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Kinetic analysis of biogas produced from kitchen waste conducted using population growth & first order analytical models

L. Feng[1], T.Y. Gao[1], S.Y. Gu[2*], W. Kou[3], P. Gao[2], X.Y. Dong[3], M.L. Yu[3], D.L. Zhang[3], J.Z. Wang[4]

[1]*Liaoning Province Clean Energy Key Laboratory, Shenyang Aerospace University, Shenyang, China*
[2]*Shenyang Agricultural University,China*
[3]*Liaoning Institute of Energy Resources, Yingkou,China*
[4]*Liaoning haosheng biogas power generation co. LTD, Liaozhong, ,China*

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Sequencing batch anaerobic digestion (AD) of kitchen waste at 37 ºC was studied. The classic population growth equations and the first-order biogas production were used to analyze the characteristics of biogas production in kitchen waste anaerobic digestion process under the condition of initial total solids (TS) = 4, 5, 6 and 7 wt %. Logistic equation was better fitted to the experimental data for kitchen waste of initial TS=7 wt % comparing with the modified Gompertz equation. For kitchen waste (AD) process at other TS concentrations in this research to the Modified Gompertz equation was preferred. No lag phase time appeared in the experiment, k of kitchen waste of initial TS= 4, 5, 6 and 7 wt % were 0.2179, 0.1430, 0.1170, and 0.0954, respectively. The kitchen waste of initial TS=4 wt % gave the highest biogas production, followed by initial TS=6 wt % and initial TS=5 wt %. The kitchen waste of initial TS=7 wt % displayed the worst characteristics of biogas production.

Key words: Kitchen waste; Population growth equation; First order model; Kinetics

INTRODUCTION

Undesirable kitchen waste accounts for 30%–50% of municipal solid waste [1]. In China, the production of kitchen waste reached 110 million t in 2012 [2]. Traditionally, kitchen waste can not only be used for feeding pigs [3,4] but also be disposed by landfill or composting with other wastes. The landfill or composting occupies a lot of valuable land and pollutes the surroundings [5-7]. Kitchen waste is composed of starch, proteins, fibers, fat and other organic substances and contains a large amount of moisture and organic matter, rendering it subject to acidification [8]. Based on these characteristics of kitchen waste, anaerobic digestion technique has advantages. Anaerobic digestion technique can dispose solid organic wastes and produce biogas as a source of clean energy [9-12]. After anaerobic digestion, the biogas residue is rich in nitrogen, phosphorus and other elements, the emissions of which will cause eutrophication of waters, and hence the residue can serve as a fertilizer for agricultural production [13,14]. Moreover, the residue can also be utilized to cultivate microalgae to produce biodiesel [15].

In a typical sequencing batch anaerobic digestion process, biogas production has a certain relationship with the growth of microorganisms. The logistic equation and the revised Gompertz equation are classic and prevalent models for the description of population growth in the anaerobic digestion for biogas production. Pommier, Brullmann, Gao *et al.* [16-18] used the revised Gompertz equation to model the process of anaerobic digestion for biogas production. Yusuf *et al.* [19-21] modeled the process of anaerobic digestion for biogas production with the Gompertz equation. In addition, the first-order hydrolysis model is the simplest model for the hydrolysis of complex organic compounds, assuming that the substrate is a limit, and the rate of hydrolysis is proportional to the concentration of unhydrolyzed organic matter. This model fits well with the actual hydrolysis behavior of particulate organic matter. In this paper, a first-order biogas production model was obtained on the basis of the first-order hydrolysis model. By combining the classic population growth model with the first-order gas production model, the behavior and characteristics of biogas production were analyzed using kitchen waste with different concentrations of total solid (TS) to find out under which initial TS kitchen waste can produce the highest biogas amount. This study is meaningful for industrial applications of the anaerobic digestion of kitchen waste and gives practical guidance for the actual operation.

EXPERIMENTAL

Experiments

The kitchen waste was derived from the Canteen of Shenyang Aerospace University in China, and cut into particulates with a diameter of 10 mm. The inoculated sludge which was domesticated at a temperature of 37^{o}C was obtained from a waste water treatment plant in north Shenyang. The initial kitchen

*To whom all correspondence should be sent:
E-mail: fl_iceee@163.com

waste weight and the inoculated sludge volume are shown in table 1. Water was added to the reactor to a level of 1L. Mass fractions of TS and volatile solids (VS) in the kitchen waste were 23.31 and 92.84 wt %, respectively. Mass fractions of TS and VS in the inoculated sludge were 11.95 and 78.05 wt %, respectively. The C/N ratio of the raw material was 21.38. VS was calculated on the base of TS.

