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Taking Advantage of Waste Heat Resource from Vinasses for Anaerobic Co-digestion of Waste Activated Sludge under the Thermophilic Condition: Energy Balance and Kinetic Analysis

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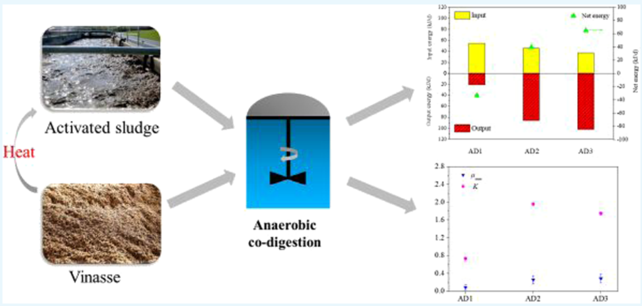
ABSTRACT: Vinasses are not only an easily biodegradable substrate but also a heat energy resource. In this study, the energy balance and kinetic model of anaerobic co-digestion of waste activated sludge (WAS) with vinasses have been investigated in semicontinuous reactor experiments at 55 °C. Herein, the maximum energy balance value, the ratio of energy to mass, and the kinetic constants μ_{max} and K of anaerobic digestion of WAS were -33.44 kJ·day^{-1}, -5.72 kJ·VS^{-1}·day^{-1}, and 0.0894 day^{-1} and 0.7294, respectively, at an organic loading rate (OLR) of 1.17 VS·L^{-3}·day^{-1}; when the mixture ratio of WAS to vinasses was 2:1 (dry VS) for co-digestion, the maximum energy balance value, the maximum ratio of energy to mass, and the kinetic constants μ_{max} and K of anaerobic co-digestion of WAS and vinasses were +39.73 kJ·day^{-1}, 8.1 kJ·VS^{-1}·day^{-1}, and 0.2619 day^{-1} and 1.9583, respectively, at an OLR of 1.73 VS·L^{-3}·day^{-1}. The positive energy balance was obtained for two reasons: one is for making the best use of the high-temperature heat energy resource of vinasses and the other is for enhancing the amount of biogas yield. The bottleneck of the negative energy balance of thermophilic digestion of WAS can be broken by anaerobic co-digestion of WAS and vinasses. The results indicate a promising future in the application of anaerobic thermophilic co-digestion of WAS and vinasses. Methane production from digestion and co-digestion was also predicted by the Chen−Hashimoto kinetic model.



1. INTRODUCTION

In the last few years, the number of municipal wastewater treatment plants in China has significantly increased, which results in the production of large quantities of waste activated sludge (WAS) that should undergo stabilization. It has been reported that approximately 6.03 million tons of WAS (dry weight) per year is produced in China,[1] increasing the concern of public risk of environment and human health caused by pathogens, heavy metals, or persistent organic pollutants existing in WAS.[2]

Anaerobic digestion has been and continues to be one of the most widely used processes for WAS stabilization since anaerobic digestion produces methane, which can be used as a kind of renewable energy resource.[2] However, the conventional anaerobic digestion processes used in most municipal treatment plants in China still suffer from unreliable performance with low treatment efficiency, high costs, and negative energy balance[3] due to the poor hydrolysis caused by rigid cell walls and substantially secreted extracellular biopolymers.[4]

For example, leading up to 2010, a total of 50 WWTPs (wastewater treatment plants) were designed with an anaerobic digestion system in China. Still, around 80% of them were poorly operated with low volumetric biogas production rates.[5] Moreover, the existing anaerobic digesters operated at wastewater treatment plants are also oversized and underloaded.[6] Co-digestion of WAS with other kinds of wastes has been proposed extensively[4,6] to solve the above-mentioned problems and provoke the bio-energy recovery because co-digestion has unique benefits over the traditional anaerobic digestion. It balances carbon to nitrogen (C/N) ratio and nutrients,[7] increases pH buffering capacity,[8] decreases ammonia toxicity and accumulation of VFAs,[9] dilutes potential toxic matters, and increases the biogas yield.[10]

Temperature, an important factor, directly affects the dynamic situation of microorganisms. The anaerobic digestion can take place at a mesophilic range of temperatures (30−38 °C) and at a thermophilic range of temperatures (50−57 °C), and each of these biological processes has its own merits and demerits.[11] Traditionally, mesophilic (37 °C) anaerobic digestion is more

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Table 1. Elemental Characteristics of Materials

parameter	pH	C/N	TS ($g\cdot L^{-1}$)	VS ($g\cdot L^{-1}$)	TN ($g\cdot L^{-1}$)	TP ($g\cdot L^{-1}$)	VFA ($mg\cdot L^{-1}$)
WAS	6.6 ± 0.01	5.6 ± 0.2	28.6 ± 2.3	19.5 ± 2.2	1.42 ± 0.02	0.15 ± 0.01	169 ± 8.7
vinasse	4.04 ± 0.02	17.8 ± 0.4	38.4 ± 3.6	28.2 ± 2.3	1.75 ± 0.03	0.22 ± 0.02	547 ± 9.6
seed sludge	7.72 ± 0.02	8.9 ± 0.3	58.6 ± 4.2	31.3 ± 2.7	1.52 ± 0.03	0.46 ± 0.03	148 ± 5.4

