biodegradable VS, and  $VS_{NB}$  (g) is a content of non-biodegradable VS.

Degradable components are defined as easily degradable

VS ( $VS_e$ ) in an initial stage and persistent VS ( $VS_p$ ) in a later stage of decomposition (Eq. 6).  $VS_e$  accounts for a certain portion ( $f_c$ ) (Eq. 7) and  $VS_p$  is the remaining portion after leaving out the portion occupied by  $VS_e$  (Eq. 8).  $VS_B$  is expressed as shown in Eq. 9.

$$VS_B = VS_e + VS_p \quad (\text{Eq. 6})$$

$$VS_e = f_c \times VS_B \quad (\text{Eq. 7})$$

$$VS_p = (1 - f_c) VS_B \quad (\text{Eq. 8})$$

$$VS_B = f_c \times VS_B + (1 - f_c) VS_B \quad (\text{Eq. 9})$$

Where,  $VS_e$  (g) is a content of easily degradable VS,  $VS_p$  (g) is a content of persistent VS,  $f_c$  (% ,  $g\ g^{-1}$ ) is a rate of easily degradable VS.

The first order reaction rate of  $VS_e$  and  $VS_p$  is expressed as, where  $k_1$  and  $k_2$  is a rate constant of an anaerobic decomposition reaction for  $VS_e$  and  $VS_p$ , respectively,  $t$  (day) is time,  $[VS_e]_0$  (day) and  $[VS_e]_t$  (g) is an initial reaction time (0) and a content of reaction at  $t$  (Eq. 10, Eq. 11).

$$\frac{-d[VS_e]}{dt} = k_1 [VS_e] \quad (\text{Eq. 10})$$

$$\frac{-d[VS_p]}{dt} = k_2 [VS_p] \quad (\text{Eq. 11})$$

Integrating Eq. 10 and 11 and applying to Eq. 6 is same as Eq. 12.

$$[VS_B]_t = [VS_e]_0 e^{-k_1 t} + [VS_p]_0 e^{-k_2 t} = [VS_B]_0 \left\{ f_c e^{-k_1 t} + (1 - f_c) e^{-k_2 t} \right\} \quad (\text{Eq. 12})$$

A total amount of methane production ( $B_t$ ) is a methane yield produced at an initial reaction time ( $t_0$ ) and a reaction time ( $t$ ). This can be expressed as a content between a methane yield at an initial time ( $[VS_B]_0$ ) and at reaction time ( $t$ ), and it can be defined by multiplying a methane production factor ( $B_p$ ) and a methane production amount ( $B_t$ ) (Eq. 13).

$$[VS_B]_0 - [VS_B]_t = B_p \cdot B_t \quad (\text{Eq. 13})$$

Where,  $B_p$  is a methane yield constant,  $B_t$  (mL) is a methane production amount at time  $t$ .

If  $t$  approaches a limit,  $[VS_B]_t$  approaches zero and  $B$  approaches  $B_u$ . This can be expressed as Eq. 14.

$$B_u = [VS_B]_0 / B_p \quad (\text{Eq. 14})$$

Where,  $B_u$  (mL) is an ultimate methane production. If Eq. 13 and 14 are applied to Eq. 12, an amount of methane production at time  $t$  is calculated by multiplying fraction ratios of  $VS_e$  and  $VS_p$  in  $B_u$  and each constant of anaerobic decomposition. This result can estimate a content of methane production during a batch anaerobic digestion (Eq. 15). As a result, it is possible to analyze characteristics of organic matter decompositions from agricultural byproducts.

$$B_t = B_u \left\{ 1 - f_c e^{-k_1 t} - (1 - f_c) e^{-k_2 t} \right\} \quad (\text{Eq. 15})$$

Where,  $B_t$  (mL) is an amount of methane production at time  $t$ ,  $B_u$  (mL) is an amount of an ultimate methane production,  $f_c$  (% ,  $g\ g^{-1}$ ) is a ration of easily degradable VS,  $k_1$  is a kinetic constant of an anaerobic decomposition from  $VS_e$ , and  $k_2$  is a kinetic constant of an anaerobic decomposition from  $VS_p$ .

