

# Prediction of methane production performances based on determination of organic components for different vegetable wastes

Fanfan Cai<sup>1</sup>, Hu Yan<sup>1</sup>, Ruihong Zhang<sup>2</sup>, Guangqing Liu<sup>1\*</sup>, Chang Chen<sup>1</sup>

(1. Biomass Energy and Environmental Engineering Research Center, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China;

2. Department of Biological and Agricultural Engineering, University of California, Davis, CA 95616, USA)

**Abstract:** The rapid development of the economy has led to rapid consumption of fossil fuels, which results in extremely serious environmental problems. Biomass energy has been accepted as a way to reduce the usage of fossil fuels due to its cleanliness and renewability. In this study, vegetable wastes (VWs), an abundant kind of biomass resource, were treated by anaerobic digestion (AD) to be converted into methane. The total solids (TS), volatile solids (VS), elemental contents, and organic components of 17 kinds of typical VWs were systematically determined. The methane production performances were then measured and ranged from 120.1 mL/g VS (for pepper stem) to 377.7 mL/g VS (for bok choy). To easily and quickly predict the methane yields of VWs, a curvilinear relationship between different organic compositions (e.g., cellulose, hemicellulose, lignin, non-structural carbohydrate, protein, and VFA contents) and methane production was established and proved to be a useful tool for methane prediction. Four kinetic models (first-order model, Fitzhugh model, Cone model, modified Gompertz model) were applied to simulate the process of AD, and Cone and modified Gompertz models were shown to describe the AD process well. This study will not only provide basic data about the characteristics and methane production of 17 kinds of VWs but also contribute a method for predicting the methane yields of vegetable wastes, which is also valuable in future agro-industrial applications.

**Keywords:** anaerobic digestion, organic components, methane production, vegetable waste, kinetic models

**DOI:** 10.25165/j.ijabe.20191203.4705

**Citation:** Cai F F, Yan H, Zhang R H, Liu G Q, Chen C. Prediction of methane production performances based on the determination of organic components for different vegetable wastes. *Int J Agric & Biol Eng*, 2019; 12(3): 154–159.

## 1 Introduction

With the fast development of the economy, the energy demand is increasing every year, which leads to more and more depletion of fossil fuels. According to China Statistical Yearbook 2017, China, which is the second largest economic system in the world, consumed a large amount of coal, oil, and natural gas, which accounts for 86.7% of the total energy consumption in 2016<sup>[1]</sup>. Inevitably, in the process of utilizing those fossil fuels, various kinds of soil, water, and air pollutants were generated<sup>[2-4]</sup>. Biomass energy, which is renewable and clean<sup>[5]</sup>, has been regarded as one of the most popular alternatives to fossil fuels<sup>[6]</sup>.

Vegetable waste (VW) is produced in the process of vegetable planting, growing, harvesting, and processing<sup>[7]</sup>. It is an increasing biomass resource, accounting for approximately 30% of the total vegetable yield<sup>[8-10]</sup>. Most VWs are currently treated by landfilling and incineration, which lead to secondary pollutants in the environment<sup>[7]</sup>. Anaerobic digestion (AD), which can

efficiently convert biomass wastes to methane<sup>[11,12]</sup>, has been applied in managing many conventional agricultural residues, such as lignocellulosic materials and animal manures<sup>[13-16]</sup>. VW has a high moisture content, organic content, and high biodegradability, which make it a desired feedstock for AD<sup>[7,17]</sup>.

Prior studies have assessed the AD of VWs, and most of them used mixed VWs<sup>[10,18-20]</sup>. However, AD performance of mixed VWs will be greatly influenced by the vegetable variety, location, season, and even collection method. These factors can cause fluctuations in feedstock and AD performance. It is scientifically necessary and important to investigate waste characteristics and methane production performances, which were rarely reported before. Moreover, as an important energy conversion parameter, the methane yield is directly influenced by the organic components, such as cellulose, hemicellulose, protein, and non-structural carbohydrate<sup>[12,21]</sup>. It will be very helpful if the methane production of VWs could be quickly estimated by simply measuring the organic components.

The major objectives of this study were as follows: 1) to systematically investigate the characterization and methane production of 17 representative kinds of VWs in China; 2) to explore the correlation between biochemical components and methane yields to predict the methane production performance easily through properties analysis; and 3) to provide some basic data and useful reference for future scientific research and industrial utilization of VWs.

## 2 Materials and methods

### 2.1 Feed and inoculum

Seventeen typical kinds of VW, which were massively

**Received date:** 2018-10-10 **Accepted date:** 2019-05-02

**Biographies:** Fanfan Cai, Master candidate, research interest: environmental engineering, chemical engineering, Email: 931451931@qq.com; Hu Yan, PhD candidate, research interest: environmental engineering, chemical engineering, Email: yanhu1101@163.com; Ruihong Zhang, PhD, Professor, research interest: agricultural engineering, environmental engineering, Email: rhzhang@ucdavis.edu; Chang Chen, PhD, Professor, research interest: environmental engineering, biological engineering, agricultural engineering, Email: chenchang@mail.buct.edu.cn.

\*Corresponding authors: Guangqing Liu, PhD, Professor, research interest: agricultural engineering, environmental engineering, 505 Zonghe Building, Beijing University of Chemical Technology, 15<sup>th</sup> North 3<sup>rd</sup> Ring East Road, Beijing 100029, China. Tel/Fax: +86-10-6444-2375, Email: gqliu@mail.buct.edu.cn.

produced or abandoned in the field, were collected from farms in Shandong province, China, where the output of vegetables is enormous. The common and Latin names, the used parts and the abbreviations are shown in Table 1. After collection, some vegetable wastes were divided into leaves and stems. All the samples were shredded to 3-5 mm using a grinder (JOYOUNG, China). They were then stored at 4 °C in a refrigerator.