Table 2. Feeding Mode and Digestion Performance Results

digester	feeding mode	OLR ($g\cdot VS\cdot L^{-3}\ day^{-1}$)	SRT (days)	VFA ($mg\cdot L^{-1}$)	accumulated biogas yield (L)	daily biogas yield ($L\cdot g\cdot VS\cdot day^{-1}$)
AD1	once a day	1.17	16.7	24.5 ± 0.10	1.2 ± 0.01	0.21
AD1	once every 2 days	0.58	33.4	34.8 ± 0.12	1.9 ± 0.01	0.16
AD1	once every 3 days	0.39	50.1	185.2 ± 1.54	2.1 ± 0.02	0.12
AD1	once every 4 days	0.29	66.8	214.7 ± 1.30	2.2 ± 0.02	0.09
AD2	once a day	1.73	12.5	84.3 ± 0.88	4.7 ± 0.03	0.54
AD2	once every 2 days	0.86	25.0	108.4 ± 0.94	7.5 ± 0.03	0.43
AD2	once every 3 days	0.58	37.5	215.6 ± 1.64	8.0 ± 0.03	0.31
AD2	once every 4 days	0.43	50.0	346.0 ± 2.76	8.2 ± 0.03	0.24
AD3	once a day	2.30	10.0	1653.7 ± 12.8	5.6 ± 0.02	0.49
AD3	once every 2 days	1.15	20.0	154.3 ± 1.21	9.5 ± 0.03	0.41
AD3	once every 3 days	0.77	30.0	210.6 ± 1.76	10.3 ± 00.4	0.30
AD3	once every 4 days	0.58	40.0	398.1 ± 2.65	10.6 ± 0.04	0.23

widely used compared to thermophilic one (55 °C) due to better process stability with less energy demand.[7] Nevertheless, several studies have reported the attractive advantage of the thermophilic processes to operate at reduced hydraulic retention times with higher organic matter removal and higher methane yields,[12,13] ensuring complete hygienization.[14] Moreover, several studies have shown that the thermophilic range of temperature should be preferred for the co-digestion process because of its superior performance compared to the mesophilic process.[15,16]

However, the main problem in thermophilic anaerobic digestion of WAS is the high heating requirements for sustaining the process compared with mesophilic digestion.[17] In other words, the thermophilic reactor needs a slightly higher temperature input to maintain the thermophilic temperature range; hence, if an extra external waste heat resource can be utilized for maintaining the reactor temperature in thermophilic digestion, a better result of energy balance will be acquired from anaerobic thermophilic digestion of WAS, which can realize a waste-to-energy strategy.

Ethanol production for biofuel, industrial use, pharmaceutical use, and alcoholic beverages has increased in recent years in China, especially for biofuel, bioethanol-blended petrol, which accounted for 20% of the total petrol consumption, according to the Mid- and Long-term Development Plan for Renewable Energy; the consumption of biodiesel in China will reach 2.0 million tons in 2020.[18] In general, ethanol production generates between 9 and 14 L of wastewater known as vinasses. Vinasses have a pH between 3.5 and 5, a dark brown color, and a high chemical oxygen demand (COD), which ranges between 50 and 150 $g\cdot L^{-1}$, and are discharged at a high-temperature range from 70 to 80 °C.[19]

Vinasses have been reported to be used for irrigation and fertilization due to their high nutrient and matter content; though many different technologies exist for treating vinasses, they must initially be treated with anaerobic processes due to their high organic loads. When vinasses are treated by anaerobic digestion at 55 °C usually, the high-temperature vinasses require expensive precooling before they are fed into the anaerobic digester, which means a process of energy-wasting.

Nanyang Tianguan Group Co., Ltd. (Henan province, China) has not only a capacity to produce 30×10^4 m^3 bioethanol per year but also a capacity of 10×10^4 m^3 municipal sewage wastewater treatment per day, which was carried out by a build–operate–transfer (BOT) model at the same location. Hence, there are large amounts of WAS and vinasses (of high temperature) in the same company, and both of them need to be anaerobically treated separately. At present, vinasses are treated by cooling to about 55 °C before being fed into the thermophilic upflow anaerobic sludge bed (UASB) reactor, which has been the amount of heat energy wasted for many years. Therefore, we can take advantage of the amount of heat energy of vinasses for sustaining the anaerobic thermophilic digestion of WAS; at the same time, vinasses can be used as a co-substrate for anaerobic thermophilic co-digestion with WAS together, the waste heat energy will be utilized, and the dominances of anaerobic thermophilic digestion can appear accordingly.