### 3. Results and Discussion

#### 3.1 Characteristics of substrate

Chemical properties of testing materials in this study is shown in Table 1. Testing materials, cucumbers, tomatoes, and paprika, had greater amounts of total solids (TS) from stalks, while smaller amounts from their fruits. Volatile solids (VS) which is an organic matter indicator of biogas conversion during an anaerobic digestion were range of 83~88% of TS content from stalks and 87~93% of TS amount from fruits. This result explains that fruits had

greater amounts of available organic matters. Adlays, upland crops, had 390 g kg<sup>-1</sup>, 351 g kg<sup>-1</sup> of TS content and radishes had 122 g kg<sup>-1</sup>. Rinds of juice process wastes, apples, pears and tangerines had 158–249 g kg<sup>-1</sup> of TS content and overall greater organic matter contents.

### 3.2 Ultimate methane potential (B<sub>u</sub>)

The results of methane production potentials are shown in Table 2. Vegetable by-products from green houses

showed that stalks had significantly smaller methane productions than fruits as a result of cumulative methane production calculation. This result can be explained as slow microbial decompositions because stalks of vegetable crops have mainly greater amounts of hard tissues and lignin. Previous studies reported that the lignin do not decompose as easily as easily biodegradable organic matters and have a great rate of corrosion conversion. The greatest B<sub>u</sub> value from green house crops was

Table 1. Chemical Characteristics of the Agricultural Waste Biomass

Byproducts	TS <sup>1)</sup>	VS <sup>2)</sup>	TN	TP	K	Ca	Mg	Na	Fe	Co	Ni	Mo	Cu	Zn
	g kg <sup>-1</sup>									mg kg <sup>-1</sup>				
Cucumber	32.8	28.5	36.0	0.62	1.75	0.23	0.13	0.01	0.02	0.02	0.13	0.09	1.00	6.78
Cucumber stem	103.3	85.1	18.5	2.30	6.07	2.12	0.66	0.03	0.10	0.05	0.76	0.17	3.22	35.89
Tomato	79.7	72.8	18.4	0.57	1.16	0.11	0.14	0.03	0.16	0.02	0.51	0.19	57.1	15.76
Tomato stem	108.3	94.7	15.8	0.79	4.79	1.52	0.50	0.11	0.09	0.04	0.43	0.30	2.39	24.76
Paprika	74.43	69.0	22.6	0.63	2.34	0.10	0.11	0.02	0.07	0.02	0.17	0.11	1.40	22.29
Paprika stem	164.4	144.4	24.6	1.16	9.77	1.56	0.49	0.10	0.10	0.07	0.66	0.41	5.43	39.39
Adlay straw	390.0	351.6	13.7	4.27	5.03	1.36	0.65	0.09	0.32	0.39	4.42	5.02	0.39	45.3
Radish	165.1	121.5	48.4	1.37	1.98	1.99	0.28	0.81	0.14	0.04	1.04	0.06	22.37	12.41
Apple sludge	162.4	157.5	0.8	0.26	0.86	0.08	0.06	0.04	0.13	0.06	1.41	3.10	2.07	10.53
Pear sludge	219.7	211.2	8.7	1.63	0.64	0.09	0.31	0.01	0.16	0.03	1.69	0.25	90.81	22.6
Tangerine peel	296.3	249.1	11.1	1.18	1.40	0.52	0.64	0.07	0.32	0.03	1.94	0.25	306.5	61.97

TS : total solid content, VS : volatile solid content.

Table 2. Parameters of Methane Production Curve Estimated by the Modified Gompertz Equation in the Agricultural Waste Biomass

Byproducts	B <sub>u</sub>	P	R <sub>m</sub>	λ
	Nm <sup>3</sup> kg <sup>-1</sup> -VS <sub>added</sub>	mL	mL day <sup>-1</sup>	day
Cucumber	0.398	397.3	38.2	0.4
Cucumber stem	0.317	427.7	31.2	0.5
Tomato	0.300	237.9	17.2	-
Tomato stem	0.250	197.5	19.5	0.7
Paprika	0.343	391.8	33.3	0.4
Paprika stem	0.207	167.2	16.7	0.8
Adlay straw	0.364	291.8	25.4	-
Radish	0.279	131.5	8.8	0.3
Apple sludge	0.393	405.9	32.0	0.6
Pear sludge	0.176	83.1	3.5	-
Tangerine peel	0.279	160.2	8.7	-

B<sub>u</sub> : ultimate methane potential, P : methane production, R<sub>m</sub> : specific methane production rate,  
λ : lag phase time.