The sludge was obtained from Donghuashan biogas plant, where only pig manure was used as feedstock. Before use, the inoculum was placed in room temperature. Then, the supernate was removed and the precipitate was used as inoculum.

**Table 1 Common and Latin name, the used parts, and the abbreviations of 17 kinds of VWs**

Latin name	Common name	Used parts	Abbreviations
<i>Lactuca sativa</i> L.	Lettuce	Whole	VW1
<i>Spinacia oleracea</i> L.	Spinach	Whole	VW2
<i>Brassica chinensis</i> var. <i>chinensis</i>	Bok choy	Whole	VW3
<i>Brassica chinensis</i> L.	Chinese cabbage	Whole	VW4
<i>Chrysanthemum coronarium</i> L.	Crown daisy	Whole	VW5
<i>Cucurbita pepo</i> L.	Zucchini	Leaf	VW6
<i>Pisum sativum</i> var. <i>saccharatum</i>	Snow peas	Leaf	VW7
<i>Apium graveolens</i> L.	Celery	Leaf	VW8
<i>Apium graveolens</i> L.		Stem	VW9
<i>Solanum tuberosum</i> L.	Potato	Leaf	VW10
<i>Solanum tuberosum</i> L.		Stem	VW11
<i>Capsicum annuum</i> L.	Pepper	Leaf	VW12
<i>Capsicum annuum</i> L.		Stem	VW13
<i>Capsicum annuum</i> L. var. <i>grossum</i> (Willd.) Sendtn.		Leaf	VW14
<i>Capsicum annuum</i> L. var. <i>grossum</i> (Willd.) Sendtn.	Bell pepper	Stem	VW15
<i>Solanum melongena</i> L.	Eggplant	Leaf	VW16
<i>Solanum melongena</i> L.		Stem	VW17

Note: VW1-VW5, VW8, and VW9 were edible parts; the others were inedible parts left in the field.

## 2.2 Characterization methods

### (1) Determination of total solids (TS) and volatile solids (VS)

TS and VS contents of substrates and inoculum were determined using the APHA standard method<sup>[22]</sup>. The TS and VS contents of inoculum were measured as (6.00±0.02)% and (2.57±0.00)% (w/w), respectively.

### (2) Elemental analysis

The elemental contents of C, N, and H were detected using an organic element analyzer (Vario EL cube, Germany). The oxygen elemental content was then calculated by the equation: C + H + N + O = 99.5% (VS based)<sup>[23]</sup>.

### (3) Determination of cellulose, hemicellulose, and lignin contents

The neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) were determined using an ANKOM 2000 fiber analyzer (ANKOM, USA)<sup>[24]</sup>. The ash ( $A_{ADL}$ ) content containing in ADL was measured using the APHA standard method<sup>[22]</sup>. The cellulose, hemicellulose, and lignin contents were calculated as: cellulose = NDF-ADF, hemicellulose = ADF-ADL, lignin = ADL- $A_{ADL}$ .

### (4) Determination of non-structural carbohydrate, protein, and VFA

The non-structural carbohydrate contents were determined by DNS colorimetric method using 3,5-Dinitrosalicylic acid (DNS) reagent<sup>[25]</sup>. The protein contents were tested by Branford method

using Coomassie Brilliant Blue G250<sup>[26]</sup>. The volatile fatty acid (VFA) contents of the raw materials were measured using a gas chromatograph (GC, Agilent 7890A, USA) equipped with a flame ionization detector and DB-wax capillary column (30 m×530 μm×1.0 μm).

All the characterizations were measured with three parallels.

## 2.3 Anaerobic digestion experiments

The organic loading and the feed-to-inoculum ratio of all the anaerobic digesters were set to 5 g VS/L and 1:1<sup>[14]</sup>. The inoculum and the substrate were firstly added into each digester. Tap water was then poured in to get a working volume of 250 mL. Nitrogen was filled into each digester to remove the oxygen and create an anaerobic condition. All the digesters were put in an incubator with the temperature of 37 °C. The blank control without raw material added was also set in the same condition to detect the methane produced by inoculum. Every condition has three parallels.

## 2.4 Biogas analysis

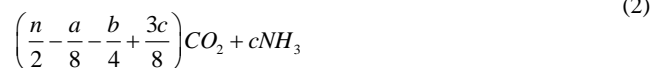
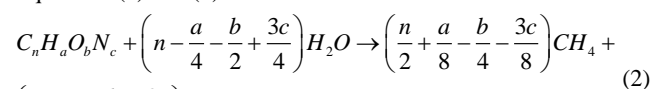
The biogas production was calculated by incorporating the pressure difference measured by a 3151 WAL-BMP-Test system pressure gauge (WAL Messund Regelsysteme GmbH, Germany) with the following Equation (1)<sup>[27]</sup>:

$$V_b = \frac{\Delta p \cdot V_h \cdot C}{R \cdot T} \quad (1)$$

where,  $V_b$  means the daily biogas production, L;  $\Delta p$  stands for the absolute pressure difference, kPa;  $V_h$  represents the headspace volume of the anaerobic digester, L;  $C$  is the molar volume in normal temperature-pressure, 22.4 L/mol;  $R$  refers to the thermodynamic constant, 8.314 kPa/K mol, and  $T$  is the temperature of the incubator, 310.15 K. The biogas compositions were then tested by a GC (Agilent 7890B, USA) equipped with a thermal conductivity detector and an analytical column of Agilent Hayesep Q.

