Thermophilic anaerobic digestion of model organic wastes: Evaluation of biomethane production and multiple kinetic models analysis

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Abstract

The main aim of this work was to test various organic wastes, i.e. from a livestock farm, a cattle slaughterhouse and agricultural waste streams, for its ability to produce methane under thermophilic anaerobic digestion (AD) conditions. The stability of the digestion, potential biomethane production and biomethane production rate for each waste were assessed. The highest methane yield (110.83 mL CH_4/g VS_{added}·day) was found in the AD of crushed animal carcasses on day 4. The experimental results were analyzed using four kinetic models and it was observed that the Cone model described the biomethane yield as well as the methane production rate of each substrate. The results from this study showed the good potential of model organic wastes to produce biomethane.

Keywords: Organic wastes; biomethane potential; first-order model; modified Gompertz model; Cone model; dual pooled first-order kinetic model.

1. Introduction

With the growing concern around global warming and in order to confront the persisting global energy crisis, the search for alternative energy resources has been a topic of major concern in the developed and developing nations (Moon et al., 2018). Bioenergy can reduce the demand for fossil energy sources that are depleting at a faster rate (Atelge et al., 2018). Conventional exploitation and use of fossil energy sources contribute to serious environmental problems such as global warming, climate change, and environmental pollution (He et al., 2017; Liu et al., 2015; Whiting and Azapagic, 2014). Anaerobic digestion (AD) has proven to be a sustainable energy producing technology that presents the opportunity and potential for enhancing the reduction, recycling, and recovery of resources from several types of organic wastes (Khalid et al., 2011; Mata-Alvarez et al., 2000; Zou et al., 2016). AD process involves three main phases (including hydrolysis, acidogenesis, and methanogenesis) that require complicated coordination of multiple groups of anaerobic bacteria during each stage. Meanwhile, the quantities and activities of these bacterial groups vary depending on different factors such as the reactors operation conditions, substrate properties and composition, and digester configuration (Yu et al., 2014). The important roles and benefits of AD technology have been widely recognized and applied worldwide. Not only does AD provide beneficial transformation of organic solid wastes into more useful solids (organic amendment), it also produces large amounts of biogas, which is a primary source of sustainable bioenergy (Donoso-Bravo et al., 2011; Ferreira et al., 2013; Nguyen et al., 2016; Romero-Güiza et al., 2016; Yu et al., 2014).

Large quantities of organic solid waste are being generated daily from livestock farms, slaughterhouses, and from intense agricultural activities around the world (Liu et al., 2015; Tauseef et al., 2013). Such wastes contain high levels of organic matter that is biodegradable, representing a valuable and economical feedstocks (biomass) for AD (Khalid et al., 2011; Nguyen et al., 2017a; Saxena et al., 2009). The biochemical methane potential (BMP) test is an effective analytical method by which the potential for biological methane production, and the biodegradability of the substrates can be assessed (Kafle and Chen, 2016; Triolo et al., 2011; Triolo et al., 2014). Modeling AD processes can provide optimal solutions for predicting and evaluating the performance of an AD system (El-Mashad, 2013; Yang et al., 2016). Such models can also be used to describe the kinetics of methane production during the AD of different substrates, and can also be helpful for interpreting the effects of changing parameters on the efficiency of the AD system (Xie et al., 2016). The combination of BMP test data and a statistical model can provide substantial benefits in terms of time and cost and can provide an estimation of the optimum design parameters required to support and develop new reactor configurations or to upgrade an existing anaerobic digester (Abudi et al., 2016; Donoso-Bravo et al., 2011; Jurado et al., 2016; Kafle and Chen, 2016; Yang et al., 2016). Several attempts have been made in the literature to describe the dynamics of AD for organic waste treatment (Abudi et al., 2016; Kafle and Chen, 2016; Kouas et al., 2019; Yang et al., 2016; Zhen et al., 2016). However, the models remain underdeveloped because most of the previous studies have focused on the use of a very limited number of substrates and kinetics models, which stimulated the interest of this study in evaluating the utilization of wide range of organic substrates for biomethane production.

The main objectives of this study were to: (i) investigate the biomethane production potential from nine different organic waste using a series of batch tests in thermophilic AD, (ii) determine the substrate biodegradable fraction through the measurement and calculation of the elemental composition, and (iii) apply and evaluate four kinetic models, i.e. the Cone model, a first-order kinetic model, the modified Gompertz model, and the dual pooled first-order kinetic model, to describe the kinetics and mechanisms of AD. A comparative evaluation of the four kinetic models was performed to estimate the most suitable one for accurately predicting the biomethane production.

2. Materials and methods

2.1. Feedstock and inoculum

Different organic wastes were collected from livestock farms, cattle slaughterhouses, and agricultural wastes in various cities of South Korea and ground using a mixer grinder (Dae Sung Artlon Co., Ltd., South Korea), equipped with a fine filtering screen. This process produced a homogeneous mixture with particle sizes < 2.0 mm that was used as the feedstock in the experiments. The characteristics and elemental composition of each type of organic waste are presented in Table 1.

Table 1. Characteristics of typical organic wastes used in this study.

[Insert Table 1]

The inoculum for all BMP tests was obtained from a digester using thermophilic anaerobic bacteria to process sewage sludge at the Jinguen biogas plant (Namyangju City, South Korea). The inoculum was sieved through a 1.0 mm mesh and stored in an incubator at 55 °C until further use. Its main characteristics are presented in Table 2. The collection, preservation, and storage of all the samples, including the substrates and the inoculum, followed proper laboratory protocols.

Table 2. Characteristics of the inoculum used in this study.

