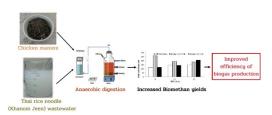


Kinetic model of anaerobic digestion from chicken manure and Thai rice noodle wastewater in continuous reactors

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Graphical abstract



Abstract

A kinetic model was used to describe the anaerobic codigestion of chicken manure (CM) and Thai rice noodle wastewater (TRNW) in continuous reactors. This research investigated the effects of mixing interval and hydraulic retention time (HRT) on methane production and other related kinetic parameters. Experiments were carried out in three identical reactors with different mixing conditions: 1) without mixing, 2) mixing every 6 hours, and 3) mixing every 12 hours. Each reactor was operated at HRT of 10, 20, and 30 days, respectively. The anaerobic co-digestion was conducted at room temperature (28-30 °C). The results showed that the co-digestion provided suitable initial conditions for anaerobic microorganisms in terms of pH level (7.1 ± 0.04), alkalinity (3,420 ± 20.00 mg/LasCaCO₃), and volatile fatty acid (VFA) concentration (480 ± 10.00 mg/LasCH3COOH). The co-digestion experiment with the mixing interval of every 12 hours and HRT of 10 days provided the highest methane production potential with an average of 261 mLCH₄/gCOD. The model was validated statistically and can provide beneficial information for designing co-anaerobic wastewater treatment plants in the mixing interval and HRT suitable for biogas production.

Keywords: Kinetic model, anaerobic digestion, chicken manure, Thai rice noodle wastewater

1. Introduction

Currently, energy is a critical issue worldwide. Studies have shown that energy consumption is constantly increasing in every sector of society. For example, the consumption of liquefied petroleum gas (LPG) in Thailand increased by 2.9% in 2018 compared to 2017. Household consumption is the highest contributor at 34%, despite the constant increase in the price of LPG since August 2017 (Ministry of Energy 2018). Consequently, the energy crisis is intensifying and has become a major concern when compounded with environmental degradation. Therefore, finding alternative energy sources and saving energy is vital in addressing this problem. Recently, Thailand and other developing countries have been increasingly utilizing biogas as a renewable energy source substitute for LPG on the household and community scale. In the past, the deployment of biogas digesters was restricted to rural areas. Using a digester in urban areas is not convenient as it requires raw materials, such as food waste, to be fed into it all the time. Therefore, LPG gas tanks have become the definitive source of energy in such areas (Rajendran et al. 2012). Practically, households and communities produce a lot of organic waste, such as food, wastewater, and animal waste, which can be utilized in biogas production for energy need of households and communities. Thus, biogas production can reduce waste and LPG dependence, mitigating water and pathogen contamination.

Agricultural and food industries, such as raising broilers, laying hens or other food processing plants, also increase daily waste loading and environment problems, particularly in urban areas. In particular, it is essential for cooking because most people consume eggs, and chickens because they are easily accessible, affordable, and highly nutritious. Consequently, raising chicken was the primary industry of Thailand, being raw material used in food industry and other related industries (Srichat and Suntivarakorn 2016; Srichat 2017). The main problem in raising chickens is the management of chicken manure. Most chicken farms raise many chickens in cages, leading to the accumulation of chicken manure. Accumulated manure in cages produces ammonia, which can evaporate and affect the raised chickens negatively (Wilawan et al. 2014; Hussaro, Intanin, and Teekasap 2017). Chicken manure is also used as fish food (Elsaidy et al. 2015) and plant fertilizer. However, when not adequately treated,

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chicken manure used as fish food may contaminate fishpond water with harmful chemicals. To use chicken manure as a fertilizer, traditionally it must be dried beforehand. This is difficult to do during the rainy season. In addition, the process can cause problems for the nearby communities because of the unpleasant smell during the fermentation and drying of chicken manure. Large farms solve the problem by spraying/injecting chemicals to reduce the odors. However, the smell cannot be permanently eliminated, and therefore, chemical injection must be done regularly. When the profit from selling fertilizers is evaluated, odor management may not be worthwhile. In addition, chicken manure drying will affect the community by supporting the life cycles of germ carriers such as flies, resulting in decease transmission which increase the unhealthy life in the surrounding communities. Currently, these problems are solved by cleaning the farms daily and using the manure for other benefits such as fish-raising, worm culture, red-miteraising, and plant fertilizer and raw material for biogas production. Among these options, in many case biogas production is the most effective way because it benefits entrepreneurs, reduces the environmental impact and conserves energy (Aggarangsi et al. 2013).