Generally speaking, the energy balance is a critical issue for the assessment of feasibility in anaerobic digestion of WAS. If the net energy balance, in which the energy output is more than the energy input, is a positive value, it indicates that the technique has advantages in practical application; otherwise, the technique exists with some defects in practical application.[20] However, to our knowledge, there are no studies on the evaluation of the energy balance by taking advantage of waste thermal resource from vinasses for anaerobic thermophilic co-digestion of waste WAS. This research has been conducted to address this limitation.

The present study was conducted to investigate the performance of anaerobic thermophilic digestion of WAS and co-digestion of WAS and vinasses. Moreover, to assess the energy balance by taking advantage of waste heat resources from vinasses based on biogas is utilized in the combined heat and power (CHP) unit; simultaneously, the kinetic evaluation was carried out using the Chen–Hashimoto methane production model.[21]

2. MATERIALS AND METHODS

2.1. Materials. WAS used in this experiment was taken from the returned residual sludge of the Nanyang Tianguan Group Co., Ltd. (China) municipal sewage treatment plant, which treated 20×10^4 tons of municipal sewage daily by the activated sludge process. The residual sludge used for the experiment was naturally precipitated by gravity for 48 h, and the sludge with the supernatant removed was stored at 4 °C for use. Vinasses were extracted from Nanyang Tianguan Group Co., Ltd. After separation of solid–liquid distiller's grains, the wastewater was retrieved and allowed to stand for 24 h. Then, the sedimentation part was discarded and the supernatant reserved for later use. The seed sludge used as an inoculum for the reactors was collected from anaerobically thermophilic (55 ± 1 °C) digestion of the food wastewater. The elemental characteristics of the materials are shown in Table 1.

2.2. Experimental Methodology. Three laboratory-scale digesters (AD1, AD2, and AD3), each with a total volume of 6 L and a working volume of 5 L, were operated at a controlled temperature of 55 ± 1 °C in a water bath. Each digester was fitted with a stainless steel stirrer, which was powered by a motor and stirred continuously at 80 rpm, equipped with a thermometer and a gas collection system. Some operational parameters of the semicontinuous system are provided in Table 2.

The feeding mode and digestion performance results are shown in Table 2. At the beginning of the experiment, 5 L of seed sludge was added to each of the three anaerobic digestion reactors AD1, AD2, and AD3, and then the anaerobic digestion operation was maintained at 55 ± 1 °C and the stirring speed was set at 80 rpm. From the second day, different substrates were added using a peristaltic pump; AD1, AD2, and AD3 were fed with 300 mL of WAS, 400 mL of WAS/vinasses mixture (2:1 (dry VS)), and 500 mL of WAS/vinasses mixture (1:1 (dry VS)), respectively. The experiments were carried out to allow feeding after effluent discharge; that is 300, 400, and 500 mL of the reactor contents in AD1, AD2, and AD3 were replaced with new substrates when feeding, respectively.

The anaerobic digestion experiment underwent four feeding modes: daily feeding for the first mode, every 2 days feeding for the second mode, every 3 days feeding for the third mode, and every 4 days feeding for the fourth mode. After the first mode was completed, the next running mode was entered; the rest could be done in the same manner. Hence, each feeding mode has its own corresponding SRT and OLR. In each feeding method, three SRTs were continuously run until the system reached a stable state. After the last SRT was run, the properties of the anaerobic sludge were determined for six consecutive times and the average value was taken in the fourth SRT. The measurement of gas production was done on-line, and the pH values of all of the anaerobic digested sludge were determined. When each feed mode index measurement was completed, the next feeding mode was started. Reactors were operated in triplicate for each condition, and the results were calculated as an average obtained from the three replicate reactors.

2.3. Analytical Techniques. The following parameters were measured for each process: biogas production (wet-tip gas meter), pH (pH-3C acidity meter), and volatile fatty acids (VFAs, HP 6890/FID Chromatographer). Total solid (TS) and volatile solid (VS) were measured according to the methods for monitoring and analysis of water and wastewater.[22] Analyses of all of the above-mentioned parameters were performed in triplicate.

2.4. Statistical Analysis. Analysis of the variance was used to evaluate the effect on the investigated parameters, and the test data were tested for significant differences using a 95% least significant difference.

3. RESULTS AND DISCUSSION

3.1. Biogas Production at Different SRTs. The accumulated biogas yield and daily biogas yield in AD1, AD2, and AD3 under different conditions are summarized in Table 2. A similar changing trend was observed in each digester. First, the accumulated biogas yield increased as the SRT was increased. The accumulated biogas production increased from 1.2 to 2.2 L as the SRT was increased from 16.7 to 66.8 days in AD1, the accumulated biogas yield increased from 4.7 to 8.2 L as the SRT was increased from 12.5 to 50 days in AD2, and the accumulated biogas production increased from 5.6 to 10.6 L as the SRT was increased from 10 to 40 days in AD3. The C/N ratio of WAS is relatively low, only 5.6, while that of vinasse is relatively high, 17.8 (Table 1). This can explain why the gas production of WAS is low and the co-anaerobic gas production is high after the addition of vinasses, which is consistent with the results of other studies.[6,7,10] This indicates that with respect to biogas production, anaerobic co-digestion of WAS and vinasses is superior to the anaerobic digestion of WAS.