[Insert Table 2]

2.2. Practical biochemical methane potential test procedure

A series of practical biochemical methane potential (PBMP) tests were performed in this study. The batch experiments were carried out for 26 days under conditions that favored thermophilic anaerobes (55 °C). The experiments were performed to determine the potential for methane production from the nine organic wastes, according to previously established protocols (Owen et al., 1979). A PBMP test was conducted for each type of organic waste in 500 mL serum bottles (working volume 300 mL), in which the inoculum size was 20% (*v/v*), the substrate was 2 g VS/L, and a suitable nutrient medium for the growth and activity of anaerobic microorganisms (Jeong et al., 2019; Nguyen et al., 2017b; Shelton and Tiedje, 1984). The nutrient medium had the following composition: phosphate buffer (to adjust the pH to 7.0 ± 0.1), 270 mg/L KH_2PO_4, 350 mg/L K_2HPO_4, mineral salts including 530 mg/L NH_4Cl, 75 mg/L $CaCl_2 \cdot 2H_2O$, 100 mg/L $MgCl \cdot 6H_2O$, and 20 mg/L $FeCl_2 \cdot 4H_2O$, and trace metals including 0.50 mg/L $MnCl_2 \cdot 4H_2O$, 0.05 mg/L H_3BO_3, 0.05 mg/L $ZnCl_2$, and 0.03 mg/L $CuCl_2$. The nutrient medium was sterilized in a high-pressure autoclave for ~15 min. The residual oxygen was removed by purging nitrogen gas through a heated (250-300 °C) pipe wound with copper ribbon. To avoid a sudden drop in pH during the acidogenic phase of anaerobic digestion, 1200 mg/L of $NaHCO_3$ was injected into the medium after it was cooled to 55 °C.

The oxygen remaining in the headspace of all bottles was flushed with nitrogen gas for 3-5 min to create the desired anaerobic condition and avoid aerobic respiration (Koch et al., 2015a). The bottles were sealed air-tight with screw caps fitted with butyl rubber septa stoppers and were then placed upside down in an incubator in the dark, at 55 ± 2 °C for 26 days. Each digester (bottle) was monitored daily to note the degree of bulging of the rubber septa caused by biogas generation. The biogas pressure generated was controlled, and each bottle was manually shaken, once a day, to mix the contents. Under the same experimental conditions, the control digester containing only the inoculum and the nutrient medium (without substrate added) was also used to determine and correct for methane generated from the inoculum alone.

The samples were collected at regular intervals of time until the cumulative biomethane curve almost reached a plateau. The amount of biogas produced in each digester was extracted and measured using a 5 or 10 mL gas-tight syringe until the biogas pressure in the digesters matched the atmospheric pressure. The composition of the biogas collected was analyzed according to previously reported protocols.

The volume of biomethane produced during two consecutive measurements, t-1 and t, was calculated as follows (Eq. 1) (El-Mashad, 2013):

$$V_{C,t}^{CH_4}(55^o C) = C_{C,t} \times V_{G,t} + V_{head} \times (C_{C,t} - C_{C,t-1}) \quad \text{Eq. 1}$$

where $V_{c,t}$ is the volume of biomethane produced in the time interval between *t-1* and *t* (in mL), $C_{c,t}$ and $C_{c,t-1}$ are the biomethane concentrations measured at *t* and *t-1*, respectively, by gas chromatography (%). $V_{G,t}$ is the volume of biogas produced in the time interval between t-1 and t (%), and V_{head} is the volume of the head space of the digester (mL).

The biomethane (CH_4) production (V_{CH4}, mL) was normalized to volume at standard temperature and pressure conditions (STP: 0 °C and 1 bar) using the ideal gas law (Eq. 2). The specific CH_4 production (mL CH_4/g VS_{add}) was expressed as the volume of CH_4 produced per g of VS of the substrate added to digesters at the beginning of the BMP tests, as follows:

$$V_{CH_4}(STP) = V_{C,t}^{CH_4}(55^o C) \times \frac{(273\ K)}{(273K + 55K)} \times \frac{(760mmHg - 118mmHg)}{760mmHg} \quad \text{Eq. 2}$$

The saturated vapor pressure at 55 °C was 118 mm Hg.

2.3. Theoretical methane yield and biodegradability calculation

The theoretical biochemical methane potential (TBMP) under standard conditions (0 °C, 1 bar) was calculated based on the elemental composition of the substrates, according to Buswell's formula (Eqs. 3 and 4):

$$C_cH_hO_oN_n + \left(\frac{4c-h-2o+3n}{4}\right)H_2O \rightarrow \left(\frac{4c+h-2o-3n}{8}\right)CH_4 + \left(\frac{4c-h+2o+3n}{8}\right)CO_2 + nNH_3 \quad \text{Eq. 3}$$

$$CH_4^{TBMP}\ (\text{ml } CH_4 / g\ VS_{added}) = 22.4 \times \left[\frac{\left(\frac{4c+h-2o-3n}{8}\right)}{12c+h+16o+14n}\right] \times 1000 \quad \text{Eq. 4}$$

The substrate biodegradability was calculated according to Eq. 5 (Browne et al., 2014):

$$Biodegradability\ (\%) = \frac{Cumulative\ methane\ yield\ (L/kgVS)}{Theoritical\ methane\ yield\ (L/kgVS)} \times 100 \quad \text{Eq. 5}$$

The deviation between the experimental values and the simulated values for AD of the substrates was calculated according to Eq. 6:

$$D_{experimental\ vr.\ simulated}(\%) = \frac{\left|X_{i,Experimental\ value} - X_{i,Simulated\ value}\right|}{X_{i,Experimental\ value}} \times 100 \quad \text{Eq. 6}$$

where *D* is the deviation between the experimental and the simulated values, $X_{i,experimental}$ is the experimental value at time *i*, and $X_{i,simulated}$ is the simulated value from the model at time *i*.

2.4. Kinetic model analysis

A model that was able to describe the complex metabolic processes in the AD and accurately assess the methane yield from the AD of various organic substrates was identified. Four kinetic models including, the Cone model (Eq. 7), a first-order kinetic model (Eq. 8), the modified Gompertz model (Eq. 9), and the dual pooled first-order kinetic model (Eq. 10), were used to fit the cumulative methane production obtained from the experimental data. These models were selected because they have often been used in recent years to describe and predict the kinetics of methane production in AD processes (Brulé et al., 2014; Dennehy et al., 2016; El-Mashad, 2013; Koch and Drewes, 2014; Shin and Song, 1995; Zhao et al., 2018; Zhen et al., 2016; Zhen et al., 2015). The models kinetic parameters were determined and analyzed statistically using Microsoft Excel™ 2010, with a Solver add-in program (Microsoft, USA) and Origin V8.1 (OriginLab Corporation, USA) *via* non-linear curve fitting of the experimental data. Statistical analyses of the models were evaluated, and the significance was indicated at $p < 0.05$.