0.398 Nm<sup>3</sup> kg<sup>-1</sup>-VS<sub>added</sub> from cucumbers and the lowest ones was 0.207 Nm<sup>3</sup> kg<sup>-1</sup>-VS<sub>added</sub> from paprika stalks. Adlays, upland crops, had the B<sub>0</sub> value of 0.364 Nm<sup>3</sup> kg<sup>-1</sup>-VS<sub>added</sub> and this had no significant difference from green house crops. Sludge from process plants had overall smaller methane production potentials. Particularly, sludge from pear process plants showed smaller value of a methane production potential, 0.176 Nm<sup>3</sup> kg<sup>-1</sup>-VS<sub>added</sub>, while ones from apple process plants had 0.393 m<sup>3</sup> kg<sup>-1</sup>-VS<sub>added</sub> of a methane production potential. This result can be interpreted as process of two fruits in plants. The sludge of apples are sludge after squeezing juices, while pears are boiled with various additives and this causes consumption of organic matters for microbes to use. The daily ultimate methane production (R<sub>m</sub>) was 38.2, 31.2 mL day<sup>-1</sup> from cucumber fruits and stalks. The R<sub>m</sub> value was smaller as 17.2, 19.5 mL day<sup>-1</sup> from tomato fruits and stalks and 33.3, 16.7 mL day<sup>-1</sup> from leaves and stalks of paprika. The lag phase time was overall shorter and tomatoes, adlays, pear sludge and apple sludge had no lag phase time. The rest by-products had shorter lag phase times than 1 day. This result showed that cellulose contents in agricultural biomasses did not affect a lag growth phase.

### 3.3 Analyses of organic matter components by reaction rate

Anaerobic biodegradability of organic matters (AB) was analyzed by methane production potential test of biomass and interpreted by German VDI4630. The AB values were 87.1% and 71.5% from cucumber fruits and stalks, 68.8% and 58.0% from tomato fruits and stalks, and 91.1% and 48.2% from paprika fruits and stalks. These results showed that stalks had significantly smaller decomposition rate than fruits (Table 3, Fig. 1). These results were caused because plant organic matters were blocked by cell walls and it required longer time for anaerobic digestion bacteria to produce methane and carbon dioxide.<sup>7)</sup>

The factor (k) of the anaerobic decomposition rate was calculated by substrate decomposition analyses before the analyses of the batch methane potentials. All the biomasses applied in this study showed rapid decomposition in the initial stage. Then the decomposition rate began to slow down for a certain period and the rate became 10 times slower than the initial decomposition rate. This trend of decomposition rate changes is typical conditions of biomass decompositions.<sup>6)</sup> Therefore, the factor of the rapid decomposition rate in the initial stage, (k<sub>1</sub>) and

Table 3. Parameters of Methane Production Curve Estimated by the Double First Order Kinetics Model on Agricultural Waste Biomass

Byproduct	biodegradability	f <sub>e</sub>	k <sub>1</sub>	k <sub>2</sub>	R <sup>2</sup>
	(%)	-	(day <sup>-1</sup> )	(day <sup>-1</sup> )	
Cucumber	87.1	0.42	0.152	0.002	0.9892
Cucumber stem	71.5	0.76	0.097	0.018	0.9851
Tomato	68.8	0.69	0.145	0.024	0.9902
Tomato stem	58.0	0.75	0.147	0.020	0.9640
Paprika	91.1	0.49	0.144	0.005	0.9498
Paprika stem	48.2	0.82	0.138	0.018	0.9414
Adlay straw	81.5	0.78	0.149	0.019	0.9865
Radish	44.0	0.79	0.097	0.021	0.9828
Apple processing sludge	89.3	0.77	0.114	0.023	0.9705
Pear processing sludge	30.8	0.52	0.128	0.021	0.9756
Tangerine peel	55.3	0.80	0.094	0.029	0.9886

biodegradability: biodegradability by VDI4630 method, f<sub>e</sub>: easily degradable VS ratio (g/g), k<sub>1</sub>: easily biodegradable reaction kinetic constant, k<sub>2</sub>: persistently biodegradable reaction constant.