However, two apparent phenomena were noted during the digestion. First, in AD1 at a feeding mode once a day, if the feeding volume was more than 300 L, i.e., OLR was more than $1.17\ \mathrm{g{\cdot}VS{\cdot}L^{-3}{\cdot}day^{-1}}$, acidification phenomenon (pH < 6.5) was observed and the digestion process was a failure and biogas was not produced in the end, which was caused by higher OLR than it can endure the maximum OLR. Second, the same acidification phenomenon (organic overload) was observed in AD3 (SRT of 10 days, OLR of $2.30\ \mathrm{g{\cdot}VS{\cdot}L^{-3}{\cdot}day^{-1}}$). In the experiments, to keep the process steady for continuous biogas production and to allow the collection of the completed data, neutralization measures were taken in AD3. Otherwise, the digestion process would fail for the acidification phenomenon.[7,16]

During the process of the acidification phenomenon, the pH of the effluent is below 6.5, and thus the biogas production will cease in the end; in this study, the acidification phenomenon and pH of 6.5 were also observed simultaneously.

For this reason, although the anaerobic thermophilic co-digestion of WAS and vinasses produces more daily biogas and accumulated biogas than those in the anaerobic thermophilic digestion of WAS alone, organic overload should be avoided. In practice, based on 300 mL of WAS for digestion alone, the optimum mixed ratio of WAS to vinasses to be fed into AD2 should be selected for the co-digestion of WAS and vinasses.

Besides, the VFAs in the three digesters were found to exhibit a similar trend result, except for the date in AD3 for SRT of 10 d; the VFA increased as the SRT was increased or the OLR decreased in the same digester; for example, in AD1, when the SRTs were 16.7, 33.4, 50.1, and 66.8 days, the VFAs were 24.4, 34.8, 185.2, and 214.7 $\mathrm{mg{\cdot}L^{-1}}$, respectively. However, in AD3, the highest VFA of 1653.7 $\mathrm{mg{\cdot}L^{-1}}$ and the pH below 6.5 appeared with an SRT of 10 days and $2.30\ \mathrm{g\ VS{\cdot}L^{-3}{\cdot}day^{-1}}$. Xu et al.[23] suggested that the excessive accumulation of VFA caused by high organic loads will inhibit anaerobic digestion intensively. The methanogenic activities were wholly inhibited at a VFA concentration of 5.8–6.9 $\mathrm{g{\cdot}L^{-1}}$ in the anaerobic thermophilic digestion of kitchen wastes. Compared with their results, it is

Table 3. Calculation Results of Energy Balance

digester	SRT (days)	cumulative methane yield (L)	methane content (%)	$E_{\text{input,heat}}$ (kJ·day^{-1})	$E_{\text{input,electricity}}$ (kJ·day^{-1})	$E_{\text{output,heat}}$ (kJ·day^{-1})	$E_{\text{output,electricity}}$ (kJ·d^{-1})	net energy (kJ·day^{-1})	the ratio of energy to mass (kJ·VS^{-1}·day^{-1})
AD1	16.7	1.2 ± 0.01	55.4 ± 1.8	52.82	2.04	13.09	8.33	−33.44	−5.72
AD1	33.4	1.9 ± 0.01	56.2 ± 1.7	57.04	54	10.5	6.69	−43.39	−15.0
AD1	50.1	2.1 ± 0.02	56.1 ± 1.6	61.27	5.04	7.73	4.92	−53.66	−27.5
AD1	66.8	2.1 ± 0.02	54.3 ± 1.6	65.50	6.54	5.88	3.74	−62.42	−43.0
AD2	12.5	4.7 ± 0.03	56.8 ± 1.9	44.06	2.22	52.56	33.45	+39.73	8.1
AD2	25.0	7.5 ± 0.03	55.3 ± 1.8	47.58	3.72	40.83	25.98	+15.51	3.6
AD2	37.5	8.0 ± 0.03	55.1 ± 1.7	51.11	5.22	28.93	18.41	−8.99	−3.1
AD2	50.0	8.2 ± 0.03	56.7 ± 1.9	54.63	6.72	22.89	14.56	−23.9	−11.1
AD3	10.0	5.6 ± 0.03	56.6 ± 1.5	34.76	2.40	62.41	39.71	+64.96	5.6
AD3	20.0	9.5 ± 0.03	54.2±1.8	37.54	3.90	50.69	32.26	+41.51	7.2
AD3	30.0	10.3 ± 0.04	54.3 ± 1.9	40.32	5.40	36.71	23.36	+14.35	3.7
AD3	40.0	10.6 ± 0.04	55.1 ± 1.7	43.03	6.90	28.75	18.30	−2.88	1.0

evident that the VFA concentration, which leads to a drop in pH, is slightly lower than their result mentioned above; this is because the substrates used in anaerobic thermophilic digestion are different. The serious VFA inhibition on the activity of methanogens is caused by a pH drop in the reactor, which may lead to the activity loss of acid-sensitive glycolytic enzymes.[24,25]

If the stable operation of the co-anaerobic system is to be maintained, appropriate OLR and SRT should be considered. Hence, AD2 was selected as an optimum selection for anaerobic thermophilic co-digestion of WAS and vinasses in practical application.