## 2.5 Maximum theoretical methane production and biodegradability

Maximum theoretical methane production (TMP) means the maximum methane production of the substrate in theory. It was calculated based on the compositions of organic elements, such as carbon (C), hydrogen (H), oxygen (O), and nitrogen (N), as shown in Equations (2) and (3)<sup>[28]</sup>:



$$TMP \left( \frac{\text{mL } CH_4}{\text{g VS}} \right) = \frac{22.4 \times 1000 \times \left( \frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8} \right)}{12n + a + 16b + 14c} \quad (3)$$

The biodegradability (BD) was calculated as the ratio of the cumulative methane production (CMP) to TMP, as shown in Equation (4):

$$BD = \frac{CMP}{TMP} \quad (4)$$

## 2.6 Kinetic models

Many models have been applied to simulate the AD process<sup>[29-32]</sup>, among which the following four commonly used kinetic models (first-order model, Fitzhugh model, Cone model, and modified Gompertz model) were employed, shown as Equations (5)-(8)<sup>[31,33-35]</sup>:

$$B = B_o [1 - \exp(-k_{hyd} t)] \quad (5)$$

$$B = B_o[1 - \exp(-k_{hyd}t)^n] \quad (6)$$

$$B = \frac{B_o}{1 + (k_{hyd}t)^{-n}} \quad (7)$$

$$B = B_o \cdot \exp\left\{-\exp\left[\frac{R_{max}}{B_o} \cdot e(\lambda - t) + 1\right]\right\} \quad (8)$$

where,  $B$  represents the CMP, mL/g VS, for a anaerobic digestion time  $t$ , d;  $B_o$  represents the simulated maximum methane yield, mL/g VS;  $k_{hyd}$  stands for hydrolysis rate constant, 1/d;  $R_{max}$  is the maximum methane production rate, mL/(g VS d);  $e$  equals to 2.7183;  $\lambda$  is the lag phase time, d, and  $n$  stands for a dimensionless factor.

### 3 Results and discussions

#### 3.1 Characteristics of VWs

As seen from Table 2, all the selected VWs had extremely different characteristics. Relatively low TS contents of 3.93% ± 0.05% to 18.74% ± 0.14% (w/w) and VS contents of 2.56% ± 0.05% to 14.36% ± 0.20% (w/w) were obtained, which were close to other reported mixed VWs<sup>[7,18]</sup> and indicating the high moisture contents of VWs. In particular, leaf vegetable wastes (e.g., lettuce, spinach, bok choy, Chinese cabbage, crown daisy) had a moisture content of more than 90%<sup>[10,20]</sup>. In addition, it was found that the leaves of a single species had higher TS contents and VS contents than stems

of the same species in this study, except for pepper, whose VS content of stem (13.67% ± 0.42%, w/w) was slightly higher than that of leaf (12.36% ± 0.01%, w/w). Generally high values of VS/TS ranging from 65.23% to 84.20% were calculated for all raw materials, implying high organic matter contents, which were desirable for AD<sup>[36]</sup>. The C/N ratios ranged from 5.05 to 16.46, most of which were slightly lower than the ideal range of C/N (from 15 to 30)<sup>[15,37]</sup>.

The organic compositions of cellulose, hemicellulose, lignin, non-structural carbohydrate, protein, and VFA are also shown in Table 2. For some stem samples such as celery stem, pepper stem, bell pepper stem, and eggplant stem, lignocellulosic contents were determined to be 57.68%, 66.40%, 46.05%, and 54.11%, respectively, among which cellulose accounted for the majority (35.12% ± 0.95%, 36.06% ± 0.01%, 27.14% ± 0.99%, and 35.13% ± 1.13%, respectively). The lignocellulosic contents for the rest of the substrates were less than 45%. For majority of the samples, the contents of non-structural carbohydrate were less than 2%, except for Chinese cabbage, snow pea leaf, celery stem, and eggplant stem, whose contents were 2.83% ± 0.28%, 4.01% ± 0.09%, 3.52% ± 0.05%, and 2.41% ± 0.17%, respectively. All the VWs had relatively low protein and VFA contents of 0.06% ± 0.00% - 1.47% ± 0.01% and 0.19% ± 0.01% - 1.76% ± 0.06%, respectively.