Beside rice, a popular meal in the South of Thailand is rice noodles called Khanom Jeen. Khanom Jeen producers can be found throughout Thailand – both in households and large-scale factories. Khanom Jeen production results in wastewater with high organic content (Jijai and Siripatana 2017). If this wastewater is released into public water sources, it will affect water quality, aquatic ecology negatively and cause unwanted odors in the nearby communities. Therefore, treating the wastewater before releasing it into the environment is essential. Most Khanom Jeen factories have installed wastewater treatment systems, which control the water quality according to the Department of Industrial Works standards. However, the unmonitored production of Khanom Jeen in households and small-scale industries cause environmental issues due to the producers' lack of technical knowledge and investment in wastewater treatment. Khanom Jeen is produced from rice, and its production requires a lot of water, resulting in large amount of wastewater.

This research studies the co-digestion of chicken manure (high pH (pH 7.0 - 8.4) and nitrogen content (0.38-0.57 %w/w)) with Thai rice noodles wastewater (with a low pH (pH 3.9 - 4.5) and COD/N = 21.21) in an anaerobic process for biogas production. In many cases, both types of waste are available in the same proximity, and the logistic cost is minimal. Moreover, the digester sites should be located at the Thai rice noodles (COD_{average} = 4,200 mg/L) factories because their COD content is relatively low compared to chicken manure (COD_{average} = 10,740 mg/L). and average of COD concentration for mix rice noodle wastewater and chicken manure was 7,470 mg/L. This way, only a small amount of chicken manure will be transported, albeit commonly available in Thailand.

Anaerobic co-digestion requires an appropriate carbon-tonitrogen (C/N) ratio for efficient biogas production. Thai rice noodles, being rich in carbonaceous compounds, can balance the C/N ratio of chicken manure, which often has a high nitrogen content. A well-balanced C/N ratio supports microbial activity and prevents the formation of inhibitory substances, ensuring a stable digestion process (Jijai and Siripatana 2017). Co-digestion balances the environmental condition and the harmful effects of biogas production, and the low cost of the system's operation. The co-digestion process is beneficial for maximizing biogas production compared to the anaerobic digestion of animal manure alone (Ameen et al. 2021; Pečar et al. 2021; Hakimi et al. 2021). From the previous works, mono-digestion of chicken manure (CM) is not stable and trends to fail because of the accumulation of free ammonia, and VFA and carbon exhaustion. On the other hand, mono-digestion of Thai-rice noodle wastewater (TRNW), which is carbon-rich but nitrogen-deficit, gives very low methane yield and is generally unstable. Appropriate mixing ratio between CM and TRNW makes creates a favorable condition for C/N ratio, reducing free ammonia and VFA accumulation and increase methane yield. (Jijai and Siripatana 2017; Shapovalov et al. 2020; Jurgutis et al. 2020). This experiment investigates the optimum mixing interval and HRT of the anaerobic co-digestion process to improve the efficiency of biogas production and determines the kinetics of microbes in biogas production from the co-digestion of the CSTR process.

2. Materials and methods

2.1. Chicken manure

Chicken manure was collected from a layer chicken farm in Yala, Thailand. The sample was sealed in a Polyethylene plastic bag (Ziploc[®]) and stored at room temperature (28-30 °C) in the Laboratory of Environmental Science of the Faculty of Science, Technology, and Agriculture of Yala Rajabhat University before physical and chemical analyses.