3.2. Calculation of Energy Balance in Anaerobic Digestion/Co-digestion. In the treatment of WAS by anaerobic digestion, whether the production of positive energy balance can be obtained or not is key to sustain the performance in municipal sewage treatment plants. During anaerobic digestion, energy consumption is mainly involved in the following factors: sludge for heating, sludge for transforming with pump, sludge for mixing, and the heat loss through the boundaries and pipe of the digester. Although the production energy in anaerobic digestion of the sludge is the heat energy derived from methane combustion, conventionally, biogas is used in a cogeneration internal combustion engine. This engine, here called a CHP, is used for the production of energy (electricity). The waste heat from the CHP system process is the main source of heat for the digestion. The results showed that most of the heat requirements in the thermophilic sludge digestion were inflow sludge heating, and the heat loss of the sludge digester was only to 2−8% of heat requirements. The energy requirements for pumping and mixing were estimated to be 1.8×10^3 kJ·m^{-3} and 3.0×10^2 kJ·(m^3·d)$^{-1}$, respectively.[26,27]

To calculate the energy balance in sludge digestion, the technique used in the CHP system must be considered. Based on the CHP, about 35% of the biogas energy is converted to electrical power, heat losses are about 10%, and the portion of the heat that can be utilized is 55%; the specific heat of WAS and vinasses was 4.18×10^{-3} kJ·(g·°C)$^{-1}$, and the calorific value of methane was 35.8 kJ·L^{-1}.[26,27] The specific density of WAS and vinasses was 1 g·L^{-1}.

For calculations, the average outside temperature of 16 °C in Nanying City was considered across many years of meteorological recordings. Hence, the initial temperature of WAS was assumed to be 16 °C, the initial temperature of the vinasses was 75 °C, and the temperature for anaerobic thermophilic digestion was 55 °C.

According to the volume that need to be digested in the three digesters, the mixed sludge temperature can be calculated as

$$T_{\text{mixed,sludge}} = (T_1V_1 + T_2V_2)/(V_1 + V_2) \tag{1}$$

Here, $T_{\text{mixed,sludge}}$ is the mixed sludge temperature before feeding in the reactor; T_1 is the temperature of WAS before mixing; V_1 is the volume of WAS before mixing in mL; T_2 is the temperature of vinasses before mixing; and V_2 is the volume of vinasses before mixing in mL. The temperatures of the mixed sludge before feeding in the three anaerobic digesters are 16 °C for AD$_1$, 30.8 °C for AD$_2$, and 39.6 °C for AD$_3$. Because the temperature in the three anaerobic digesters is 55 °C, the temperature difference between a mixture and anaerobic digestion (55 °C) must be compensated from the production energy derived from CH$_4$ combustion. If the production energy is not sufficient for compensation, the necessary heat must come from elsewhere.

Consequently, the energy input in the form of heat and electricity for the compensation is calculated using the following equations[28,29]

$$E_{\text{input,heat}} = \rho Q \gamma (t_2 - t_1)(1 - \varphi)(1 + k) \tag{2}$$

$$E_{\text{input,electricity}} = Q \times \theta + V_{\text{p}} \cdot \omega \tag{3}$$

Here, $E_{\text{input,heat}}$ is the heat requirement for compensation, kJ·day^{-1}; $E_{\text{input,electricity}}$ is the electricity requirement for compensation, kJ·day^{-1}; ρ is the specific density of WAS and vinasses, which can be regarded as 1 g·mL^{-1}; Q is the sludge flow fed to the digester, m^3·day^{-1}; γ is the specific heat of WAS and vinasses, 4.18 kJ·(kg·°C)$^{-1}$; t_1 the temperature of the mixing sludge (i.e., $T_{\text{mixed,sludge}}$), °C; t_2 is the temperature of anaerobic digestion, 55 °C; φ is the relative amount of heat recovered, 85%; k is the relative amount of heat loss from the piping and binding of the digester, 8%; V_{p} is the volume of the digester, 5 L; θ is the electrical energy consumption for pumping, 1.8×10^3 kJ·m^{-3}; and ω is the electrical energy consumption rate for stirring, 3.0×10^2 kJ·(m^3·d)$^{-1}$.