Cone model: $$M(t) = \frac{M_m}{1 + (k \times t)^{-n}}$$ Eq. 7

First-order kinetic model: $$M(t) = M_m \times \left(1 - e^{-k \times t}\right)$$ Eq. 8

Modified Gompertz model: $$M(t) = M_m \times \exp\left\{-\exp\left[\frac{R_m \exp(1)}{M_m}(\lambda - t) + 1\right]\right\}$$ Eq. 9

Dual pooled first-order kinetic mode: $$M(t) = M_m \times \left(1 - \alpha \times e^{-k_f t} - (1 - \alpha) \times e^{-k_L t}\right)$$ Eq. 10

where *M(t)* is the cumulative biomethane production at a given time *t* (mL CH_4/g VS_{added}), M_m is the maximum biomethane production potential of the substrate (mL CH_4/g VS_{added}), *k* is the hydrolysis rate constant (1/day), *t* is the time (day), *n* is the shape factor, R_m is the maximum specific methane production rate (mL CH_4/g VS_{added}·day), λ is the lag phase time (day), k_f and k_L are the respective rate constants for a rapidly degradable substrate and slowly degradable substrate, respectively, and α is the ratio of rapidly degradable substrate to the total degradable substrate.

2.5. Analytical methods

2.5.1. Sample analysis

The volume of biogas production in each digester was measured using a gas-tight syringe at regular intervals of time. The gas was collected and the methane concentration was measured using a gas chromatograph (GC) (Agilent 7890A, Agilent Technologies, Inc., USA), equipped with a HP-PLOT/Q capillary column (split ratio 3:1) (30 m length × 0.53 mm inner diameter, 40 μm film) and a thermal conductivity detector (GC-TCD). Each sample of biogas (~250 μL) was injected into the GC with helium as a carrier gas at a flow rate of 30 cm/s. The initial temperature of the GC column was 60 °C, which was increased to 270 °C at the rate of 30 °C/min. The injector temperature was set at 230 °C, while the flame ionization detector (FID) was set at 250 °C.

The inoculum samples were analyzed for pH, TCOD, SCOD, TS, VS, TN, TAN, FAN, and Alk. according to the procedure outlined in standard methods (Apha, 2005). The elemental composition (C, H, N and O) of each substrate was analyzed using an elemental analyzer (Flash EA1112, CE Instruments, Italy), and the results were reported as percentage of dry weight. Samples were subjected to pyrolysis at high temperature (900 °C), which decomposed them into gases containing the various elements and allowed measurement of the thermal conductivity of these gases. The C/N ratio was calculated based on the results of this analysis.

2.5.1. Data analysis and model evaluation

To determine the best model, the following statistical indicators were determined and compared: the coefficient of determination (R^2), the *F*-test, the root mean square prediction error (rMSPE) (Eq. 11) (Kafle et al., 2013), the second-order Akaike information criterion (AIC) test (Eq. 12) (Akaike, 1974; El-Mashad, 2013), and the Bayesian information criterion (BIC) test (Eq. 13) (Schwarz, 1978).

$$rMSPE = \left(\frac{1}{m} \sum_{j=1}^{m} \left(\frac{d_j}{Y_j} \right)^2 \right)^{\frac{1}{2}} = \sqrt{\frac{1}{m} \sum_{j=1}^{m} \left(\frac{d_j}{Y_j} \right)^2} \qquad \text{Eq. 11}$$

where *m* is number of data pairs, *j* is the j^{th} value, *Y* is the measured biomethane production (mL/g VS_{added}), and *d* is the deviation between the experimental and the model fitted methane production.

$$AIC = \begin{cases} N \times \ln\left(\frac{RSS}{N}\right) + 2K, & when \frac{N}{K} \geq 40 \\ N \times \ln\left(\frac{RSS}{N}\right) + 2K + \frac{2K(K+1)}{N-K-1}, & when \frac{N}{K} < 40 \end{cases} \qquad \text{Eq. 12}$$

$$BIC = N \ln\left(\frac{RSS}{N}\right) + K \ln(N) \qquad \text{Eq. 13}$$

where RSS is the residual sum of squares, *N* is number of data points, and *K* is the number of model parameters.

3. Results and discussion

3.1. Biomethane generation potential and TBMP of various organic wastes

A series of practical biochemical methane potential (PBMP) tests were conducted under thermophilic conditions. The TBMP for nine different organic substrates was calculated to assess the overall methane production rates, biomethane yields, and anaerobic biodegradability of the substrates. As shown in Fig. 1, the daily methane yield (DMY) and cumulative biomethane yield

(CMY) were obtained for batch anaerobic digesters after 26 days of operation. The DMY and CMY are the values obtained after subtracting the corresponding biogas yield generated from the control digester. The results of the daily methane yield during the batch anaerobic digestion clearly shows that two peaks appeared for most of the studied substrates (Fig. 1a). The two peaks appeared over a period of 4 to 18 days of digestion, except for OW3, OW5, and OW6 that did not clearly exhibit one or two peaks, due to the biodegradability of the substrates. This mainly depended on the simultaneous processes of hydrolysis and metabolism of accumulated acid and intermediates (e.g. VFAs) (Koch et al., 2015b). The highest daily methane production of all substrates was also observed during this period. There was a gradual decline in the methane production during the end of the experiments, due to the depletion of the substrates. Methane yields were observed in all the digesters, almost instantly after incubation, indicating rapid acclimatization of the anaerobic microbial populations (e.g. methanogenesis) in each digester (Fig. 1a).

[Insert Figure 2]

Fig. 1. Daily methane yield (a) and cumulative biomethane yield (b) from biochemical methane potential tests of various organic substrates during the study period.