2.2. Thai rice noodle wastewater

Thai Rice Noodle wastewater was collected from a household producer in Yala Province of Thailand having the production rate of 100 kg Noodle/day. The sample was stored in a refrigerator in the laboratory at 0-4 °C before it was used in this study.

2.3. Experiment design

The digester was made from a 2 L glass bottle (1-L working volume). The produced biogas is captured by a gas outlet tube connected to a gas counter as show Figure 1. The water displacement method was used and the amount of biogas produced by the process was measured by a gas counter which is produced and calibrated locally. Biogas composition was analysed by Gas Chromatography (GC-8A Shimadzu), and confirmed that the methane content was in the range of 48 - 52%. The digester was operated at different mixing intervals (once every 0, 6, and 12 hours), controlled by a stirrer with a magnetic bar. A higher mixing frequency means that the microbe is mixed more thoroughly in the system, enhancing the intimate contact between the microorganisms and the substrate in the wastewater, thus causing the digestion process to occur at

a higher rate and giving a high methane yield. A timer was used to set the time interval for mixing. A schematic diagram of the experiment is shown in Figure 1.

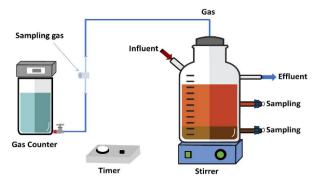


Figure 1. Schematic diagram of the experiment

2.4. Sample analysis

Physical and chemical analyses of samples were conducted before and after each experiment. Properties such as pH, alkalinity, volatile fatty acid (VFA), total kjeldahl nitrogen (TKN), total phosphorus (TP), mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solid (MLVSS), and chemical oxygen demand (COD) were measured according to the standard methods of water examination (APHA 1999). The biogas production potential can be obtained by calculating the biochemical methane potential (BMP) through the following Equation (1) (Angelidaki *et al.* 2009).

$$BMP\left(\frac{mL_{CH_4}}{gCOD_{remove}}\right) = \frac{mL_{CH_4} \text{ Produced}}{\frac{gCOD}{L} * L \text{ (substrate}_{\text{in bottle}})}$$
(1)

2.5. Kinetics of a continuous stirred tank reactor (CSTR)

Raposo *et al.* (2004) developed and proposed the substrate balance model. Considering the COD of the initial substrate, the following equation calculates the incoming total COD (TCOD)₀.

 $(TCOD)_0 = (SCOD)_e + (TCOD)biogas + (TCOD_{VSS})_e + (TCOD)_m$ (2)

where,

(SCOD)e = Outgoing soluble COD

(TCOD) = Fraction of (TCOD)₀ converted into biogas

(TCOD_{VSS})_e = Fraction of (TCOD)₀ converted into biomass

 $(TCOD)_m$ = Fraction of $(TCOD)_0$ consumed for cell maintenance

Generally, the measurement of the viable biomass in the system is complex. Using the MLVSS amount, the biomass quantity in the system was measured. Some of the non-digested solids remain in the digester. Consequently, the difference between the outgoing total and soluble COD may indicate the viable biomass in the system (Borja *et al.* 2003).

$$qS_{t0} = qS_{Se} + q_{CH4}Y_{S/G} + q[S_{te}-S_{Se}] + k_mXV$$
(3)

where,

q is the Flow rate (L/d)

 S_{t0} is the Incoming TCOD concentration (g TCOD/L)

 S_{te} is the Outgoing TCOD concentration (g TCOD/L)

 S_{Se} is the Outgoing SCOD concentration (g SCOD/L)

 q_{CH4} is the Daily methane production (L CH₄/d) Y_{S/G} is the Biomass coefficient for cell maintenance

X is the Biomass concentration in the reactor

V is the Reactor volume

From Equation 3, the following can be obtained:

 $q[S_{t0} - S_{te}] = q_{CH4}Y_{S/G} + k_mXV$

where,

HRT is the Hydraulic retention time (V/Q)