The biogas is a merely rich energy source, which is generated during the anaerobic digestion because the chemical energy of methane can be converted to heat and electricity by a combined heat and power (CHP) unit. Supposing that the CHP was used in this study for calculation, according to a previous study, about 35% of the chemical energy of methane can be converted to electrical energy, 55% to heat, and the remaining 10% is lost. Here, the output energy can be calculated using the following equations

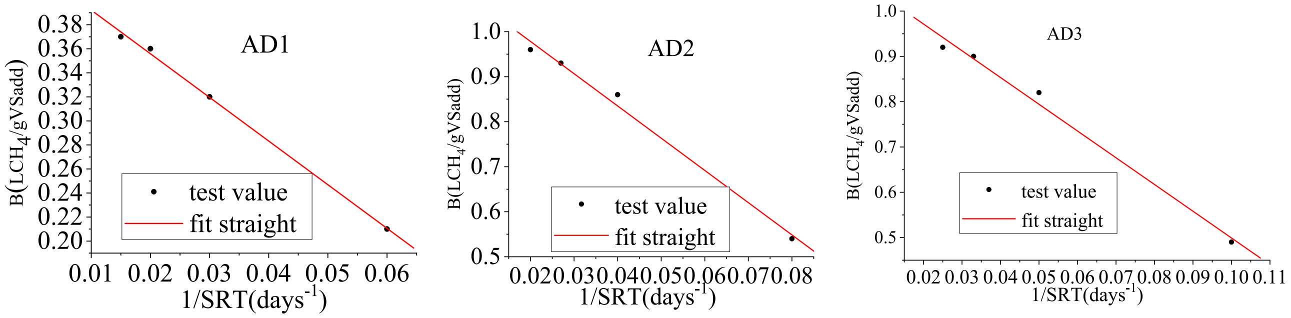

Figure 1. Linear fitting of B with $1/\Theta$ in AD1, AD2, and AD3.

$$E_{\text{output,heat}} = 35\% \times H \times V \times C \tag{4}$$

$$E_{\text{output,electricity}} = 55\% \times H \times V \times C \tag{5}$$

Here, $E_{\text{output,heat}}$ is the heat production from methane produced by a process, kJ; $E_{\text{output,electricity}}$ is the electricity produced from the extra methane produced from a process, kJ; H is the calorific value of methane, 35.8 kJ·L^{-1}; V is the yield of methane in the process in L; and C is the proportion of methane in %.

The calculated values of heat and electricity requirements and net energy balance are shown in Table 3. The calculated values of the heat and electricity requirements for the compensation of the mixing sludge to the digester ($E_{\text{input,heat}}$ and $E_{\text{input,electricity}}$) and the heat and electricity production from the extra methane produced by the process ($E_{\text{output,heat}}$ and $E_{\text{output,electricity}}$) are presented in Table 3.

As shown in Table 3, when SRT increased in AD1, AD2, and AD3, the cumulative methane yield also increased, while the change in the methane content in the three digesters is not significant. Through calculation, the $E_{\text{input,heat}}$ and $E_{\text{input,electricity}}$ in each digester increased as SRT increased. This is because, as the viewer moves from AD1 and AD2 to AD3, the temperature of the mixing sludge before anaerobic digestion increased gradually, and the compensation heat for thermophilic digestion decreased gradually. The $E_{\text{output,heat}}$ and $E_{\text{output,electricity}}$ in each digester decreased gradually as the SRT increased. That is, although the methane yield increased with SRT, the methane production rate decreased as SRT increased, and the heat loss and energy consumption increased accordingly. The net energy decreased as SRT increased in each digester.

In AD1, a negative energy balance was observed during overall experiments; for example, with 300 mL of WAS for anaerobic thermophilic digestion, net energy values were negative for all SRTs. The energy balance ranged from −33.44 to −62.42 kJ·day^{-1}, which indicates that there are no possible practical applications for them in the anaerobic thermophilic digestion of WAS alone.

In AD2, 300 mL of WAS and 100 mL of vinasses were mixed for anaerobic thermophilic co-digestion. Consequently, the cumulative methane yield increased compared with AD1, and net energy transitioned from a negative value to a positive value as SRT increased. For example, the positive energy values are +39.73 and +15.51 kJ·day^{-1} at SRT of 12.5 and 25 days, respectively. This illustrates that the positive energy balance can be created in anaerobic thermophilic co-digestion of WAS and vinasses, which breaks through the bottleneck of negative net energy balance. As SRT approached 37.5 days, the net energy resulted in negative energy balance; the reason is that though the cumulative methane yield increased with the prolonging of SRT, the rate of methane production decreased rapidly, causing energy consumption to increase rapidly.

In AD3, 300 mL of WAS and 200 mL of vinasses were mixed for anaerobic thermophilic co-digestion, and the cumulative methane yield was higher than that in AD2. The net energy changed from a positive value to a negative value as SRT increased, and the positive energy values +64.96 and +41.51 kJ·day^{-1} appeared at SRT of 10−20 days. However, there is an acidification phenomenon for the overloading mentioned above in AD3, and some alkali must be added to the digester on schedule to avoid the acidification to maintain the regular operation. For this reason, this result is desirable as it is required for comparing AD3 with AD1 and AD2. When the SRT increased to 30 and 40 days, the net energy value was +14.35 and −2.88 kJ·day^{-1}, respectively. Compared with these net energy balance results of co-digestion for AD2 and AD3, the AD2 with 12.5 days of SRT was used as an optimum selection.