The highest peak of methane yield (110.83 mL CH_4/g VS_{added}·day) was observed using OW3 as the substrate on day 4. However, the highest PBMP was achieved by the OW1 digester (390.05 mL CH_4/g VS_{added}), and it was higher than those obtained from substrates OW2 (5.28%), OW3 (2.01%), OW4 (17.95%), OW5 (55.33%), OW6 (56.87%), OW7 (37.37%), OW8 (10.01%), and OW9 (22.91%) digesters, respectively. Approximately 86-90% of the PBMP after 26 days of digestion was obtained at the end of 21 days for all the substrates studied. This is because of the low substrate concentration available in the digesters after 21 days. The corresponding methane production was very low (0.86 to 5.78 mL CH_4/g VS_{added}·day), depending on the complex organics present in the substrates (Fig. 1b). Compared with the other studied substrates, the PBMP obtained in the OW7, OW6, and OW5 digesters were lowest (244.31, 168.23, and 174.23 mL CH_4/g VS, respectively). This can be attributed to either one of the following reasons: (i) differences in substrate structure and composition (e.g. protein, lignin, and cellulose content) (Koch et al., 2015b), (ii) some portion of the substrate was easily biodegradable as they were already metabolized by the animals digestive systems in the case of OW6 and OW7 (Triolo et al., 2011; Zheng et al., 2015), and (iii) biological conversion processes in the wastewater treatment system for OW5. This would make the remaining portions more difficult or impossible to digest (hydrolyze and biodegrade) by the anaerobic bacteria. In such cases, pretreatment (including chemical, physical, biological, or combinations) of these substrates is essential to enhance anaerobic digestion to simultaneously increase biogas production and reduce the solids content (Nguyen et al., 2017c; Ometto et al., 2014). Detectable biomethane was produced in all the digesters after 12 h of operation, and the CMY increased steadily thereafter irrespective of the type of substrate. This result demonstrates that the digesters were properly prepared (nutrient medium, trace metal, inoculum, and environmental conditions) to enhance the growth of anaerobic bacteria. The theoretical ultimate methane yield of each substrate was calculated (Fig. 2). Using Buswell's equation, the results showed that the yield varied significantly (239.7 to 482.0 mL CH_4/g VS_{added}) depending on the chemical composition of the substrates tested. The highest TBMP value calculated was 482.0 mL CH_4/g VS for OW2, while the lowest value was 239.7 mL CH_4/g VS_{added} for OW6.

[Insert Figure 2]

Fig. 2. Theoretical and experimental biochemical methane potential of various organic substrates during the study period (**a**) and their biodegradability fraction (**b**) (error bars represent 5% of the data).

The TBMP values were always higher than the PBMP values for all the substrates tested (Fig. 2a). This is because the TBMPs were calculated based on the chemical composition of both the biodegradable and the non-biodegradable fraction/components of the waste, whereas, only the biodegradable portion was metabolized into biogas through the anaerobic bioconversion process (Kafle and Chen, 2016; Labatut et al., 2011). The anaerobic biodegradability of the substrates was also calculated based on the ratio between the PBMP and the TBMP (Eq. 5) to assess the biological metabolism capacity or methane conversion efficiency of organic substrates under the experimental conditions. The highest biodegradability was 93.04% for OW8, and the lowest was 51.51% for OW5; whereas OW4, OW1, OW3, OW2, OW7, and OW6 were 82.30%, 81.77%, 79.43%, 76.64%, 71.62%, and 70.18%, respectively (Fig. 2b). These results clearly indicated that these substrates (except OW5, OW6, and OW7) could be suitable for biodegradation under conditions favoring thermophilic anaerobes, to produce renewable energy and mitigate gaseous emissions. However, pretreatment of OW5, OW6, and OW7 prior to feeding and performing anaerobic digestion was deemed necessary in order to accelerate the anaerobic biodegradability.

3.2. Validation and evaluation of the tested kinetic models

The selection of an appropriate dynamic model is necessary to simplify and accurately explain the mechanisms and metabolic pathways involved in AD of the substrates under different operating conditions and to predict the performance of individual digesters (Donoso-Bravo et al., 2011; Kafle and Chen, 2016; Prajapati and Singh, 2018). A suitable model is essential for the design, process intensification and long-term AD operation.

The experimental data and model predicted curves of cumulative biomethane yield from batch thermophilic AD of nine organic substrates are shown in Fig. 2. The kinetic parameters of the models used to describe the rates of substrate degradation and biomethane production were determined by fitting the experimental data (see Supplementary material). According to the results shown in Fig. 2 and Supplementary material, all the tested models provided reasonable fit to the experimental data. This was confirmed by the high values of determination coefficients (R^2), which were all >0.97. This indicates that the models employed could explain >97% of the variations in the results. However, the dual pooled first-order kinetic model was only found to be satisfactory for the substrates OW2, OW3, OW5, and OW9. It appears that the dual pooled first-order kinetic model is probably less flexible and diverse than the other models presented in this work for predicting biomethane production under the study conditions. Hence, it was ascertained that the three other proposed models (Cone model, First-order kinetic model, and Modified Gompertz model) are appropriate for describing the biomethane yield as a function of residence time for the substrates tested in this study. However, each model has its own distinct advantages. For example, the Cone model provides more information on the shape factor, whereas the Gompertz model provides information on the lag phase and the maximum specific methane production rate.

The relationship of CMY as a function of AD time with different organic substrates was described by the polynomial regression models (Fig. 3). The relationship was characterized by three main phases: (i) a lag phase (one or two days) in which methane production was detected; however, still at low intensity, (ii) a logarithmic phase during which CMY increased steeply from 2 to 21 days due to the rapid growth of the anaerobic bacterial populations, and (iii) the stationary and death phase (after 21 days) wherein the CMY tended to slowly increase until the CMY curve reached a plateau. This plateau may be due to the depletion of the substrate and cell death, owing to which the biomethane production almost ceased.

[Insert Figure 3]

Fig. 3. Experimental data (symbols) and model simulation/prediction (lines) of cumulative biomethane yield from different organic substrates.

The hydrolysis rate constant (k) of the substrates determined from the Cone model varied in the range 0.091-0.233 (L/day), which was 25.17-45.07% higher than those obtained from the first-order model. This finding is in accordance to the values reported by Zhao et al. (2016), wherein the value of the hydrolysis rate constant obtained from the Cone model was higher than those obtained using the first-order model. The hydrolysis rate constant varied between substrates, probably due to differences in the composition and structure of the substrate. The results also showed that a lower hydrolysis rate constant was correlated with the decreased biodegradability and longer degradation times required for methane production to reach its maximum value. This observation is also consistent with previously published works (Koch et al., 2015b).