V is the Reactor volume

Q is the Flow rate

When Equation (4) is divided by (XV), the following equation can be obtained:

$$\frac{[\text{St0} - \text{Ste}]}{(\text{HRT x X})} = \frac{q\text{CH}_4 Y_{\text{S/G}}}{XV} + k_m$$
(5)

Equation (5) is linear where the slope is equal to the substrate-methane conversion coefficient $(Y_{S/G})$. Consequently, the inverse of the slope $(1/Y_{S/G})$ can be calculated as the methane coefficient $(Y_{G/S})$, while the y-intercept is equal to the coefficient for cell maintenance (k_m) .

Considering the Monod equation (Doran 2013), the relation between the specific growth rate and the concentration of the substrate is as follows:

$$\mu = \mu_{\text{max}} \frac{S_{\text{te}}}{(K_{\text{s}} + S_{\text{te}})}$$
(6)

where,

 $\boldsymbol{\mu}$ is the Specific growth rate

 μ_{max} is the Maximum specific growth rate

Ks is the Substrate constant

Monod equation is developed based on microorganism culture, which is a pure culture. On the other hand, anaerobic wastewater treatment is a process characterized by the substrate's inhomogeneity, as well as complex and viable microbes. This complex nature affects the system kinetics due to the high variability of the growth constant. However, many researchers found that the relation between μ and St₀, as determined by Equation (6), can describe the system's kinetics reasonably well. Hu *et al.* (2002) proposed an equation to describe the rate of conversion of biomass concentration in CSTR for a steady-state system as the following.

$$q(X-X_0) = \mu XV - k_d XV \tag{7}$$

where,

VSS/L)

q is the Flow rate (L/d)

X₀ is the Concentration of biomass in the influent (g VSS/L) X is the Concentration of biomass in the reactor/effluent (g

 k_d is the Death rate constant (d⁻¹)

V is the Volume of the reactor (L)

(4)

If we consider the biomass concentration in the feed to be eqal to zero and substitute HRT into Equation (7), the following can be obtained:

$$\mu = \frac{1}{HRT} + K_d \tag{8}$$

he relation between the rate of conversion of substrate and biomass in a steady-state system is described by Equation (9):

$$\frac{[S_{to} - S_{te}]}{HRT} = \mu \frac{X}{Y}$$
(9)

Where,

Y = The coefficient of biomass.

Therefore, when we substitute Equation (8) into Equation (9), the following equation can be obtained:

$$\frac{[\mathbf{S}_{to} - \mathbf{S}_{te}]}{\mathbf{HRT} \times \mathbf{X}} = \frac{1}{\mathbf{Y} \times \mathbf{HRT}} + \frac{\mathbf{K}_{d}}{\mathbf{Y}}$$
(10)

Equation (10) also gives an equation of a line when [S_{t0} - S_{te}]/(HRT \times X) is plotted as a function of 1/(HRT). The inverse of the slope can be calculated as the coefficient of biomass, and the death rate can be calculated from the y-intercept on the graph (Hu *et al.* 2002).

Equations (5) and (10) can be used to analyze the different parameters of the kinetic model and to study and predict the operation of anaerobic wastewater treatment by CSTRs.

3. Results and discussion

The physical and chemical characteristics of chicken manure and Thai rice noodle wastewater, such as pH, COD, TKN, TP, TS, VS, SS, VSS, alkalinity, and VFA parameters, is shown in Table 1. The wastewater from Thai rice noodle production can be described as cloudy white liquid with a sour smell from fermented flour used in the production. It is partially decomposed into VFA by acid-producing as the result of the intermediate volatile acid produced by fermentation bacteria or acidogenic bacteria which break down organic polysaccharides under an anaerobic process. The pH of Thai rice noodle wastewater was approximately 4.3 which is unsuitable for viable microbes to convert the feed to methane via anaerobic digestion. Generally, the wastewater produced from flour fermentation has a low pH and contains easily degradable organic compounds. Researchers have found that the BOD and COD of fermented flour wastewater were in the range of 3,060-28,300 mg/L and 5,568-33,969 mg/L, respectively (Siripattanakul-Ratpukdi 2012; Jijai et al 2017; Pongjinapeth et al. 2020). According to Metcalf and Eddy (2003), production of biogas is feasible when a wastewater have a COD of higher than 1,000 mg/L and a pH in the range of 6.8-7.2 (Speece 1996). In this study, the average COD of Thai rice noodle wastewater was 4,200 mg/L, so it could be used to produce biogas. The average pH of chicken manure was 7.6. The co-digestion of these two substrates balances the pH level at 7.1±0.04 for the microbes to undergo the anaerobic digestion process. A few chemicals can be added to adjust the pH.