There are two main reasons for the positive net energy balance value in anaerobic thermophilic co-digestion of WAS and vinasses than that in anaerobic thermophilic digestion of WAS alone. One is that the high-temperature heat resource from vinasses was utilized fully and compensated the heat energy requirement for the mixture, and the other reason is that co-digestion of WAS and vinasses can improve the efficiency and obtain more gas production.

3.3. Kinetic Evaluation of Anaerobic Thermophilic Digestion/Co-digestion. Anaerobic digestion processes are generally described using the first-order kinetic model. Several kinetic models can be used to understand the performance of anaerobic digestion; the model used in the present study was proposed by Chen and Hashimoto. Its main characteristics are as follows: (a) the specific growth rate of microorganisms, μ, is defined from Contois's equation; (b) continuous or semi-continuous completely mixed flow systems are considered; (c) predominant microorganisms in the influent; (d) the yield coefficient is constant; (e) cellular lysis is not taken into account; (f) effluent concentration is directly proportional to influent concentration; and (g) methane production is directly proportional to biodegradable substrate assimilation.

The kinetic equation governing this anaerobic digestion model is given as follows

$$\Theta = 1/\mu_{\max} + (K/\mu_{\max}) \times [B/(B_0 - B)] \tag{6}$$

Here, Θ is the sludge retention time (SRT), in days; K is a dimensionless kinetic parameter related to the rate and stability of the anaerobic digestion; B is the volume of methane produced under normal conditions of pressure and temperature per gram of substrate (VS) added to the digester, L CH$_4$ STP/g VS added; B_0 is the volume of methane produced under normal conditions of pressure and temperature per gram of substrate added at infinite retention time, LCH_4 STP/g VS added; and μ_{max} is the maximum specific microbial growth rate, in $days^{-1}$.

Thus, by first calculating the values of B_0, the graph of Θ versus $B/(B_0 - B)$ produces a straight line with an intercept of $1/\mu_{max}$ and a slope of K/μ_{max}.

To attain the parameter B_0, the following equation is easily derived from eq 6.

$$B = B_0|1 - K/(\mu_{max}\Theta - 1 + K)| \tag{7}$$

This equation shows that, in fact, $\mu_{max}\Theta \gg |1 - K|$. The plot of B versus $1/\Theta$ should be a straight line with $B \to B_0$ as $\Theta \to \infty$ since the plot of B versus $1/\Theta$ was found to be linear for the above-mentioned ranges of SRT; linear regressions were used to determine the intercept B_0.

To use eqs 6 and 7, the data in Table 1 were alternated B as LCH_4/g VS added.

Figure 1 shows the linear fitting of B with $1/\Theta$ in AD_1, AD_2, and AD_3; since the plots of B versus $1/\Theta$ were found to be linear, test values and fit straight values (predication value) have a good correlation, and the linear regressions factor (R) was used to determine the intercept B_0 in Table 4.

Table 4. Results of the Fit Linear Straight Equation for Plot of B Versus $1/\Theta$

digester	correlation coefficient (R)	linear intercept $(B_0)/L\cdot g^{-1}\cdot$ VS	linear slope
AD1	−0.9944	0.4285	−3.6308
AD2	−0.8895	1.3899	−11.1962
AD3	−0.9948	1.0895	−5.9035

The results for all digestion trail correlation coefficients (R) ranging from −0.8895 to −0.9948 are given in Figure 1 and Table 4. These results indicate that the Chen−Hashimoto kinetic model fitted well to the cumulative methane yield in this study. The maximum productive amounts of $CH_4(B_0)$ in AD1, AD2, and AD3 are 0.4285, 1.3899, and 1.0895 $L\cdot g^{-1}$ VS, respectively. It is obvious that the B_0 value in the co-anaerobic system is significantly greater than the sludge anaerobic value alone.

From the values of B and B_0 in the digester, the value of $B/(B_0 - B)$ can be easily calculated, and the graph of SRT(Θ) against $B/(B_0 - B)$ can be plotted. The graph of Θ against $B/(B_0 - B)$ in AD1, AD2, and AD3 is shown in Figure 2 and Table 5. This indicates the best fit for the measured value and deviations between the measured and predicted values.

The results for all digestion trail correlation coefficients (R) ranging from 0.9752 to 0.9863 are given in Figure 2 and Table 5. These results indicate that the Chen−Hashimoto kinetic model fitted well to the SRT with $B/(B_0 - B)$ in this study. This shows the best fit for the measured value and deviations between the measured and predicted values.

Table 5. Linear Fitting of SRT with $B/(B_0 - B)$

reactor	correlation efficient (R)	linear intercept	linear slope
AD_1	0.9861	11.1843	8.1578
AD_2	0.9863	3.8914	7.6207
AD_3	0.9752	3.5197	6.1156

According to the results shown in Table 5 and eq 6, the kinetic equation parameters μ_{max} = 1/linear intercept and k = linear slope/linear intercept. The values of the kinetic parameters (μ_{max} and K) for the three substrates considered are shown in Table 6. The methane production model was the best fit for the measured value and deviations between the measured and predicted values.

