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Kinetic Model of Biogas Production from Co-digestion of Thai Rice Noodle Wastewater (Khanomjeen) with Chicken Manure

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Abstract

This study aimed to evaluate the bio-methane potential (BMP) of Thai rice noodle wastewater co-digested with chicken manure. Batch anaerobic digestion systems were operated at room temperature (28-30 ºC) for 45 days. Five different amounts of chicken manure were added to Thai rice noodle wastewater operating in 5 digesters (10g, 20g, 30g, 40g and 50g of chicken manure added respectively). Time-rate derivative models including Gompertz model and its related extensions were used to represent the experimental data. In the biogas production, the Gompertz model becomes popular to describe growth and product formation data because it is simplicity and well-fitting to batch data. Chemical analysis showed that all digesters had the higher nitrogen content (or low COD: N ratio) which was in the range of 16.15-17.62. It was also found that, the digester supplemented with 30g of chicken manure gave highest BMP. This was due to more suitable pH and the ratio of volatile fatty acid to alkalinity (VFA/ALK). The initial pH and alkalinity had a strong effect on the BMP. In general, well nutrient balance, suitable initial pH, and VFA-to-ALK ratio promoted the growth of microorganisms and hence increased the biogas production rate. These were indicated by the kinetic parameters such as the maximum methane production rate (R_m, ml/d) and the methane production potential (P, ml) but not for the shorter lag-phase period (λ, day).

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Keywords: Biogas production, Co-digestion, Anaerobic digestion, Kinetic model, Chicken manure ;

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1. Introduction

Biogas is a clean renewable energy produced by an anaerobic process which can substitute conventional sources of energy such as fossil, fuels, oil, and etc [1]. The anaerobic digestion is one of the most widely used to produce biogas whereby the organic material will be converted by bacteria into the biogas [2]. In Thailand, the sources of biogas production cover a wide range of feedstock such as municipal solid waste, animal waste, agricultural waste, agro-industry waste and wastewater, industrial wastewater, sewage sludge and landfill waste [3]. Many researchers studied biogas production from alternative feedstock such as waste from agro-industry, solid waste, animal waste, industrial wastewater etc [4-6]. The traditional Thai rice noodle wastewater causes considerable environmental problems and largely ignored because many of them are small in size. When this wastewater enters into the river without pre-treatment, it may create the severe problem due to its high chemical oxygen demand (COD) [7]. In the wastewater treatment of Thai rice noodle wastewater, aerobic process are mainly used for the organic removal. However, the aerobic process is not regarded as a suitable treatment option because of high energy requirement for aerobic treatment [8]. The anaerobic co-digestion of wastewater with animal waste has recently been considered as a promising alternative. So, it not only has a potential to produce biogas for local energy need but also decreases the environmental pollution. The scope of this research is to study the bio-methane potential from different amount chicken manure added into Thai rice noodle wastewater (TRW) in anaerobic digestion (AD), whereas important factors for the anaerobic process is C/N ratio and buffer capacity [9]. The Thai rice noodle wastewater (TRW) has lowest of nitrogen content and pH and should preferably be co-digested with chicken manure which has high nitrogen content and pH. The co-digestion would balance nutrients and increase the buffer capacity and improve biogas production. Then we compared the different addition using the modified Gompertz model and other more, including Shnute, Gompertz power law, Grau n-order and Monod model [10]. The preliminary results in this work could be valuable for planning in start-up biogas plant in the large scales.

2. Materials and methods

2.1 Wastewater and Seed

The wastewater sample was collected from the community in Yala province and chicken manure was collected from the layer chicken farm. Characteristics of wastewater and chicken manure are shown in Table 1. The wastewater and chicken manure were kept at 0-4 ºC until used in the experiments.

2.2 Experimental set-up

The experiments were conducted at room temperature (28-30 ºC) until batch completion. The 300-ml-volume serum bottles were used as reactors and a working volume of 200 ml was used in all experiments. The serum bottles were covered with the rubber stoppers and sealed with aluminum caps. The volume of biogas was measured daily by using water displacement method [11-13]. The methane content was measured using Gas Chromatography (GC-8A Shimadzu). The experiments were duplicated in all experiments. The experiment setup is shown in Fig. 1.