Table 1. Initial kitchen waste weight and inoculated sludge volume

Initial TS weight content (wt %)	Initial kitchen waste weight (g)	Inoculated sludge volume (mL)
4	17.8	300
5	60.7	300
6	103.6	300
7	146.5	300

Experimental apparatus and method

A self-designed anaerobic fermentation reactor was used. Two wide-mouthed 1L bottles acted as a gas collecting bottle and a water collecting bottle. Total volume of the reactor was 1.1 L. The bottleneck was sealed with a rubber stopper and sealant. The apparatus was placed in airtight and anaerobic environment.

The fermentation reactor was heated with a thermostated water bath. In this study, the initial mass fraction of TS was separately set as 4, 5, 6, and 7 wt%. Triple experiments were performed with the same initial mass of 17.8 g, 60.7 g, 103.6 g, and 146.5 g of kitchen waste and 300 mL of inoculated sludge was aslo added into the reactor as the inoculum. Water was added to the fermentation reactor to a level of 1L, then the bottles were sealed and cultured at 37 ºC for 30 days in the water bath.

The fermentation liquor was withdrawn with a syringe and the pH was measured with a digital pH meter once a day before adding new kitchen waste during the experimental peroid. The fermentation liquor was then returned into the reactor. When the pH was less than 6.8, pH was adjusted to 7.0 with the addition of $NaHCO_3$ at about 5 pm. Stirring was performed 2 times per day by hand shaking during 5 min each time. pH of the $NaHCO_3$ solution was 9. During the anaerobic process, the pH of the fermenting liquid was below 7. The ideal value pH of the fermenting liquid was 7. Volume of $NaHCO_3$ solution injected was calculated and added according to the rule above. The production of biogas was determined once per day, and the volume of water in the water-collecting bottle was that of produced biogas. Biogas production of the sequencing batch reactor was further revised with the production of control group where only inoculum was added without any substrates. TS and VS were determined by using the drying method at 103–105 ºC and 600 ºC, respectively.

Models

Population Growth Model: The logistic equation can be described as follows:

$$P = \frac{P_{\max}}{1+\exp[\frac{4R_{\max}(\lambda - t)}{P_{\max}} + 2]} \qquad (1)$$

where P is the cumulative biogas production ($mL \cdot g^{-1}$ VS) at time t. P_{max} is the maximum biogas production ($mL \cdot g^{-1}$ VS). R_{max} is the maximum biogas production rate ($mL \cdot g^{-1}VS \cdot d^{-1}$). t represents reaction time (d). Lag-phase time is denoted by λ.

The Gompertz equation is given by:

$$M = P \times \exp\{-\exp[\frac{R_m \times e}{P}(\lambda - t) + 1]\} \qquad (2)$$

where M is the cumulative biogas production ($mL \cdot g^{-1}$ VS) at time t. P is the maximum biogas production ($mL \cdot g^{-1}$ VS). Rm is the maximum biogas production rate ($mL \cdot g^{-1}VS \cdot d^{-1}$). t represents reaction time (d). Lag-phase time is denoted by λ.

Evidently, P, P_{max}, and R_{max} in the logistic equation correspond to the counterparts of M, P, and Rm in the revised Gompertz equation. Kinetic parameters of the logistic equation and the revised Gompertz equation were fitted and analyzed with nonlinear regression by using an Origin8.0 software, whose producter is OriginLab company.

First-order biogas production model: A first-order biogas production model proposed by Lei Feng et al. [23] was used herein and expressed as follows:

$$\frac{1}{t}\ln(\frac{dy_t}{dt}) = \frac{1}{t}(\ln(y_m) + \ln k) - k \qquad (3)$$

where y_m represents the maximum biogas production per gram of volatile substances ($mL \cdot g^{-1}$ VS); y_t represents the biogas production per gram of volatile substances at time t ($mL \cdot g^{-1}$ VS); t represents reaction time (d) and k is the hydrolysis constant (d^{-1}).

The experimental data were analyzed based on the above equation with an Origin8.0 software, which gave the values of $\ln y_m$ + lnk and k of relevant organics.

RESULTS AND DISCUSSION

Data analysis based on the logistic equation and revised Gompertz equation

Under optimal conditions such as temperature, pH, amount of inoculum, etc., the experimental data in an anaerobic digestion process were nonlinearly fitted

with the Origin software (Figure 1). The fitting parameters of anaerobic digestion of different materials based on the logistic equation and revised Gompertz equation are tabulated in Tables 2 and 3.