**Table 2 Characteristics of different VWs**

TS /%	VS /%	VS/TS /%	Elemental contents/%				C/N	Organic compositions/%					Ash /%		
			C	H	N	O		Cellulose	Hemicellulose	Lignin	Non-structural carbohydrate	Protein		VFA	
VW1	4.87±0.06	3.77±0.05	77.30	38.61	5.49	4.61	28.21	8.38	14.36±0.59	11.91±0.33	15.18±0.96	1.05±0.13	1.00±0.02	1.45±0.02	22.70
VW2	8.89±0.14	6.81±0.18	76.68	37.77	5.24	4.70	28.58	8.04	12.22±0.37	12.36±0.22	7.47±0.37	0.62±0.06	0.60±0.05	1.48±0.10	23.32
VW3	3.93±0.05	2.56±0.04	65.23	33.35	5.01	6.34	15.95	5.26	15.82±0.80	10.20±0.25	4.83±0.06	0.25±0.03	0.55±0.03	0.97±0.01	34.77
VW4	5.67±0.06	3.94±0.07	69.62	32.36	4.80	5.55	26.56	5.83	14.70±0.24	9.48±0.37	6.46±0.39	2.83±0.28	0.19±0.02	1.34±0.01	30.38
VW5	6.40±0.05	4.77±0.05	74.58	37.58	5.33	5.07	26.22	7.41	10.64±0.39	10.94±0.11	12.23±0.09	0.88±0.05	0.81±0.03	1.76±0.06	25.42
VW6	15.31±0.23	11.50±0.30	75.15	38.94	5.65	4.59	25.59	8.48	12.27±0.63	12.83±1.14	11.50±0.59	0.58±0.11	0.33±0.04	0.63±0.01	24.85
VW7	18.01±0.02	14.36±0.20	79.73	39.68	5.59	3.12	30.94	12.72	19.73±0.46	13.96±0.38	4.10±0.38	4.01±0.09	0.27±0.03	1.74±0.12	20.27
VW8	11.41±0.01	8.21±0.05	72.00	34.79	5.23	3.14	28.48	11.08	13.79±0.56	10.19±0.11	5.65±0.15	0.81±0.02	0.52±0.02	1.01±0.01	28.00
VW9	3.95±0.15	2.71±0.16	68.50	29.95	4.59	1.82	31.77	16.46	35.12±0.95	10.30±0.46	12.26±0.35	3.52±0.05	0.97±0.07	1.43±0.04	31.50
VW10	10.50±0.27	8.36±0.25	79.68	39.47	5.62	5.63	28.56	7.01	12.66±0.43	12.42±0.98	7.80±0.41	0.50±0.12	1.47±0.01	1.67±0.01	20.32
VW11	5.28±0.15	3.68±0.13	69.64	27.91	4.05	5.53	31.80	5.05	17.23±0.97	5.90±0.32	3.14±0.06	1.39±0.13	0.60±0.08	0.96±0.01	30.36
VW12	17.55±0.06	12.36±0.01	70.44	33.57	4.67	4.23	27.62	7.94	11.93±0.25	12.85±0.85	6.73±0.22	0.18±0.02	0.22±0.03	0.59±0.01	29.56
VW13	16.39±0.44	13.67±0.42	83.42	36.80	5.27	2.84	38.08	12.96	36.06±0.01	14.72±0.16	15.62±0.78	1.02±0.21	0.06±0.00	0.33±0.01	16.58
VW14	16.59±0.45	13.02±0.43	78.49	38.67	5.42	5.74	28.26	6.74	12.17±0.70	17.69±1.43	5.08±0.11	0.07±0.04	0.90±0.03	0.44±0.01	21.51
VW15	12.52±0.38	10.07±0.39	80.44	35.19	5.19	4.10	35.55	8.58	27.14±0.99	12.14±0.16	6.76±0.55	0.13±0.02	0.38±0.01	0.19±0.01	19.56
VW16	18.74±0.14	14.00±0.53	74.70	40.44	5.40	4.74	23.72	8.53	15.08±0.52	15.75±1.07	5.50±0.65	0.45±0.01	0.48±0.01	1.51±0.02	25.30
VW17	14.79±0.18	12.46±0.23	84.20	37.81	5.36	2.33	38.27	16.23	35.13±1.13	11.42±0.38	7.56±0.29	2.41±0.17	1.02±0.02	0.78±0.01	15.80

Note: TS and VS were tested based on total materials; elemental contents, organic compositions, and ash contents were measured based on TS.

#### 3.2 Methane production performance and biodegradability

As seen from Figure 1a-1d, the CMP of all the VWs were in the range of 120.1±1.8 mL/g VS to 377.7±12.1 mL/g VS. The majority of the substrates showed a CMP of more than 150.0 mL/g VS, and nearly half of them had methane yields higher than 200.0 mL/g VS. Among the substrates, leaf vegetable wastes performed especially well, and the highest CMP was produced by bok choy with a value of 377.7±12.1 mL/g VS, which might be attributed to the low TS contents. Generally, the stems of one single species had significantly lower CMP than the leaves of the same species for most VWs. The hardness of stems could be the main reason as they were difficult to dissolve in water. However,

the CMP of celery stem was obviously higher than celery leaf, which might be because of the much higher non-structural carbohydrate content of celery stem (3.52% ± 0.05%) than leaf (0.81% ± 0.02%)<sup>[12]</sup>. The lowest CMP was produced by pepper stem (120.1±1.8 mL/g VS) due to its high lignin content of 15.62% ± 0.78%, which might influence the methane production<sup>[32]</sup>.

BD means the proportion of organic matters of substrates that are converted during the AD process<sup>[13]</sup>. A higher BD always indicates a higher conversion efficiency during AD<sup>[28]</sup>. The BD of studied VWs ranged from 29.25% to 64.04% as shown in Figure 2. It was found that those substrates (e.g., spinach, bok choy, crown daisy, celery stem, and potato leaf) that had the high CMP of more

than 250 mL/g VS (296.3±19.5, 377.7±12.1, 275.6±4.3, 275.2±7.0, and 256.1±1.5 mL/g VS, respectively) also showed relatively high BD which exceeded 50% (60.93%, 64.04%, 54.14%, 65.56%, and 51.78%, respectively). The lowest BD was found in pepper stem which also performed the lowest CMP, probably due to the very low nitrogen content (2.88%) which might limit the growth of anaerobic microorganisms<sup>[34]</sup>, and high lignin content (15.62%±0.78%) which was hard to be utilized in AD<sup>[37]</sup>. Some other VWs, such as Chinese cabbage, zucchini leaf, and eggplant

leaf, also showed relatively low BD (37.33%, 32.98%, and 34.82%, respectively), which could be partly because of the low C/N (5.83, 8.48, and 8.58, respectively) that were extremely less than the optimal C/N ratio for AD<sup>[15]</sup>.

In conclusion, the high CMP and BD for the majority of the selected VWs verified that VWs would be suitable feedstock for methane production during AD. It is worthwhile to employ AD to manage the huge amount of VWs that were left in the field in the future.