Table 1. Characteristic of wastewater and chicken manure

Parameter	**Waste**	
	Thai rice noodle wastewater	**Chicken manure**
pH	4.3	6.7
COD (mg/l)	4,200	10,740
TKN (mg/l)	198	690
TP (mg/l)	18	-
TS (mg/l)	1,610	8,430
VS (mg/l)	1,106	6,759
SS (mg/l)	1,500	9,240
VSS (mg/l)	583.5	7,250
Alkalinity (mg/ las$CaCO_3$)	519	920
VFA (mg/ lasCH_3COOH)	294	1,240
C/N	-	12.40
VS (%w/w)	-	50.20

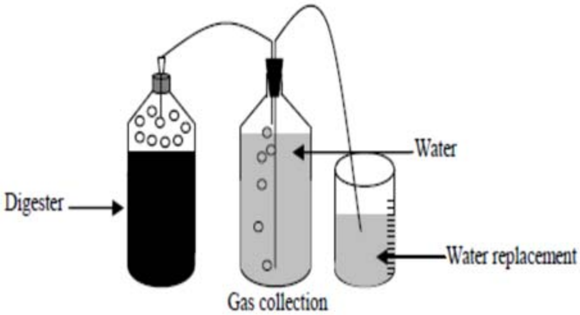

Fig. 1. Schematic view of the experimental set-up

2.3 Experimental design

All experiments were operated in batch mode. Each reactor contains different of amounts of chicken manure (10g, 20g, 30g, 40g, and 50g) which added to Thai rice noodle wastewater. The anaerobic digester having a total working volume of 200 ml. The variables designed in this study were shown in Table 2. The experiments were duplicated in all digesters.

Table 2. Experimental design of this study

Digester	Thai rice noodle wastewater (ml)	Chicken manure (g)
1	200	10
2	200	20
3	200	30
4	200	40
5	200	50

2.4 Analytical procedures

In all experiments, we analysed pH, Chemical Oxygen Demand (COD), Total Khjdhal Nitrogen (TKN), Total Phosphorus (TP), Total Solids (TS), Volatile Solids (VS), Suspended Solids (SS), Volatile Suspended Solids (VSS), Alkalinity, Volatile Fatty Acids (VFA) and C/N ratio. All analytical procedures are performed in accordance with standard methods for the examination of water and wastewater APHA [14]. The biochemical methane potential can calculate by maximum cumulative methane divided by gCOD added [15]

3. Kinetic model of biogas production

One of the most widely-used semi-empirical models for kinetic study the methane production is the modified Gompertz equation as shown in Eq. (1) [16-17]

$$P = P_{\infty} \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{P_{\infty}}(\lambda - t) + 1\right]\right\} \tag{1}$$

where P is Cumulative methane production (ml), P_{∞} is Methane production potential (ml), R_m is the maximum specific methane production rates (ml/d), λ is lag phase period or minimum time to produce biogas (days) and e is mathematical constant (2.718282)

From the original form Gompertz equation

$$P = P_{\infty} \exp\left(\frac{-r_0}{\alpha}\exp\left(-\alpha t\right)\right) \tag{2}$$

where r_0 and α are parameter in Gompertz which directly related to R_m and λ in Eq. (1)

Another, more generalized time-derivative Gompertz extension, the Schnute model which have the following from.

$$P = P_\infty \exp\left(\frac{-\alpha t}{\beta}\right)\left(\exp(\alpha t) - \frac{\beta r_0}{\alpha + \beta r_0}\right)^{1/\beta} \quad (3)$$

where P, α, β are biogas generated, the specific biogas production rate, and the Schnute parameters respectively.