To study the effect of mixing intervals on biogas production, which utilized three reactors with different mixing intervals: without mixing (control), every 6 hours, and every 12 hours. The HRT of each reactor was operated for 10, 20, and 30 days. The results showed that the initial conditions of co-digestion were suitable for anaerobic microorganisms in terms of alkalinity (3,420 \pm 20.00 mg/LasCaCO₃), and VFA (480 \pm 10.00 mg/LasCH₃COOH). The initial COD average of 7,470 mg/L, indicating sufficient organic substrate-to-biogas production.

The experiment set with a mixing interval of every 12 hours and HRT of 10 days provided the highest biogas production rate and biogas production potential with an average value of 117 mL/d and 261 mLCH₄/gCOD respectively, as shown in Figures 2 and 3. More mixing gives the microorganisms in the system to contact and decompose organic matter more easily and make it more throughout the system. The fermentation content was more uniform and balanced because the mixing effect. Microorganisms and nutrients have a chance to meet and digest thoroughly and can produce the highest biogas production rate.

Table 1. Physical and chemical characteristics of Khanom Jeen wastewater and chicken manure.

Parameter	Khanom Jeen wastewater	Chicken manure
рН	4.3	7.6
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/LasCaCO ₃)	519	920
VFA (mg/LasCH₃COOH)	294	1,240
C/N	30.5 (Jijai <i>et al.</i> 2019)	12.40

The results showed that co-digestion of chicken manure and Thai rice noodle wastewater provided an environment with balanced nutrients (C/N ratio = 21.45) suitable for microbial growth and methane production. Mixing interval of 12 hour was found sufficient for the microbes and nutrients to distribute thoroughly, so that the contact hindrance was removed and the microbe and substrate responded well together, resulting in high methane yields and COD removal. This is consistent with the report by Lerdrattranataywee and Kaosol (2015), which studied biogas production from lock rubber wastewater and found that mixing every 12 hours/day and HRT of 10 days gave the highest biogas production. On the other hand, Li et al. (2014) studied anaerobic co-digestion of chicken manure and corn stover and found that mixing every 1 hour/day and HRT of 22.5 days gave the highest biogas production.

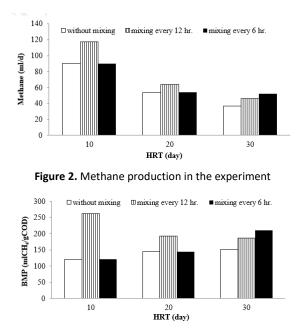
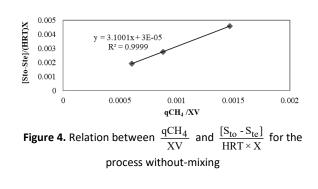
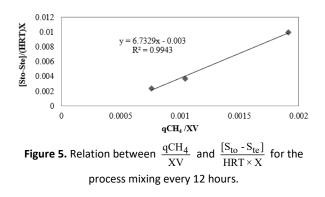