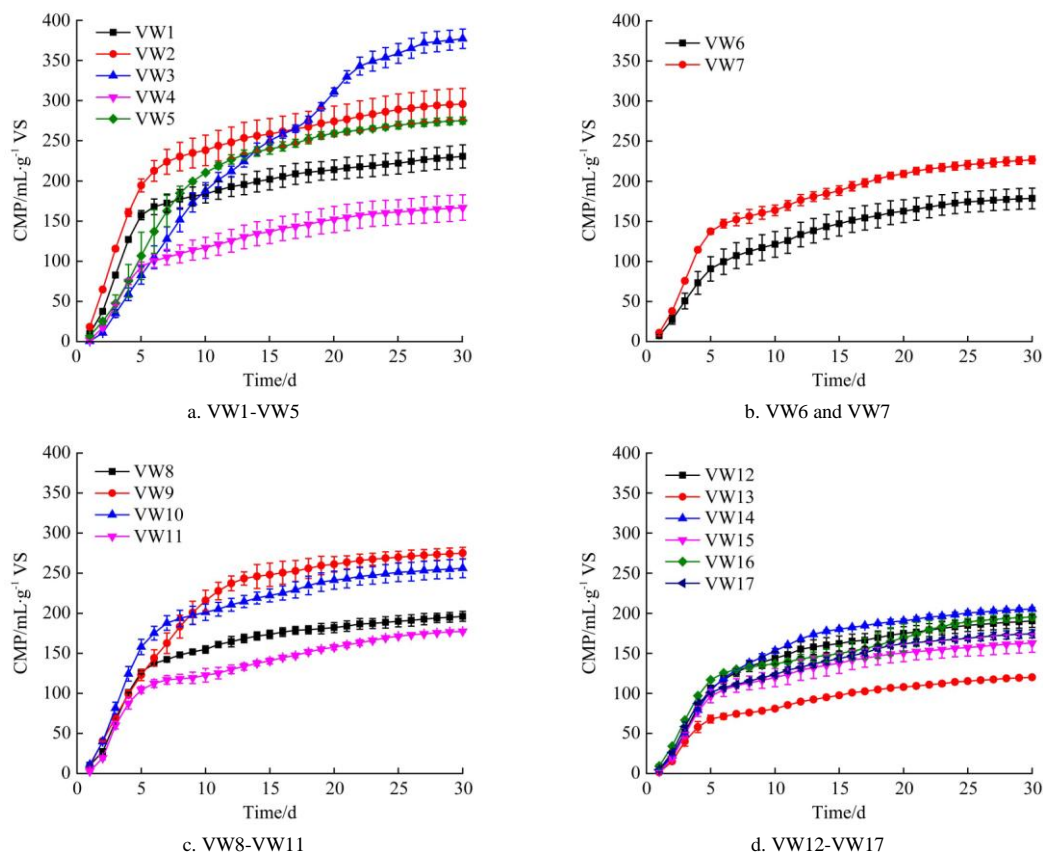
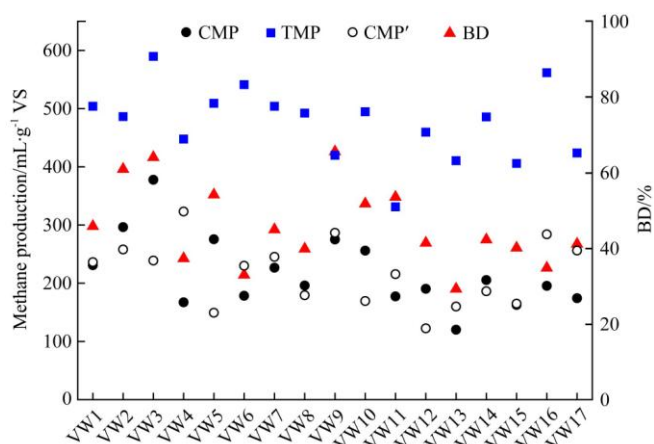


Figure 1 Cumulative methane productions (CMP) of 17 kinds of different VWs



Note: CMP: cumulative methane production; TMP: theoretical methane production; CMP': simulated methane production; BD: biodegradability.

Figure 2 Methane productions and BD of 17 kinds of VWs

### 3.3 Correlation between organic components and CMP

Organic components were completely different in all studied VWs, which resulted in the significant difference of methane production performances. To assess the correlation between organic components and methane yields, a non-linear regression relationship between different organic matters and the CMP was

established. It was found that the function forms for all the organic matters were obviously distinct, e.g., for cellulose and hemicellulose, the forms were linear function together with logarithmic function; for protein, the form was simple linear function; and for lignin, non-structural carbohydrate, and VFA, the forms were linear relation together with quadratic linear relation. Such distinction was shown as the following equation (Equation (9)), in which all the coefficients were calculated using least squares method with a software (Eviews 9.0).

$$CMP' = 641.86 + 22.11C - 431.17 \ln C - 48.63H + 422.97 \ln H - 7.31L + 1.86L^2 - 200.45N + 43.74N^2 + 30.68P + 315.45V - 110.44V^2 \quad (9)$$

where,  $CMP'$  means the simulated cumulative methane production, mL/g VS;  $C$ ,  $H$ ,  $L$ ,  $N$ ,  $P$ , and  $V$  represent cellulose, hemicellulose, lignin, non-structural carbohydrate, protein, and VFA, respectively, and all of them are the percentage contents based on TS.

The simulated curvilinear correlation ( $R^2$ ) was 0.800. In addition, as shown in Figure 2, the values of  $CMP'$  were very close to  $CMP$ , which indicated the reliability of this equation for methane production prediction. The formula contributed by this research would not only provide useful reference for future biomethane production tests as they can predict the  $CMP$  by easily estimating the organic components but also offer a co-digestion design policy to select the mixing ratio of various VWs according to the contents

of different organic compositions.