A classical way of describing growth and product formation kinetics is due to Monod (1949) [18].

$$\frac{dX'}{dt} = \mu X = \frac{\mu_m S}{K_s + S} \quad (4)$$

$$\frac{dX}{dt} = (\mu_m - k_d)X = \left(\frac{\mu_m S}{K_s + S} - K_d\right)X \quad (5)$$

$$\frac{dX}{dt} = \left(\frac{\mu_m (S_0 Y_{ps} - P)}{[(K_s + S_0)Y_{ps} - P]} - K_d\right)X \quad (6)$$

Where X' the total accumulated microbial growth assuming no death, μ_m, μ are maximum and general specific growth rate, K_d is specific death rate and K_s is the saturation constant

Using the definitions $Y_{ps} = \Delta P/\Delta S, Y_{x's} = \Delta X'/\Delta S, Y_{px'} = \Delta p/\Delta X' = Y_{ps}/Y_{x's}$ and noting that $P'_0/Y_{ps} = X'_0/Y_{x's}$

$$\frac{dS}{dt} = -\left(\frac{1}{Y_{x's}}\right)\frac{dX'}{dt} = -\left(\frac{\mu}{Y_{x's}}\right)X = -\left(\frac{1}{Y_{x's}}\right)\mu_m \frac{SX}{(K_s + S)} \quad (7)$$

$$\frac{dP}{dt} = -Y_{PS}\frac{dS}{dt} = Y_{PX'}\mu X = Y_{PX'}\frac{\mu_m S}{K_S + S}X = \frac{Y_{PS}}{Y_{X'S}}\frac{\mu_m (P_\infty - P)}{K_S Y_{PS} + P_\infty - P}X \quad (8)$$

Monod-type kinetics with constant cell density

$$\frac{dS}{dt} = -\frac{1}{Y_{XS}}\mu X_0 = -\frac{\mu_m X_0}{Y_{XS}}\frac{S}{K_S + S} = -K_1\frac{S}{K_S + S} \text{ where } K_1 = \frac{\mu_m X_0}{Y_{XS}} = \frac{\mu_m P'_0}{Y_{PS}} \quad (9)$$

Model with constant yield coefficients and no microbial death [19]

$$X = X_0 + Y_{X'S}(S_0 - S) = X_0 + (Y_{X'S}/Y_{PS})P,\ S = S_0 - \frac{P}{Y_{PS}}, S_0 = \frac{P_\infty}{Y_{PS}},\ Y_{X'S} = Y_{XS} \quad (10)$$

$$P = Y_{PS}(S_0 - S),\ C = \frac{X_0}{Y_{X'S}} + S_0 = \frac{X_0}{Y_{X'S}} + \frac{P_\infty}{Y_{PS}} = \frac{P'_0 + P_\infty}{Y_{PS}} = \frac{P'_\infty}{Y_{PS}} \quad (11)$$

$$t = \frac{1}{\mu_m}\left[\frac{K_S}{C}\ln\left(\frac{S_0(C - S)}{S(C - S_0)}\right) + \ln\left(\frac{C - S}{C - S_0}\right)\right] = \frac{1}{\mu_m}\left[\frac{K_s Y_{PS}}{P'_\infty}\ln\left(\frac{P_\infty}{P_\infty - P}\frac{P'_0 + P}{P'_0}\right) + \ln\left(\frac{P'_0 + P}{P'_0}\right)\right] \quad (12)$$

Constant biomass

$$t = \frac{Y_{XS}}{\mu_m X_0}\left[K_S \ln\left(\frac{S_0}{S}\right) + S_0 - S\right] = \frac{Y_{PS}}{\mu_m P'_0}\left[K_S \ln\left(\frac{P_\infty}{P_\infty - P}\right) + \frac{P}{Y_{PS}}\right]$$

(13)

4. Results and discussion

The result of this study in term chemical properties of Thai rice noodle wastewater (TRW) when added the different amount of chicken manure (CM) (10g, 20g, 30g, 40g and 50g) gave average COD in the range of 9,570-31,050 mg/l. The high amount of chicken manure causes to high chemical oxygen demand (COD) value. Table 3 summarizes the experiment for the study co-digestion of chicken manure with Thai rice noodle wastewater on the bio-methane potential. This study monitored biogas production for 45 days when gas generation essentially stopped. At the end of experiment period, the cumulative of biogas production from all digesters average in the range of 358-2,385 ml. And methane content was in the range of 30.38-50.66%. It was observed that digester 3 use amount of CM 30 g to TRW 200 ml, gave highest methane production and bio-methane potential were 1,216 ml and 299 ml CH_4 / $gCOD_{added}$ respectively. Digester 3 (added 30 g of CM) gave the best performance. For this digester, the alkalinity (2,500 mg/l as $CaCO_3$) higher than the stability criterion (1,500 mg/l as$CaCO_3$) and VFA (182 mg/l as CH_3COOH) less than the criterion (250 mg/l asCH_3COOH) [18]. This showed that the digester had high buffer capacity (VFA/ALK = 0.073) and pH was in the range of the criterion (6.8-7.2 pH) [9, 18]. As a result, it is the environment of digester 3 was more suitable than other digesters for the microorganism in anaerobic digestion, thus for production biogas. In most cases, pH after digestion was less than initial in all digesters, which would mean that some part of the substrate fed on to the process was not converted into methane. It is reasonable to assume that part of the particulate matter hydrolyzed and turned into volatile fatty acids (VFA), but not convert into methane. Our results were agreement with the study of Gomez et al [9].