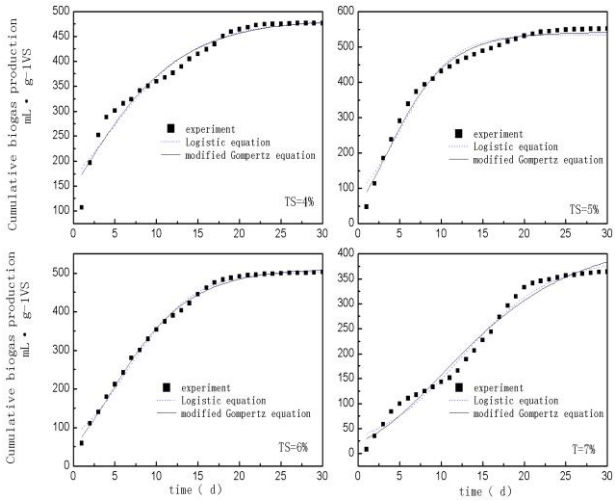

Fig. 1. Cumulative biogas production of logistic equation and modified Gompertz equation

Table 2. Model of parameters of logistic equation

Initial TS concertration (wt %)	P_{max} (mL g^{-1}VS)	R_{max} (mL g^{-1}VS·d^{-1})	λ (d)	R^2
4	480.60	21.91	-7.42	0.95125
5	534.81	42.48	-1.18	0.97202
6	503.78	32.24	-1.17	0.99414
7	389.82	18.35	1.92	0.98458

Table 3. Model of parameters of modified Gompertz equation

Initial TS concentration (wt %)	P (mL g^{-1}VS)	R_{max} (mL g^{-1}VS d^{-1})	λ (d)	R^2
4	485.10	26.52	-5.53	0.95981
5	540.94	32.18	-4.95	0.98597
6	513.09	23.67	-6.34	0.99595
7	429.87	11.70	-8.32	0.97951

The R^2 values in Tables 2 and 3 range from 0.95 to 1, indicating that the anaerobic digestion of kitchen waste with low solid concentrations for biogas generation agrees well with the population growth equation. Specifically, a good fit was obtained when the logistic equation was used for the fit of the anaerobic digestion of kitchen waste with 7 wt % of TS. In contrast, the revised Gompertz equation fitted well with the anaerobic digestion of kitchen waste with 4 wt %, 5 wt %, and 6 wt % of TS. The potential biogas production of kitchen waste with 5 wt % of TS reached a maximum of 540.94 mL·g^{-1} VS, followed by 513.09 and 485.10 mL·g^{-1} VS at 6 wt % and 4 wt % of TS respectively. The potential biogas production of kitchen waste with 7 wt % of TS had a minimum of 389.82 mL·g^{-1} VS. Except that the delay time of the anaerobic digestion of kitchen waste with 7 wt % of TS was 2 days, no delay phenomenon was observed at other contents of TS. This is because the kitchen waste contained large amounts of decomposable rice, bread and other starches as well as certain amounts of lean meat, eggs and other protein-bearing organics, resulting in a favorable C/N ratio to the anaerobic digestion. Consequently, the hydrolysis reaction was accelerated and the growth and reproduction of microorganisms was ensured to promote the progress of the reaction. The delay time at 7 wt % of TS was probably ascribed to the relatively low inoculation ratio at the beginning of the reaction, and hence the micro-organisms did not have enough time to reproduce for the production of biogas.

Analysis of results based on first-order biogas production model

First of all, considering that the anaerobic digestion process in the first-order gas production model does not involve delay time, the experimental data in the first two days were ignored at 7 wt % of TS due to it was relative short to the whole period, otherwise it can not be neglected, and the rest data were shifted to an earlier date accordingly. The experimental data were fitted with equation 8 and plotted in Figure 2, in which the linear fits of (1/t)*ln(dyt/dt) against 1/t at 4 wt %, 5 wt %, 6 wt % and 7 wt % of TS were respectively illustrated.

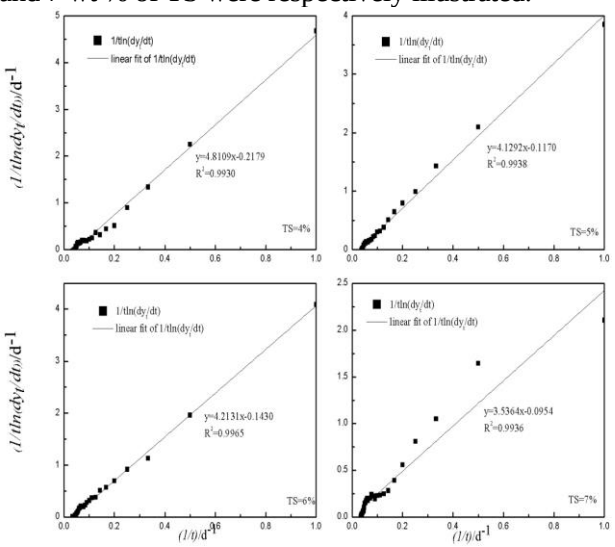

Fig. 2. Plot of 1/t(ln(dyt/dt) against 1/t for kitchen waste anaerobic digestion of different initial TS

All the coefficients of determination (R^2) were greater than 0.99, indicating that this model agreed well with the biogas production behavior of the anaerobic digestion of kitchen waste with low solid concentrations and can be used for theoretical analysis of experiments. Additionally, the values of k and $\ln y_m$ + lnk of the anaerobic digestion of kitchen waste with varied TS concentrations are depicted in Table 4.