### 3.4 Kinetic analysis

Kinetic parameters of individual VW during the AD process are important for understanding AD features<sup>[38]</sup>, but there were rare

literatures systematically reported for studied VWs. In this study, four widely used models (first-order, Fitzhugh, Cone, and modified Gompertz models) were chosen to simulate the AD process<sup>[31,34]</sup>, and all the parameters are shown in Table 3.

**Table 3 Kinetic parameters simulated by the first-order, Fitzhugh, Cone, and modified Gompertz models**

	First-order			Fitzhugh				Cone				Modified Gompertz			
	$B_o$ /mL (g VS) <sup>-1</sup>	$k$ /d <sup>-1</sup>	$R^2$	$B_o$ /mL (g VS) <sup>-1</sup>	$k$ /d <sup>-1</sup>	$n$	$R^2$	$B_o$ /mL (g VS) <sup>-1</sup>	$k_{hyd}$ /d <sup>-1</sup>	$n$	$R^2$	$B_o$ /mL (g VS) <sup>-1</sup>	$R_{max}$ (mL/g VS d)	$\lambda$ /d	$R^2$
VW1	274.8	0.12	0.911	274.7	0.11	1.1	0.911	218.6	0.27	2.4	0.999	208.2	45.9	1.2	0.999
VW2	393.2	0.07	0.813	393.1	0.08	0.8	0.813	283.0	0.28	2.1	0.999	261.0	60.4	1.0	0.995
VW3	ND	ND	ND	ND	ND	ND	ND	395.0	0.09	2.4	0.993	337.5	27.4	4.3	0.986
VW4	396.9	0.04	0.738	397.1	0.06	0.6	0.738	143.9	0.26	3.0	0.999	139.0	32.1	1.6	0.999
VW5	296.6	0.11	0.977	296.7	0.10	1.0	0.977	282.8	0.17	2.0	1.000	266.4	29.2	1.8	0.989
VW6	205.3	0.08	0.982	205.3	0.09	0.9	0.982	187.9	0.16	1.7	0.997	167.2	18.1	1.1	0.990
VW7	243.2	0.10	0.964	243.2	0.10	1.0	0.964	218.4	0.24	2.0	0.995	206.7	37.4	1.1	0.996
VW8	232.0	0.13	0.944	232.0	0.12	1.2	0.944	181.4	0.27	2.3	0.997	161.3	33.8	1.0	0.988
VW9	427.2	0.04	0.937	427.2	0.06	0.6	0.937	278.2	0.20	2.0	0.997	259.8	44.1	1.3	0.993
VW10	293.4	0.09	0.960	293.4	0.09	1.0	0.960	247.7	0.23	2.1	0.997	231.9	40.1	1.2	0.993
VW11	198.2	0.08	0.992	198.2	0.09	0.9	0.992	190.5	0.15	1.7	0.997	187.4	15.6	1.5	0.989
VW12	315.2	0.04	0.875	315.1	0.06	0.6	0.875	178.3	0.23	2.5	0.996	169.8	32.8	1.6	0.987
VW13	127.4	0.10	0.987	127.4	0.10	1.0	0.987	131.6	0.14	1.5	0.996	112.1	8.6	0.3	0.998
VW14	290.5	0.07	0.987	290.5	0.08	0.8	0.987	186.6	0.21	2.3	0.999	172.5	27.4	1.2	0.987
VW15	193.0	0.08	0.933	193.0	0.09	0.9	0.933	152.8	0.23	2.5	0.993	145.5	27.7	1.5	0.987
VW16	292.6	0.10	0.931	292.6	0.10	1.0	0.931	159.1	0.29	2.6	0.997	146.3	33.8	1.0	0.996
VW17	181.2	0.16	0.895	181.2	0.13	1.3	0.895	157.1	0.26	2.3	0.991	149.6	27.0	1.1	0.985

In the first-order and Fitzhugh models, the values of  $R^2$  were generally low, and the  $B_o$  values were much higher than the CMP. Furthermore, it was found that the experimental results of bok choy could not be simulated by these two models, indicating that first-order and Fitzhugh models might not be appropriate to simulate the AD process for some VWs.

The  $R^2$  values obtained by Cone and modified Gompertz models were in the range of 0.991 to 1.000 and 0.985 to 0.999, respectively, which were relatively high. Simulated  $B_o$  values ranged from 131.6 mL/g VS to 395.0 mL/g VS and from 112.1 mL/g VS to 337.5 mL/g VS for Cone model and modified Gompertz model, respectively, both of which were close to the experimental range of CMP (120.1±1.8 mL/g VS to 377.7±12.1 mL/g VS). These results suggested that the Cone and modified Gompertz models could simulate the AD process well.

The parameters obtained in these two models (Cone and modified Gompertz models) provided useful information for describing the AD process of VWs. In the Cone model,  $k_{hyd}$  stands for the hydrolysis rate constant<sup>[34]</sup>. A higher  $k_{hyd}$  value always implies an easier hydrolysis of the substrate and the  $k_{hyd}$  values of studied VWs were ranged from 0.09 d<sup>-1</sup> to 0.29 d<sup>-1</sup>, which were generally higher than *Salvinia molesta*, rice straw and switchgrass (0.04-0.09 d<sup>-1</sup>)<sup>[31,34]</sup>, indicating the high degradability of VWs in AD process. In the modified Gompertz model, the kinetic parameter  $R_{max}$  was the methane production rate and the  $R_{max}$  values were in the range of 8.6 mL/(g VS d) to 60.4 mL/(g VS-d). A higher  $R_{max}$  value normally means a higher methane production<sup>[34]</sup>, except for several substrates such as bok choy with high methane yield (377.7±12.1 mL/g VS) simulated a relatively low  $R_{max}$  value of 27.4 mL/(g VS-d). The  $\lambda$  value represents the lag phase time, which indicated the adaptation time of microorganisms for the substrates in AD<sup>[39]</sup>. In this study, the

majority of the substrates was found having relatively low  $\lambda$  values range (from 0.3 d to 1.8 d), suggesting the fast degradation of VWs in AD<sup>[36]</sup>. Compared to these substrates, the  $\lambda$  value of bok choy was much higher (4.3 d), which might partly due to the lowest VS/TS ratio (65.23%) among all the studied VWs. It also indicated that big difference in organic components might influence the AD process<sup>[21,40]</sup>.