The deviation (absolute value) between the experimental CMY and simulated CMY in this study was found to be within the range 0.27-6.07% for the Cone model, 0.13-7.69% for the first-order model, and 1.18-14.03% for the modified Gompertz model, respectively. This reconfirmed the fact that, all the three models can be used for estimating the biomethane potential of these substrates in AD.

The maximum predicted methane potential (*Mm*) of the substrates was estimated from the tested models, which varied depending on the substrates and the model parameter. The *Mm* predicted by the Modified Gompertz model, first-order model, and Cone model, were always slightly lower than the values obtained from TBMP calculations and were in the ranges of 0.13-0.51%, 0.00-0.45%, and 0.00-0.41%, respectively (Fig. 4).

[Insert Figure 4]

Fig. 4. Comparison of maximum biomethane production potential obtained by different model simulations and by theoretical calculations.

3.3. Comparison of proposed models and model selection

For practical applications, a model that can predict and evaluate the biomethane production exactly and provide the parameters necessary for optimal design and operation of the AD process of various substrates will save considerable time and operational costs and improve waste management strategies (Mata-Alvarez et al., 2000). Conversely, a wrong choice or inadequate evaluation of the suitability of the model could have many consequences such as incorrect design and operation, resulting in project failure or the inability to meet project requirements (Zhen et al., 2015).

The criteria parameters of χ^2, rMSPE, RSS, AIC, and BIC were calculated (Table 3) and used as the main discriminators to determine a better fit of the model to the experimental data. The lower values of χ^2, rMSPE, RSS, AIC, and BIC indicate a more appropriate model (El-Mashad, 2013; Yang et al., 2016; Zhen et al., 2015). The Cone model had the lowest of rMSPE, RSS, AIC, and BIC, followed in ascending order by the first-order model, the modified Gompertz model, and the dual pooled first-order model. Hence, it is clearly evident that the Cone model exhibited the best biomethane yield fit for the experimental data ($R^2 > 0.985$), and similar observation was also made by other researchers (El-Mashad, 2013; Zhen et al., 2016; Zhen et al., 2015).

Table 3. Criteria for analysis of the best fit of the models to the experimental data.

[Insert Table 3]

When comparing the values for methane yield derived from the Buswell's equation, the model prediction using the best model (Cone), and the experimental results are shown in Fig. 5. After 26 days of anaerobic digestion, the CMYs of substrates OW1-OW9 obtained from the Cone model prediction was compared to the experimental values (in parentheses), as follows: 399.9 (390.1), 378.0 (369.4), 383.2 (382.2), 318.6 (320.0), 173.0 (174.2), 158.0 (168.2), 248.5 (244.3), 341.2 (351.0), and 304.2 (300.7) mL CH_4/g VS_{added}. This comparison illustrates the deviation between the experimental and predicted values for the different substrates, which were relatively small (2.52%, 2.33%, 0.27%, 0.45%, 0.71%, 6.07%, 1.70%, 2.78%, and 1.16%, respectively). The experimental biomethane production values obtained after 26 days of AD of these substrates was 2.02-24.98% which is lower than the maximum biomethane production potential values (*Mm*) estimated from the Cone model, depending on their degradation rates. This observation clearly indicates that most of the biomethane produced was achieved within 26 days by the utilization of the different substrates by the anaerobic microbial consortia.

[Insert Figure 5]

Fig. 5. Comparison of biomethane production potential obtained by Buswell's calculation: Cone model prediction and experimental results (error bars represent 5% of the data).

4. Conclusions

The measured biomethane yields from thermophilic AD tests, predictions from kinetic models, and theoretical calculations of nine substrates were ascertained in this study. About 86 to 90% of the maximal biomethane yield of the substrates was achieved within 21 days. Among the different kinetic models tested, the Cone model fitted the experimental data well and described the kinetics of AD. For practical applications, the Cone model can be used to predict the biomethane production potential of organic substrates, as well as optimize process parameters to enhance the design and operation of an AD process.

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Figure captions

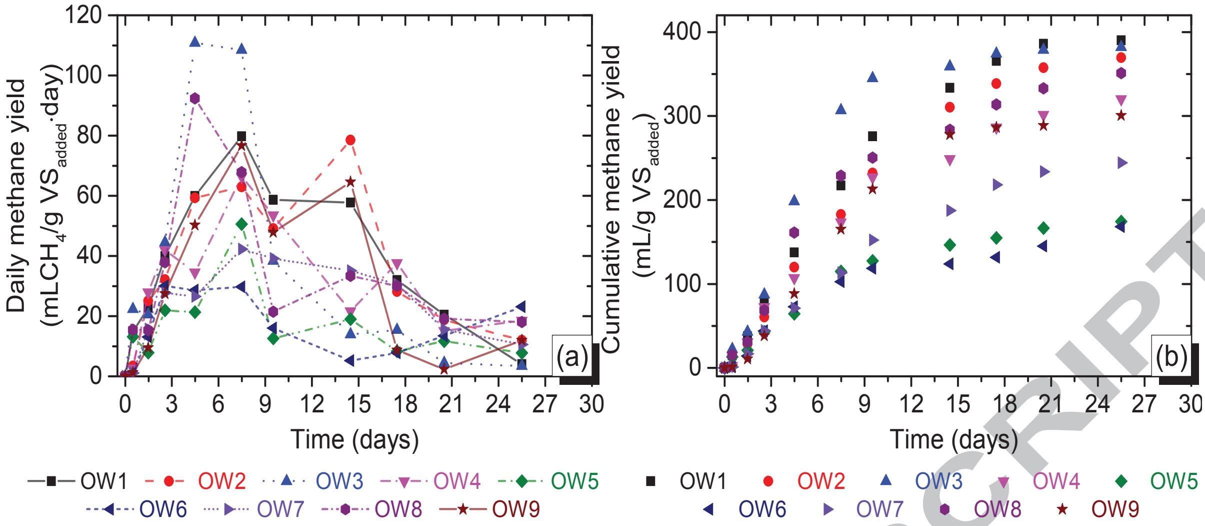
Fig. 1. Daily methane yield (a) and cumulative biomethane yield (b) from biochemical methane potential tests of various organic substrates during the study period.

Fig. 2. Theoretical and experimental biochemical methane potential of various organic substrates during the study period (a) and their biodegradability fraction (b) (error bars represent 5% of the data).