Table 6. Kinetic Parameters of Anaerobic Digestions

reactor	μ_{max}/day^{-1}	K
AD_1	0.0894 ± 0.06	0.7294 ± 0.05
AD_2	0.2569 ± 0.09	1.9583 ± 0.03
AD_3	0.2841 ± 0.10	1.7490 ± 0.04

The values of the two kinetic parameters (μ_{max} and K) with their confidence limits at 95% for the three digestions considered are shown in Table 6. As can be seen in Table 6, the values of the kinetic constants μ_{max} and K in AD1 were 0.0894 day^{-1} and 0.7294, respectively. However, the values of the kinetic constants μ_{max} and K in AD2 were 2.9 and 2.7 times higher, respectively, than those in AD1, and the values of the kinetic constants μ_{max} and K in AD3 were 3.2 and 2.4 times higher, respectively, than those in AD1. These results were shown by an enhancement of the maximum specific growth rate μ_{max} and the kinetic constant K for the co-digestion of WAS by adding vinasses; meanwhile, the anaerobic thermophilic co-digestion of WAS and vinasses had advantages over the anaerobic thermophilic digestion of WAS alone, such as the higher methane yield efficiency and positive energy production.

The value of the kinetic constant K in AD2 was greater than that in AD3, while the maximum specific growth rate μ_{max} in AD2 was less than that in AD3. The main reason for this difference was the overloading in AD3 that led to digestion acidification, which affected the methane yield efficiency.

The maximum specific growth rate μ_{max} in AD3 was the highest of the three digester values, which indicates that AD3 had the most significant organic loading compared with AD1 and AD2. However, in practice, the lower the proportion of added vinasses, the better it is for anaerobic co-digestion because lower vinasses content causes more convenience and ease of

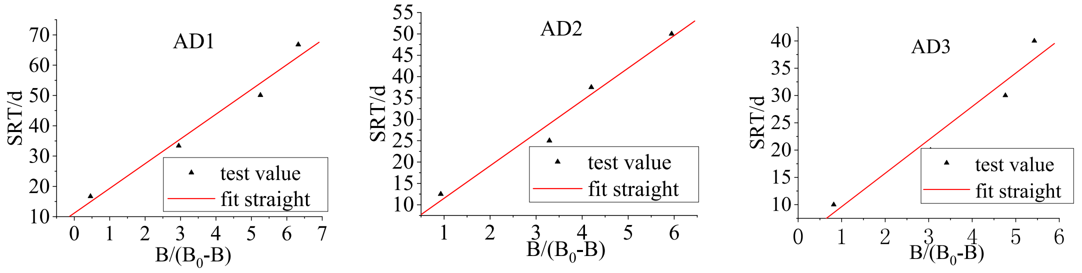

Figure 2. Linear fitting of SRT with $B/(B_0 - B)$ in AD1, AD2, and AD3.

management. Acidification was the most important factor to be considered overall. In practice, the performance of AD2 may be an optimal operation and should be selected for anaerobic thermophilic co-digestion with respect to process cost and management. The Chen−Hashimoto methane production model was best fit for the measured value, and deviations between the measured and predicted were less than 10%. The low deviations obtained between the predicted and measured values suggest that the proposed models predicted the behavior of the reactors accurately.[30]

4. CONCLUSIONS

In this study, methane production from the anaerobic thermophilic digestion of WAS and the anaerobic thermophilic co-digestion of WAS and vinasses was investigated. The results suggested that the anaerobic thermophilic co-digestion of WAS and vinasses could be a viable alternative to production in the future because the co-digestion process could not only promote methane production but also take advantage of the heat resource to realize the positive energy balance value. The main findings of this study are as follows:

1. The net energy balance value of the anaerobic thermophilic digestion of WAS ranged from −33.44 to −62.42 kJ·day^{-1} at the SRT from 16.7 to 66.8 days.
2. In the anaerobic thermophilic digestion of WAS and vinasses in AD2, the mixture proportion of WAS and vinasses of 2:1 (dry VS) can produce the positive energy balance values, which overcame the bottleneck of the negative energy balance of the thermophilic digestion of WAS.
3. In practice, the optimal process in anaerobic thermophilic co-digestion of WAS and vinasses was in AD2, with SRT of 12.5 days, a ratio of WAS/vinasses of 2:1 (dry VS), and the total volume of 400 mL.
4. The two reasons for the net energy balance of co-digestion are as follows: one is the co-digestion of WAS and vinasses can improve the productive methane yield and the other is the full use of hot energy resources from vinasses.
5. Anaerobic thermophilic digestion was evaluated using the Chen−Hashimoto model. The results showed the kinetic constants $\mu_{\max}$ and K in the anaerobic thermophilic digestion of WAS to be 0.0894 day^{-1} and 0.7294, while in the anaerobic thermophilic co-digestion of WAS and vinasses, they were 0.2569 day^{-1} and 1.9583. Anaerobic thermophilic co-digestion of WAS and vinasses has obvious advantages and an energy-saving effect.

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M.T. was responsible for writing and examination of articles. Y.T. was responsible for data collection and calculation of model equation.

Notes

The authors declare no competing financial interest.

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