## 4 Conclusions

In this study, 17 kinds of representative VWs were systematically and comprehensively analyzed. The results showed that all the substrates had different characteristics. The methane yields of all VWs were in the range of 120.1 mL/g VS to 377.7 mL/g VS, and 8 out of 17 had a significantly high methane production over 200.0 mL/g VS. The AD process of VWs was well simulated by the Cone and modified Gompertz models. A correlation between methane yields and individual organic components, which could be used as a quick and reliable tool for methane production prediction in the future, was established. In conclusion, the results obtained in this research provided fundamental knowledge of common vegetable wastes characterizations, their AD performances, and connection between biochemical components and methane yields, which could not only fill in the blanks in scientific research but also facilitate the future utilization of vegetable waste resources.

## Acknowledgements

This study was financially supported by the National Key Research and Development Program of China (2017YFD0800801). We also would like to acknowledge the support from the International Clean Energy Talent Project (iCET) provided by the China Scholarship Council (CSC).



**[References]**

- [1] NBSC. China Statistical Yearbook 2016. Beijing. China Statistics Press, 2017.
- [2] Doddapaneni T R K C, Praveenkumar R, Tolvanen H, Rintala J, Konttinen J. Techno-economic evaluation of integrating torrefaction with anaerobic digestion. *Applied Energy*, 2018; 213: 272–284.
- [3] Eteffaghi E, Ghobadian B, Rashidi A, Najafi G, Khoshtaghaza M H, Rashtchi M, et al. A novel bio-nano emulsion fuel based on biodegradable nanoparticles to improve diesel engines performance and reduce exhaust emissions. *Renewable Energy*, 2018; 125: 64–72.
- [4] Nikokavoura A, Trapalis C. Graphene and g-C<sub>3</sub>N<sub>4</sub> based photocatalysts for NO<sub>x</sub> removal: A review. *Applied Surface Science*. 2018; 430: 18–52.
- [5] Ayala-Parra P, Liu Y, Field J A, Sierra-Alvarez R. Nutrient recovery and biogas generation from the anaerobic digestion of waste biomass from algal biofuel production. *Renewable Energy*, 2017; 108: 410–416.
- [6] Luz F C, Cordiner S, Manni A, Mulone V, Rocco V. Anaerobic digestion of coffee grounds soluble fraction at laboratory scale: Evaluation of the biomethane potential. *Applied Energy*, 2017; 207: 166–175.
- [7] Li D, Chen L, Liu X, Mei Z, Ren H, Cao Q, et al. Instability mechanisms and early warning indicators for mesophilic anaerobic digestion of vegetable waste. *Bioresource Technology*, 2017; 245(Pt A): 90–97.
- [8] Ravi P P, Lindner J, Oechsner H, Lemmer A. Effects of target pH-value on organic acids and methane production in two-stage anaerobic digestion of vegetable waste. *Bioresource Technology*, 2018; 247: 96–102.
- [9] Singh A, Kuitila A, Adak S, Bishai M, Banerjee R. Utilization of Vegetable Wastes for Bioenergy Generation. *Agricultural Research*, 2012; 1(3): 213–222.
- [10] Zuo Z, Wu S, Zhang W, Dong R. Effects of organic loading rate and effluent recirculation on the performance of two-stage anaerobic digestion of vegetable waste. *Bioresource Technology*, 2013; 146: 556–561.
- [11] Ortner M, Rachbauer L, Somitsch W, Fuchs W. Can bioavailability of trace nutrients be measured in anaerobic digestion? *Applied Energy*, 2014; 126: 190–198.
- [12] Yin Y, Liu Y J, Meng S J, Kiran E U, Liu Y. Enzymatic pretreatment of activated sludge, food waste and their mixture for enhanced bioenergy recovery and waste volume reduction via anaerobic digestion. *Applied Energy*, 2016; 179: 1131–1137.
- [13] Li R, Duan N, Zhang Y, Liu Z, Li B, Zhang D, et al. Anaerobic co-digestion of chicken manure and microalgae *Chlorella* sp.: Methane potential, microbial diversity and synergistic impact evaluation. *Waste Management*, 2017; 68: 120–7.
- [14] Li W, Khalid H, Zhu Z, Zhang R, Liu G, Chen C, et al. Methane production through anaerobic digestion: Participation and digestion characteristics of cellulose, hemicellulose and lignin. *Applied Energy*, 2018; 226: 1219–28.
- [15] Sole-Bundo M, Eskicioglu C, Garfi M, Carrere H, Ferrer I. Anaerobic co-digestion of microalgal biomass and wheat straw with and without thermo-alkaline pretreatment. *Bioresource Technology*, 2017; 237: 89–98.
- [16] Croce S, Wei Q, D'Imporzano G, Dong R, Adani F. Anaerobic digestion of straw and corn stover: The effect of biological process optimization and pre-treatment on total bio-methane yield and energy performance. *Biotechnology Advances*, 2016; 34(8): 1289–1304.
- [17] Wu Y, Wang C, Liu X, Ma H, Wu J, Zuo J, et al. A new method of two-phase anaerobic digestion for fruit and vegetable waste treatment. *Bioresource Technology*, 2016; 211: 16–23.