Fig. 3. Experimental data (symbols) and model simulation/prediction (lines) of cumulative biomethane yield from different organic substrates.

Fig. 4. Comparison of maximum biomethane production potential obtained from different model simulations and from theoretical calculations.

Fig. 5. Comparison of biomethane production potential obtained by Buswell's calculation: Cone model prediction and experimental results (error bars represent 5% of the data).



Daily methane yield (mLCH$_4$/g VS$_{added}$·day)
Time (days)
(a)
Cumulative methane yield (mL/g VS$_{added}$)
Time (days)
(b)
OW1 OW2 OW3 OW4 OW5 OW6 OW7 OW8 OW9

Fig. 1

520

521

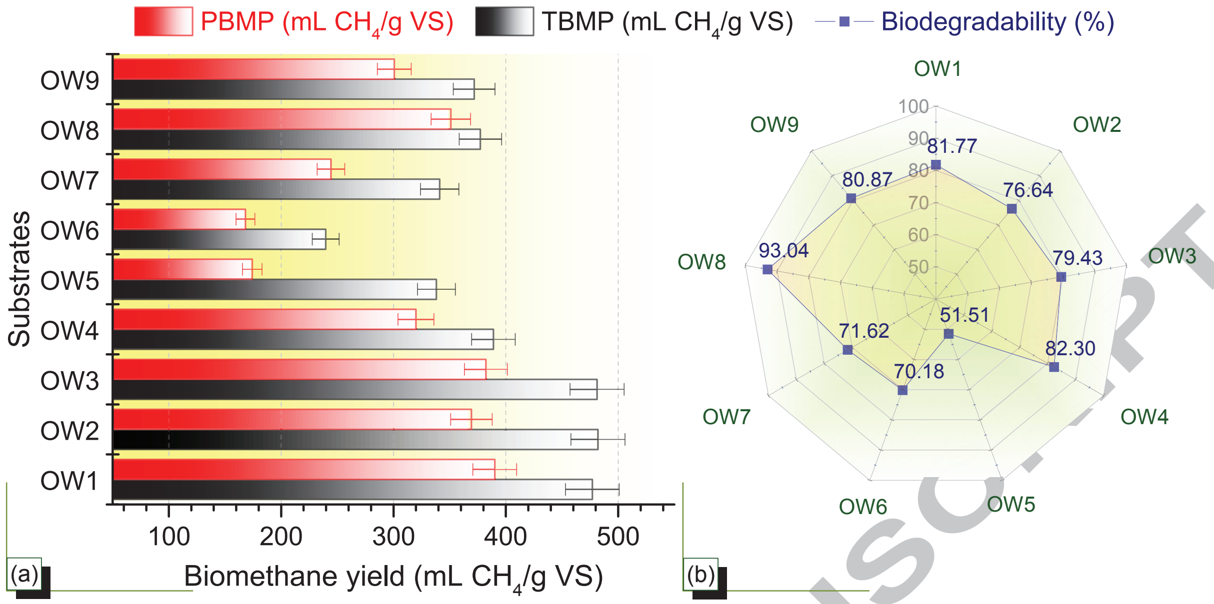

PBMP (mL CH4/g VS)
TBMP (mL CH4/g VS)
Biodegradability (%)
OW9
OW8
OW7
OW6
OW5
OW4
OW3
OW2
OW1
Substrates
100
200
300
400
500
Biomethane yield (mL CH4/g VS)
(a)
OW1
OW2
OW3
OW4
OW5
OW6
OW7
OW8
OW9
100
90
80
70
60
50
81.77
76.64
79.43
82.30
51.51
70.18
71.62
93.04
80.87
(b)