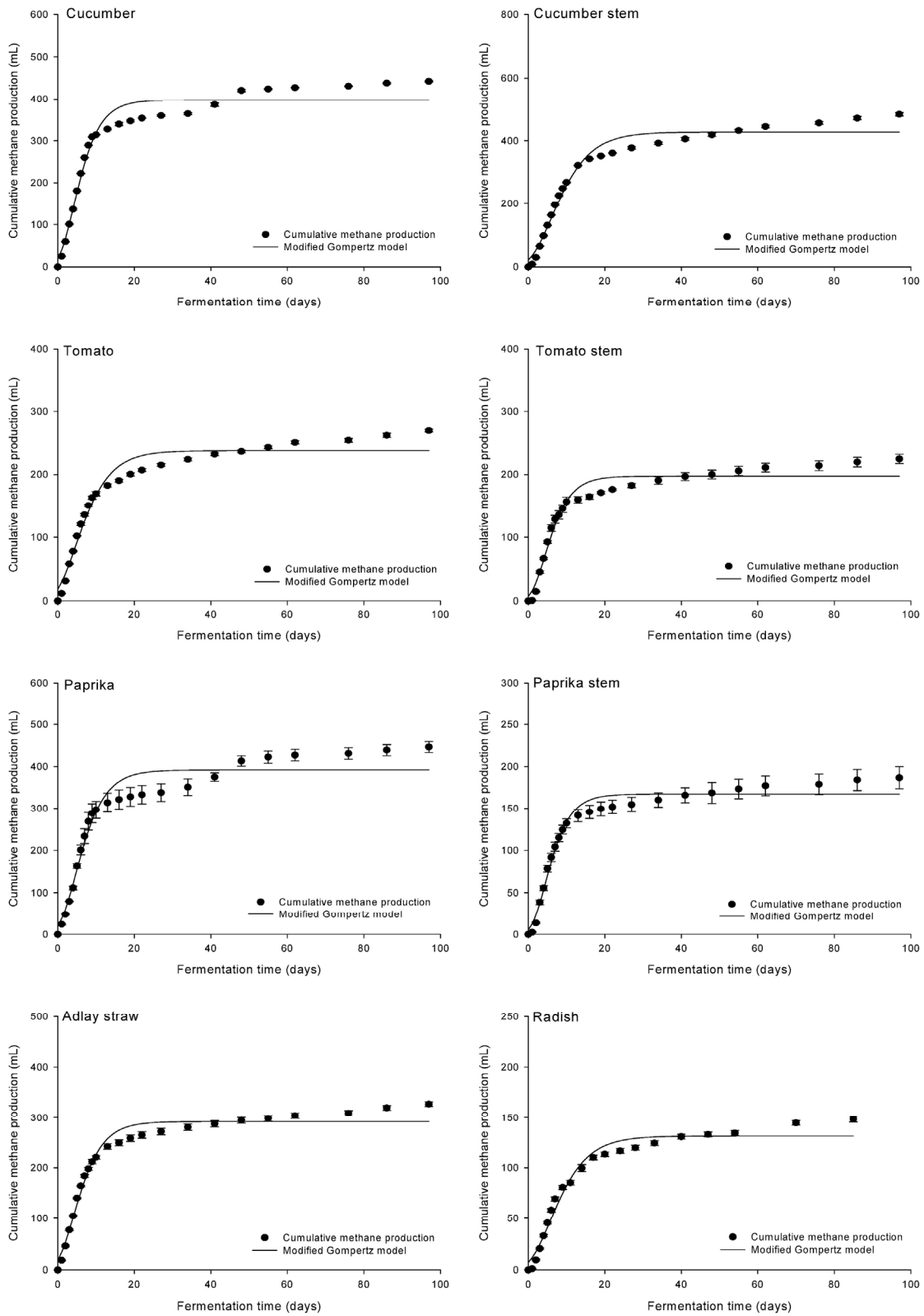


Fig. 1. Cumulative methane productions agricultural waste biomass during batch anaerobic digestion.