- [18] Li D, Ran Y, Chen L, Cao Q, Li Z, Liu X. Instability diagnosis and syntrophic acetate oxidation during thermophilic digestion of vegetable waste. *Water research*, 2018; 139: 263–271.
- [19] Dhanalakshmi Sridevi V, Rema T, Srinivasan S V. Studies on biogas production from vegetable market wastes in a two-phase anaerobic reactor. *Clean Technologies and Environmental Policy*, 2014; 17(6): 1689–1697.
- [20] Zuo Z, Wu S, Qi X, Dong R. Performance enhancement of leaf vegetable waste in two-stage anaerobic systems under high organic loading rate: Role of recirculation and hydraulic retention time. *Applied Energy*, 2015; 147: 279–286.
- [21] Xu F, Wang Z W, Li Y. Predicting the methane yield of lignocellulosic biomass in mesophilic solid-state anaerobic digestion based on feedstock characteristics and process parameters. *Bioresource Technology*, 2014; 173: 168–176.
- [22] Barbeau E M, Krieger N, Soobader M J. The American Journal of Public Health (AJPH) from the American Public Health Association (APHA) publications. *American Journal of Public Health*, 2014; 93(10): 1699.
- [23] Rincón B, Heaven S, Banks C J, Zhang Y. Anaerobic Digestion of Whole-Crop Winter Wheat Silage for Renewable Energy Production. *Energy & Fuels*, 2012; 26(4): 2357–2364.
- [24] Soest P J V, Robertson J B, Lewis B A. Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. *Journal of Dairy Science*, 1991; 74(10): 3583–3597.
- [25] Saqib A A N, Whitney P J. Differential behaviour of the dinitrosalicylic acid (DNS) reagent towards mono- and di-saccharide sugars. *Biomass and Bioenergy*, 2011; 35(11): 4748–4750.
- [26] Liang Q Q, Li Y S. A rapid and accurate method for determining protein content in dairy products based on asynchronous-injection alternating merging zone flow-injection spectrophotometry. *Food Chemistry*, 2013; 141(3): 2479–2485.
- [27] Kafle G K, Kim S H, Sung K I. Ensiling of fish industry waste for biogas production: a lab scale evaluation of biochemical methane potential (BMP) and kinetics. *Bioresource Technology*, 2013; 127: 326–236.
- [28] Yan H, Zhao C, Zhang J, Zhang R, Xue C, Liu G, et al. Study on biomethane production and biodegradability of different leafy vegetables in anaerobic digestion. *AMB Express*, 2017; 7(1): 27.
- [29] Yu L, Ma J, Frear C, Zhao Q, Dillon R, Li X, et al. Multiphase modeling of settling and suspension in anaerobic digester. *Applied Energy*, 2013; 111: 28–39.
- [30] Mani S, Sundaram J, Das K C. Process simulation and modeling: Anaerobic digestion of complex organic matter. *Biomass and Bioenergy*, 2016; 93: 158–167.
- [31] El-Mashad H M. Kinetics of methane production from the codigestion of switchgrass and *Spirulina platensis* algae. *Bioresource Technology*, 2013; 132: 305–312.
- [32] Shen J, Yan H, Zhang R, Liu G, Chen C. Characterization and methane production of different nut residue wastes in anaerobic digestion. *Renewable Energy*, 2018; 116: 835–841.
- [33] Mao C, Wang X, Xi J, Feng Y, Ren G. Linkage of kinetic parameters with process parameters and operational conditions during anaerobic digestion. *Energy*, 2017; 135: 352–360.
- [34] Syaichurrozi I. Biogas production from co-digestion *Salvinia molesta* and rice straw and kinetics. *Renewable Energy*, 2018; 115: 76–86.
- [35] Li Y, Jin Y, Li H, Borrión A, Yu Z, Li J. Kinetic studies on organic degradation and its impacts on improving methane production during anaerobic digestion of food waste. *Applied Energy*, 2018; 213: 136–147.
- [36] Zhao C, Yan H, Liu Y, Huang Y, Zhang R, Chen C, et al. Bio-energy conversion performance, biodegradability, and kinetic analysis of different fruit residues during discontinuous anaerobic digestion. *Waste Manag.*, 2016; 52: 295–301.
- [37] Li Y, Zhang R, Liu G, Chen C, He Y, Liu X. Comparison of methane production potential, biodegradability, and kinetics of different organic substrates. *Bioresource Technology*, 2013; 149: 565–569.
- [38] Zhao C, Mu H, Zhao Y, Wang L, Zuo B. Microbial characteristics analysis and kinetic studies on substrate composition to methane after microbial and nutritional regulation of fruit and vegetable wastes anaerobic digestion. *Bioresource Technology*, 2018; 249: 315–321.
- [39] Syaichurrozi I, Rusdi R, Hidayat T, Bustomi A. Kinetics studies impact of initial pH and addition of yeast *Saccharomyces cerevisiae* on biogas production from tofu wastewater in Indonesia. *International Journal of Engineering Transactions B Applications*, 2016; 29(8): 1037–1046.
- [40] Molinuevo-Salces B, González-Fernández C, Gámez X, García-González M C, Morán A. Vegetable processing wastes addition to improve swine manure anaerobic digestion: Evaluation in terms of methane yield and SEM characterization. *Applied Energy*, 2012; 91(1): 36–42.