Fig. 2

522

523

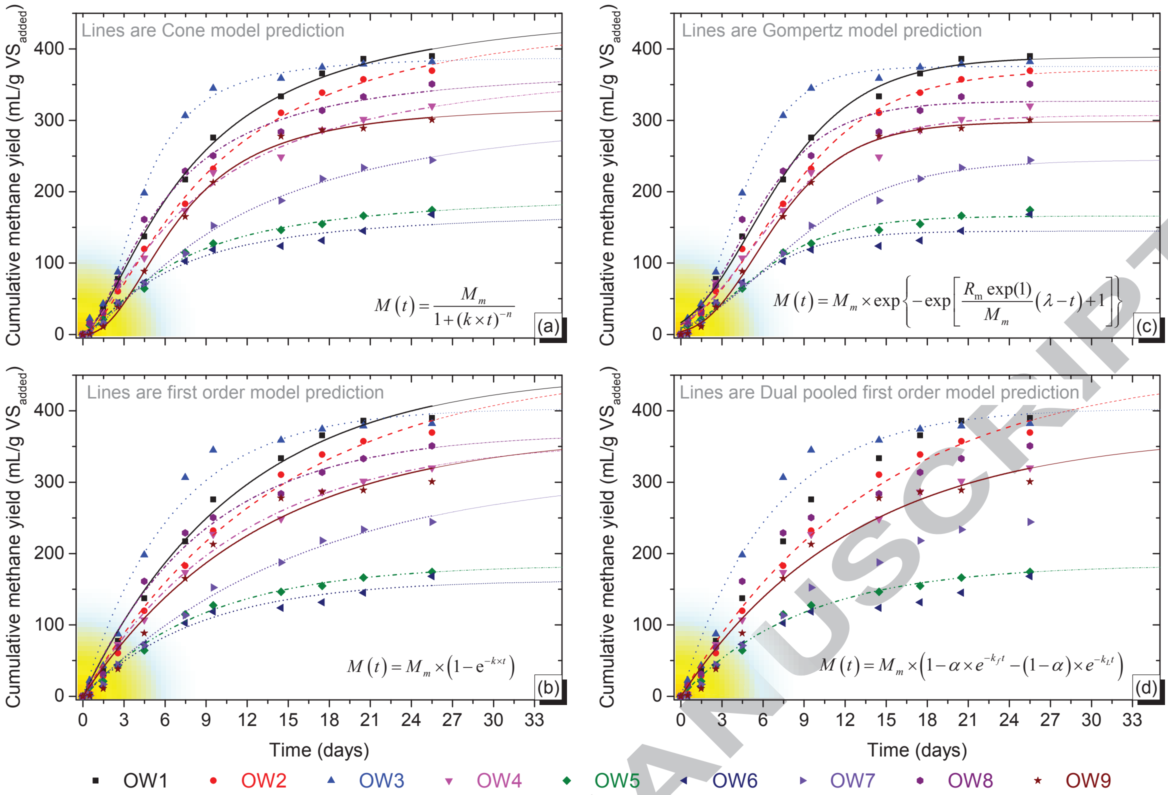
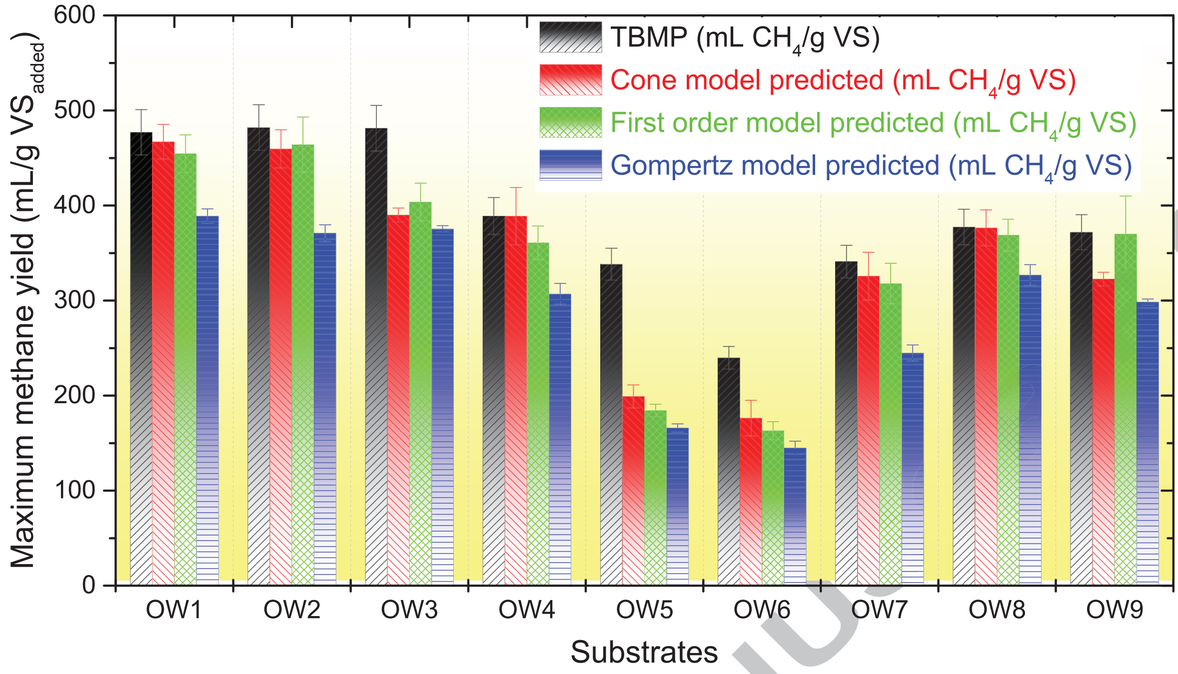

Lines are Cone model prediction
$M(t)=\frac{M_m}{1+(k\times t)^{-n}}$
(a)
Lines are Gompertz model prediction
$M(t)=M_m\times\exp\left\{-\exp\left[\frac{R_m\exp(1)}{M_m}(\lambda-t)+1\right]\right\}$
(c)
Lines are first order model prediction
$M(t)=M_m\times(1-e^{-k\times t})$
(b)
Lines are Dual pooled first order model prediction
$M(t)=M_m\times(1-\alpha\times e^{-k_f t}-(1-\alpha)\times e^{-k_L t})$
(d)
Cumulative methane yield (mL/g VS$_{added}$)
Time (days)
OW1
OW2
OW3
OW4
OW5
OW6
OW7
OW8
OW9

Fig. 3

524

525



TBMP (mL CH4/g VS)
Cone model predicted (mL CH4/g VS)
First order model predicted (mL CH4/g VS)
Gompertz model predicted (mL CH4/g VS)
Maximum methane yield (mL/g VSadded)
0
100
200
300
400
500
600
OW1
OW2
OW3
OW4
OW5
OW6
OW7
OW8
OW9
Substrates

Fig. 4

526

527

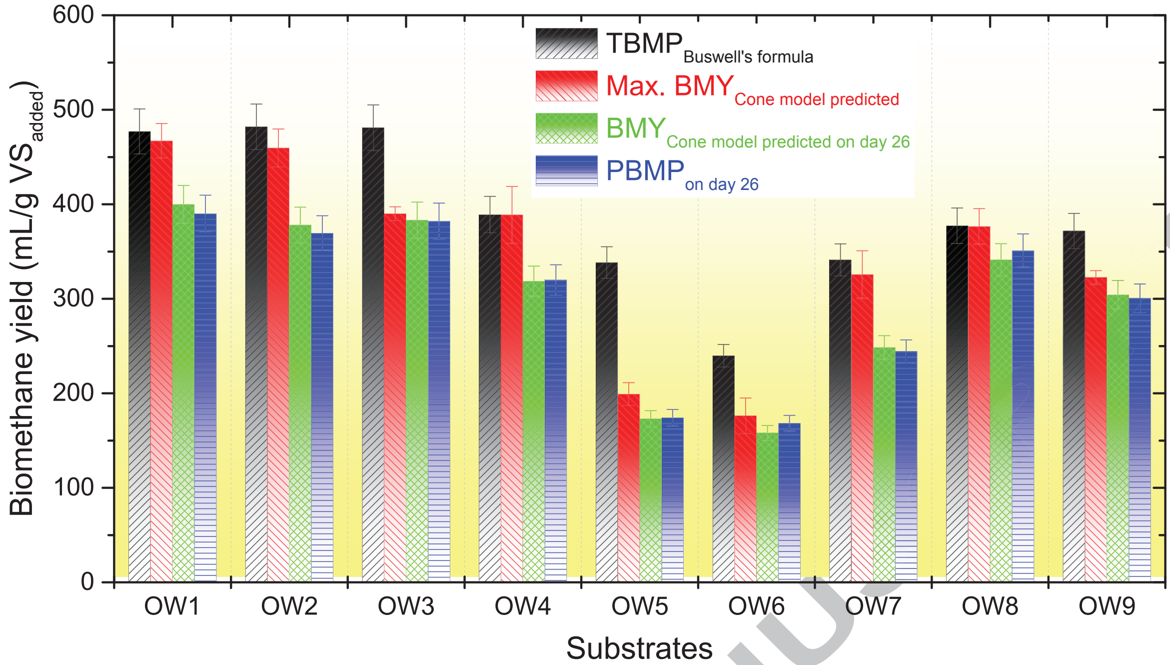


Fig. 5

50.