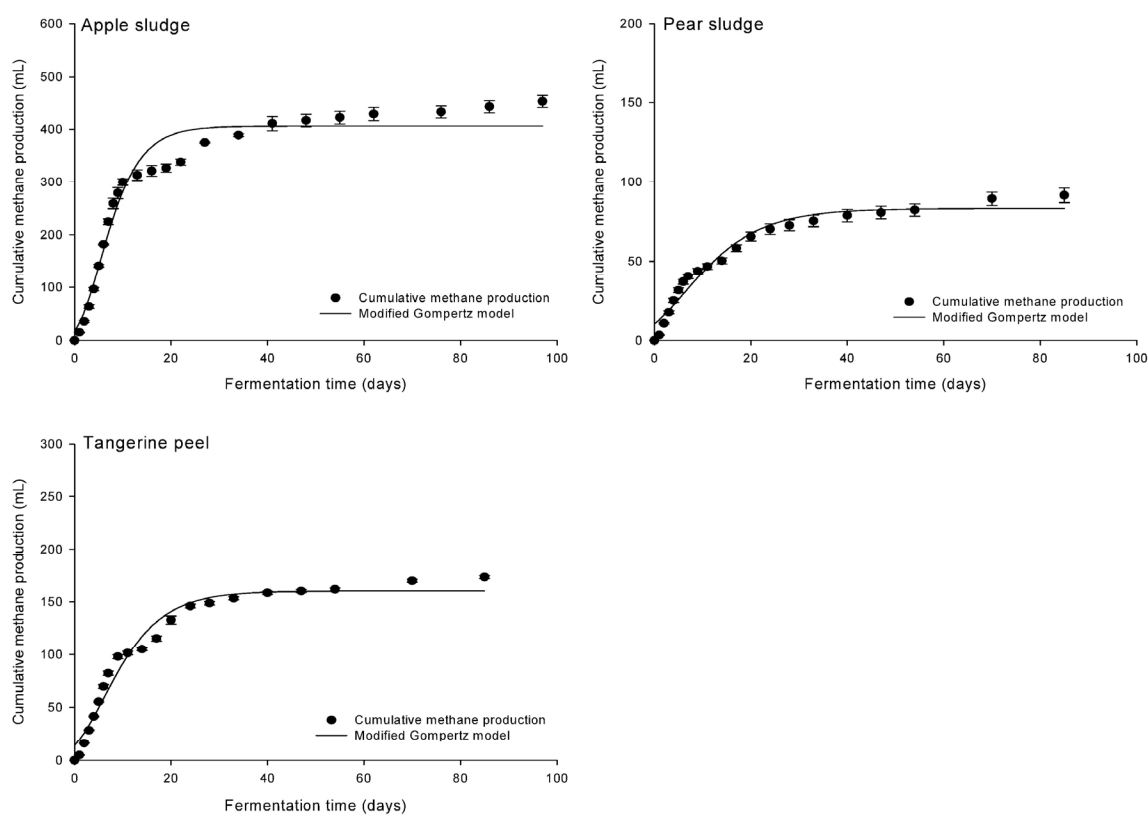


Fig. 1. Continued.

the 10 times slower rate in the later part, ( $k_2$ ) were calculated. The easily degradable factors ( $k_1$ ) were ranged between  $0.097 \sim 0.152 \text{ day}^{-1}$  from vegetable crops and persistent degradable factor ( $k_2$ ) were  $0.002 \sim 0.024 \text{ day}^{-1}$ . Among these results, greater organic matter decomposition rates from VDI4630 had greater  $k_1$  values ( $0.152, 0.144 \text{ day}^{-1}$ ) and smaller  $k_1$  values ( $0.002, 0.005 \text{ day}^{-1}$ ) from cucumbers and paprika. In a meanwhile, radishes and tangerine rinds which had low decomposition rates showed  $0.097$  and  $0.094 \text{ day}^{-1}$  of  $k_1$  values and decomposition rates seems to affect  $k_1$  values.

The ratios of the relatively rapid decomposition rate from  $k_1$  and slow decomposition rate  $k_2$  in substrates were calculated for each biomass and the results are shown in Table 4. In general, vegetables have great contents of crude fiber and it was expected to account for a large proportion of non-degradable and persistent degradable organic matters. But this study showed different results.

In Table 4, cucumber fruits had small amount of non-degradable organic matters as 12.9%, while persistent degradable organic matters occupied greater portion as 50.1%, which meant relatively small amount of easily degradable organic matters. However this trend was shown in rare cases, overall agricultural biomasses had great portions of easily degradable organic matters and non-degradable organic matters. On the other hand, persistent degradable organic matters showed relatively small contents.

Table 4. Composition of Organic Matter Divided by the Biodegradability on Agricultural Waste Biomass

Byproduct	VS <sub>T</sub>	VS <sub>B</sub>		VS <sub>NB</sub>
		VS <sub>e</sub>	VS <sub>p</sub>	
------(%)-----				
Cucumber	100	37.0	50.1	12.9
Cucumber stem	100	54.2	17.3	28.5
Tomato	100	47.4	21.4	31.2
Tomato stem	100	43.5	14.5	42.0
Paprika	100	44.6	46.5	8.9
Paprika stem	100	39.3	8.9	51.8
Adlay straw	100	63.6	17.9	18.5
Radish	100	34.8	9.2	56.0
Apple processing sludge	100	69.0	20.3	10.7
Pear processing sludge	100	16.1	14.7	69.2
Tangerine peel	100	44.1	11.2	44.7

VS<sub>T</sub>: total volatile solid, VS<sub>B</sub>: biodegradable VS, VS<sub>e</sub>: easily degradable VS, VS<sub>NB</sub>: non-biodegradable VS.

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