Table 3. The results of experiment and methane yield

Digester	TRW (ml)	CM (g)	COD (mg/l)	TKN (mg/l)	pH initial	pH final	Alkalinity (mg/l as$CaCO_3$)	VFA (mg/l asCH_3COOH)	VFA/ ALK	% CH4	Methane yield (ml.CH_4/ $gCOD_{added}$)
1	200	10	9,570	543	6.8	6.2	1,345	126	0.094	30.38	50
2	200	20	14,940	888	7.2	6.0	1,500	194	0.130	49.32	98
3	200	30	20,310	1,233	7.5	5.9	2,500	182	0.073	50.66	299
4	200	40	25,680	1,578	7.7	5.9	2,245	271	0.120	43.05	73
5	200	50	31,050	1,923	7.8	5.8	3,129	395	0.130	39.15	28

Regarding the effect of COD/N ratio base on theoretical consideration, suggested that the optimal range for anaerobic digestion is in the range 50-140 [20]. However the reports of Chen et al. state that the COD/N ratio of 70 gave the stable performance for anaerobic digestion [21]. While Sumardiono et al. reported that the biogas production showed a satisfactory performance in the range of 71.4-85.7 of COD/N ratio [22]. The results in all digesters gave COD/N in the range of 16.15-17.62 indicated the high level of nitrogen content. This too high nitrogen level may inhibit the growth of methanogenic bacteria, thus giving lower of biogas production.

The result of kinetic models is shown in Table 4. One of the most widely-used for the kinetic study of biogas production in the modified Gompertz equation as shown in Eq 1. The kinetic constant was determined by using non-linear regression, which plotting experimental data and simulation of the models have obtained the graph as shown in Fig 2 and 3. These results suggest that the pH, Alkalinity (ALK) and VFA has the strong effect on methane yield, P, and R_m but not for lag phase period or minimum time to produce biogas (λ). The digester 3 had the highest value of P and R_m which were 1,195 ml and 188 ml/d. That means the ratio of TRW: CM had optimum ratio caused the good condition and suitable for bacterial growth in the digester, thus biogas will be generating maximally. The condition in term pH, alkalinity, VFA, and buffer capacity are the necessary parameter in anaerobic digestion. In the digester 4, 5 added CM 40 and 50 g gave the nitrogen value 1,578 and 1,923 mg/l respectively. The high urea in the CM was decomposed to be ammonia/ammonium may inhibit the methanogen agreement with the study of De-Baere et al. [23] reported that concentration of ammonia of 100-140 mg/l became toxic to bacterial activity**.** And the high of pH in the digester affects the growth of microorganisms according to with the report of Chen et al. [24] reported since the fatty acid form of ammonia has been suggested to be the actual toxic agent, an increase in pH would result in increased toxicity [25].

This article compared the Gompertz-type model, Schnute and Monod model for our experiment data set. The results showed that all model fitted the experimental data well and high order did not indicate any advantage our original or modified Gompertz. However, this is the only specific conclusion and certainly Schnute, model provides much more flexibility which should be used in general and should be developed for the better insight of the process. Finally Monod model can describe the fraction of substrate in term of COD or VS, thus can result in the biogas production in more insightful explanation of co-digestion in batch anaerobic digestion corresponding the study of Rachadaporn et al. [26].