Table 1. Characteristics of typical organic wastes used in this study.

Types of organic wastes	Notation	Elemental composition (% ODM)				C/N ratio	VS (g/L)
		Carbon (C, %)	Hydrogen (H, %)	Oxygen (O, %)	Nitrogen (N, %)		
Pig blood	OW1	64.1	7.3	16.3	10.1	6.35	187.46
Cow rumen (stomach)	OW2	66.0	6.3	25.1	2.5	26.40	214.81
Crushed animal carcasses	OW3	61.9	8.2	19.4	6.4	9.67	327.29
Dehydrated slaughterhouse sludge	OW4	48.1	6.6	20.2	6.6	7.29	116.32
Excess sludge from slaughterhouse WWTP	OW5	45.0	6.1	21.6	7.5	6.00	16.92
Dairy cow manure	OW6	39.3	5.5	31.8	3.5	11.23	176.35
Cattle/animal manure	OW7	43.0	3.6	25.1	2.8	15.36	174.42
Swine manure solids	OW8	49.2	6.5	25.1	3.8	12.95	273.72
Beet leaves	OW9	52.8	6.42	30.17	1.66	31.78	75.97

Table 2. Characteristics of the inoculum used in this study.

Parameters	Seeding sludge		
	Min.	**Max.**	**Avg. ± SD**
pH	7.83	7.89	7.86 ± 0.04
Total chemical oxygen demand, TCOD (g/L)	28.04	28.83	28.44 ± 0.56
Soluble chemical oxygen demand, SCOD (g/L)	2.49	2.55	2.52 ± 0.04
Total solids, TS (g/L)	25.52	25.80	25.66 ± 0.20
Volatile solids, VS (g/L)	16.01	16.24	16.12 ± 0.16
Total nitrogen, TN (g/L)	2.92	3.06	2.99 ± 0.10
Total ammonia nitrogen, TAN (g/L)	1.16	1.23	1.20 ± 0.05
Free ammonia nitrogen, FAN (g/L)	0.261	0.275	0.268 ± 0.01
Volatile fatty acids, VFAs (g/L)	0.06	0.07	0.06 ± 0.01
Alkalinity, Alk. (g $CaCO_3$/L)	4.02	4.21	4.12 ± 0.13
VFA/Alk. ratio	0.014	0.016	0.015 ± 0.001

Table 3. Criteria for analysis of the best fit of the models to the experimental data.

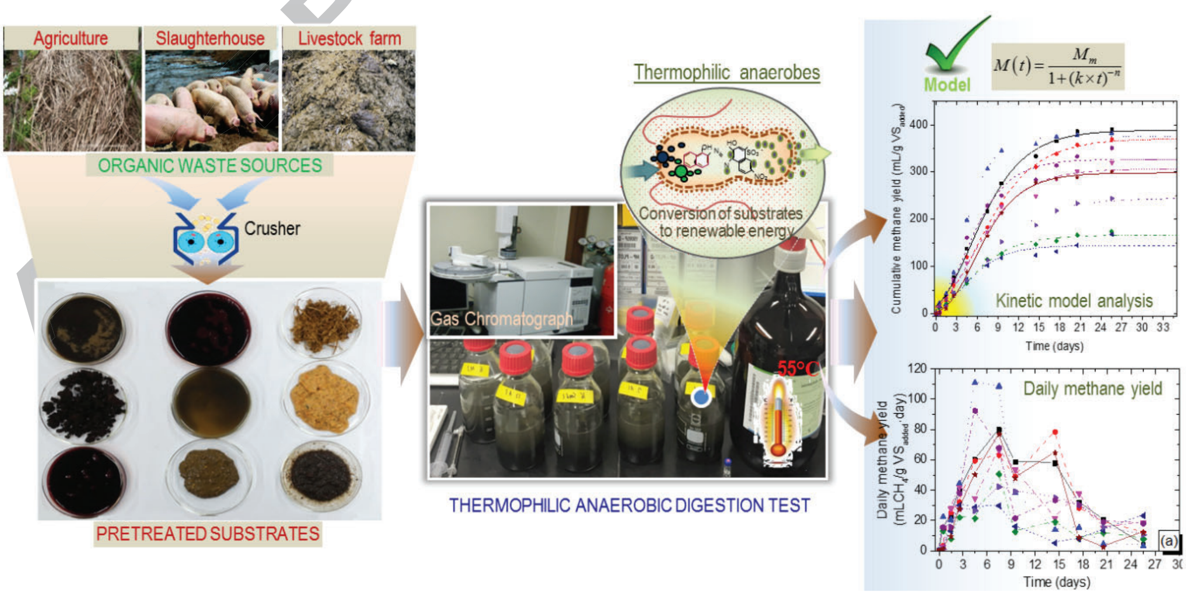
Model analysis	RSS	N	Parameter	AIC Test		BIC Test	
				AIC	Akaike weight	BIC	Diff BIC
Cone model	935.609	11	3	63.543	0.855	58.468	0
First-order model	2079.108	11	2	67.088	0.145	64.853	6.386
Modified Gompertz model	2688.253	11	3	75.153	0.017	70.078	5.224
Dual pooled first-order model	2079.108	11	4	79.660	0.0003163	69.649	11.181

51.

Thermophilic anaerobic digestion of model organic wastes: Evaluation of biomethane production and multiple kinetic models analysis

Dinh Duc Nguyen, Byong-Hun Jeon, J. Hoon Jeung, Eldon R. Rene, J. Rajesh Banu, Balasubramani Ravindran, Cuong Vu Manh, Huu Hao Ngo, Wenshan Guo, S. Woong Chang

Graphical abstract



52.

Highlights