Figure 3. Biochemical methane potential in the experiment

The kinetic parameters in this experiment can be estimated using the model proposed by Raposo et al. (2004) and Hu et al. (2002). because Monod kinetics fits well with the degradation data for soluble starch and glucose, and particularly for TRNW, as published in previous works (Jijai et al. 2017 and 2019). The regression coefficient (R²) for the three reactors was in the range of 0.9743-0.9999. The substrate-methane conversion coefficients (Y_{G/S}) calculated from Equation (5) for the process without mixing, mixed every 12 hours, and mixed every 6 hours were 0.32, 0.15, and 0.32 mLCH₄/gCOD_{removed}·d, respectively. On the other hand, the coefficients for cell maintenance (km) calculated from the y-intercept for the process without mixing, mixed every 12 hours, and mixed every 6 hours were 0.00003, 0.003, and 0.00003 gCODremove/gMLVSS·d, respectively (Figures 4, 5 and 6).





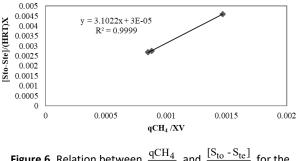


Figure 6. Relation between $\frac{qCH_4}{XV}$ and $\frac{[S_{to} - S_{te}]}{HRT \times X}$ for the process mixing every 6 hours.

The biomass yield coefficient (Y) and the death rate constant (k_d) can be calculated from the slope and intercept as shown in Figures 7, 8 and 9 for the process without mixing, mixed every 12 hours, and mixed every 6 hours, respectively. The results of kinetic values are shown in Table 2.

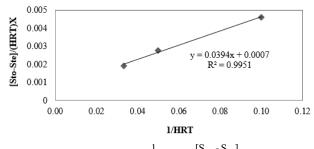


Figure 7. Relation between $\frac{1}{HRT}$ and $\frac{[S_{to} - S_{te}]}{HRT \times X}$ for the process without-mixing.

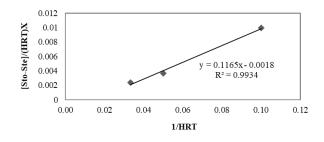


Figure 8. Relation between $\frac{1}{HRT}$ and $\frac{[S_{to} - S_{te}]}{HRT \times X}$ for the process mixing every 12 hours.

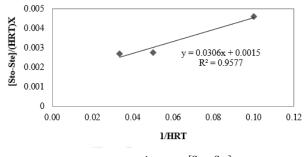


Figure 9. Relation between $\frac{1}{HRT}$ and $\frac{[S_{to} - S_{te}]}{HRT \times X}$ for the process mixing every 6 hours.

Table 2. Kinetic parameters obtained from co-digestion of chicken

 manure with Khanom Jeen wastewater in CSTR.

	Digester Characteristics		
Kinetics parameter	Without- mixing	Mixing every 12 hours	Mixing every 6 hours
Y _{G/S} (mLCH ₄ /gCOD _{remove} ·d)	0.32	0.15	0.32
k _m (gCOD _{remove} /gMLVSS·d)	0.00003	0.0030	0.00003
R ²	0.9999	0.9943	0.9999
Y(gMLVSS/ gCOD _{remove})	25.38	8.58	32.68
k _d (d ⁻¹)	0.018	0.015	0.049
R ²	0.9951	0.9934	0.9577

4. Conclusions

The kinetics of anaerobic co-digestion from chicken manure and Thai rice noodle wastewater in a CSTR were studied. The effects of mixing interval and HRT on the kinetic parameters were investigated. The results indicate that the co-digestion of these two substrates balances the pH level of the microbes in the anaerobic digestion process. Using a mixing interval of every 12 hours and HRT of 10 days provided the highest biogas production rate and biogas production potential. The kinetic values obtained from this experiment, such as the coefficient of conversion of substrate into methane $(Y_{G/S})$, the coefficient for cell maintenance (k_m), the coefficient of biomass (Y), and the death rate constant (K_d) the model was validated statistically and can be used provide beneficial information for designing anaerobic wastewater treatment plants in the range of mixing interval and HRT covered in the experiments. The results confirm that the mixing interval and HRT is a factor in biogas production and usually the limiting factor of the process.

Acknowledgements

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