Table 4. Summarized description of the models, parameters and the best-fit parameter (R^2)

Models	Parameter	Chicken manure				
		10g	20g	30g	40g	50g
General parameters	Initial COD (g l^{-1})	9.57	14.94	20.31	25.68	31.05
	P_∞(ml)	111	293	1,216	376	171
Gompertz equation	r_0(d^{-1})	0.4262	0.6997	6.7607	0.3419	0.3997
	α(d^{-1})	0.1565	0.2145	0.4298	0.1341	0.1440
	R^2	0.9930	0.9900	0.9958	0.9928	0.9943
Modified Gompertz equation	R_m(ml d^{-1})	6.4046	22.840	188.77	18.702	9.1358
	λ(d)	0.0112	0.8402	4.0841	-0.4772	0.1447
	R^2	0.9930	0.9900	0.9955	0.9930	0.9940
Schnute model	r_0(d^{-1})	0.3127	0.8158	7.8878	2.6412	21.897
	α(d^{-1})	0.1776	0.1664	0.3895	0.0890	0.1029
	β	-0.2975	0.5348	0.0346	0.8023	0.6799
	R^2	0.9932	0.9954	0.9950	0.9982	0.9977
Monod	$K = \frac{K_1}{\mu_m}$	7.45	5.66	2.00	5.24	5.88
	P'_0 (ml)	100	200	50	400	500
	μ_m (d^{-1})	0.5	0.5	1.0	0.1	0.037
	Y_{ps} (ml/mg COD)	0.386	0.209	0.562	0.158	0.087
	K_s (ml/L)	2,034	6,687	4,508	2,662	1,679
	R^2	0.9800	0.9750	0.9500	0.9820	0.9790

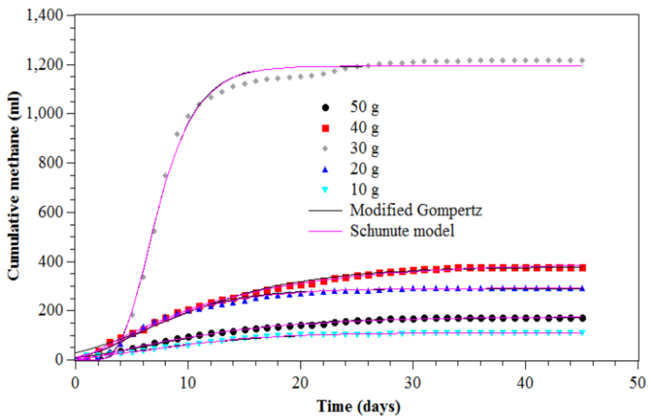

Fig. 2. Methane accumulation VS time for different kinetic models (Modified Gompertz and Schnute models)

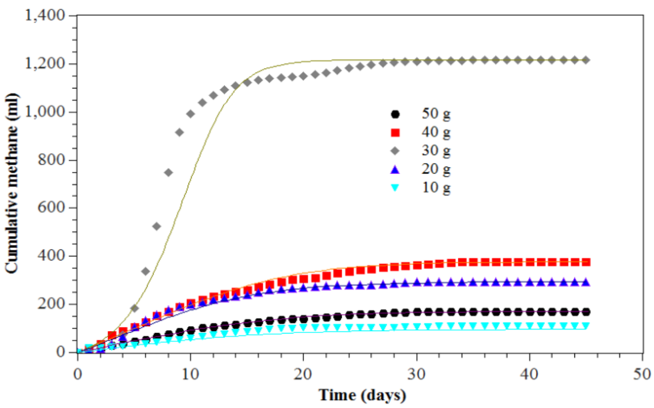

Fig. 3. Methane accumulation VS time for Monod model

5. Conclusion

The co-digestion of Thai rice noodle wastewater with chicken manure. The digester used the amount of chicken manure 30 g added into Thai rice noodle wastewater 200 ml gave highest methane yield. Because, at the ratio of TRW: CM the environmental condition (pH, VFA, ALK) was suitable for the microorganism in the anaerobic digestion process. And the results showed that pH, VFA, ALK, and buffer capacity has the strong effect on the methane yield, P, and R_m in the modified Gompertz model but not for lag phase period or minimum time to produce biogas (λ). In addition, in most cases all models Gompertz-type, Schnute and Monod fit the data well.

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