Table 4. Parameter values obtained under the condition of the model for kitchen waste anaerobic digestion of different TS concentration

Initial TS concentration (wt %)	$\ln(y_m)+\ln k$	K (d^{-1})	R^2
4	4.8109	0.2179	0.9930
5	4.1292	0.1170	0.9938
6	4.2131	0.1430	0.9965
7	3.5364	0.0954	0.9936

Where, k represents the removal efficiency of degradable substrates. A higher k value indicates a higher reaction speed. It was calculated that the hydrolysis constants of kitchen waste with a TS content of 4 wt %, 6 wt %, 5 wt %, and 7 wt % were 0.2179, 0.1430, 0.1170, and 0.0954 d^{-1}, respectively.

The item $\ln y_m + \ln k$ represents the exploitability of biodegradable substrates and is also a com prehensive index of biogas production rate and biogas production. Therefore, we could evaluate the biogas production capacity of a substrate according to the index, and a higher value indicates a greater gas production capacity of a substrate. The derived k values reflect the conversion rates of a variety of large organic molecules into small molecules, while the item $\ln y_m + \ln k$ size indicates both the biogas production rate and biogas production of various large organic molecules. The values of R^2 in the first-order hydrolysis model of kitchen waste at each TS concentration are greater than those in the population growth model. Therefore, the first-order hydrolysis model is better in the fit. The value of $\ln y_m + \ln k$ at TS concentration of 4 wt % reached a maximum of 4.8109, indicating that its biogas production capacity was the highest. Namely, both the hydrolysis rate and biogas production were high. The values of $\ln y_m + \ln k$ at a initial TS mass fraction of 6 wt %, 5 wt %, and 7 wt % were 4.2131, 4.1292, and 3.5364 respectively. He conducted a sequencing batch anaerobic digestion experiment using garbage of leafy vegetables, which demonstrated that under conditions of 3% of solids and an inoculation ratio of 3.5, the average and maximum daily biogas production rate were the highest with the shortest delay time. Moreover, at the inoculation ratio of 3.5, the biogas production rate was decreased and delay time was extended with the increase of solids percentage. In contrast, the k values in our experiments were independent on the concentrations of TS. This may be attributed to the difference between the raw materials and intermediates in the anaerobic digestion processes of different studies. The values of $\ln y_m + \ln k$ at TS mass fractions of 4 wt %, 6 wt %, 5 wt %, and 7 wt % were not in accordance with the conclusion of potential biogas production drawn from the Logistic equation and Revised Gompertz Equation. The reason may be the fitting error of the Logistic equation and Revised Gompertz Equation, which was reflected by the much lower coefficients of determination (R^2) of the Logistic equation and Revised Gompertz Equation than those of the first-order biogas production model. The dependences of the TS concentrations on k and $\ln y_m + \ln k$ agree with each other. In detail, the hydrolysis rate and biogas production capacity of the anaerobic digestion of kitchen waste were the highest at an initial TS concentration of 4 wt %, followed by those at initial TS concentrations of 6 wt %, 5wt %, and 7 wt %. The maximum of k was higher than the minimum by 128.41%, and the maximum of $\ln y_m + \ln k$ was 36.04% higher than the maximum. Hence, the initial TS content could be 4 wt % for the kinetic study of the anaerobic digestion of kitchen waste with low concentrations of solids. Other factors such as reaction temperature or pH should be adjusted afterwards in the experiment.

CONCLUSION

(1) At appropriate inoculation ratios, the anaerobic digestion process of kitchen waste with a small amount of solids almost does not have delay time. The change of k value along with TS concentrations accords with the variation of $\ln y_m + \ln k$ along with TS concentrations.

(2) The hydrolysis constants of kitchen waste at TS mass fractions of 4, 5, 6 and 7 wt % were 0.2179, 0.1430, 0.1170 and 0.0954 d^{-1}, respectively, corresponding to decreasing hydrolysis rates. The maximum of k values was higher than the minimum by 128.41%.

(3) At a TS content of 4 wt %, the biogas production capacity of anaerobic digestion of kitchen waste was the highest, followed by the capacities at TS contents of 6,5, and 7 wt %. The maximum of $\ln y_m+\ln k$ values was 36.04% higher than the minimum.

(4) Both of maximum of k values and the biogas production capacity occurred when initial TS was 4% among the four, which help researchers choose the initial TS concentration of experiment. The first-order biogas production model can be used to calculate the biogas production capacity of single component such as protein, starch, cellucose and fat. On the basic of this, the biogas production capacity of mixed organic waste can be improved by adjust the content of some organics such as adding some kind of orgaics.

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