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Kinetic model of biogas production from co-digestion of Thai rice noodle wastewater with rice husk and different type of manure with ash supplement

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Abstract. In recent decades up to now, researches on alternative energies have been intensified particularly those on biomethane and biohydrogen from agriculture wastes and municipal wastes. The objective of this research was to study the biogas production from anaerobic codigestion of Thai rice noodle wastewater with rice husk and different types of animal manure (chicken manure, cow manure, and quail manure), with and without ash supplement. There were 27 experiments conducted in batch digesters at room temperature (28-30 °C) and each experiment was triplicated. Each digester contained 10 g of animal manure, 10 g of rice husk, and 200 ml total working volumes of Thai rice noodle wastewater. Five different amounts of ashes (0, 2, 4, 6, 8 and 10 g) were supplemented. The results showed that the co-digestion of Thai rice noodle wastewater with chicken manure, rice husk, and 6 g of ash supplement gave the highest methane percentage, cumulative methane production and bio-methane potential (BMP): average value of 71.5%, 1,846 mL and 311.2 mLCH4/gVSremoved respectively. This co-digestion gave the initial pH of 7.0 and it was sustained in an optimal range (pH 6.8-7.5) until the digestion stopped (45 days). Slow release of nutrients from slowly digestible substrates helped to balance the digestion steps, sustaining pH to around 7. In contrary, other sub-optimal ratios produced the final pH was lower than its initial pH, and the AD process could fail or produced less methane. In the kinetic study, it was also found that traditional Gompertz and Monod-type models for single substrate digestion could not describe the biogas evolution curve satisfactory. Two-substrate models were used instead and able to describe the experimental data very well.

Keywords: Kinetic model, Co-digestion, Thai rice noodle, Rice husk, Ash

1. Introduction

In recent decades up to now, researches on alternative energies have been intensified particularly those on biomethane and biohydrogen from agriculture wastes and municipal wastes. In Thailand, the research topic has been flourishing thanks to the vision of ministry of energy in Thailand; "Thailand has energy security, is a leader in energy technology in the Asian region, and people can be self-reliant within the year 2036" [1]. In addition, Thailand is essentially an agricultural country where most of the



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wastes are from agricultural, agro-industrial, and community waste. These wastes can be utilized in various fields, and biogas for being a source of thermal and electrical energies is particular attractive because it not only produces the energy but also mitigate odious smell and reduce a large portion of COD in wastewater [2-4]. One of the most challenges of biogas research is how to maximize biogas production from wastewater (or other organic wastes) having varying compositions, interacting with microbial consortium dynamically. Anaerobic Co-digestion (ACoD) is an effective tool to mitigate nutrient deficiency and improve its balance, thus optimizing the biogas yield by manipulating the substrate composition and biodegradability [5].

Thai rice noodle is produced and consumed throughout Southeast Asian region. It is an industry with many hundreds small and medium factories across the country which, in overall, produce a large amount of wastewater and cause considerable environmental problems. The wastewater is characterized as acidic, carbon-riches, nutrient-imbalanced, by itself not suitable for biogas production. To obtain good biogas yield, co-digestion or nutrient supplement is required. Until now, there are very few studies on co-digestion of Thai rice noodle wastewater (TRW). Jijai et al. (2017) [6] explored TRW co-digested with chicken manure and obtained more than 50 % improvement on biogas yield. However, more complete coverage of co-digestion is still lacking for practical implementation of commercial/community scale plants.

Many works have focuses on trapping the potential of Rice husk (RH) for anaerobic digestion. It is well-known as an agriculture by-product of the rice milling industry which is generated in large quantity annually through the activities of rice harvesting and processing [7-8]. It is an important agriculture residues in term of quantity. Most of the research works on AD of rice husk take it a primary substrate and solid-state AD has been the most explored. Very few works utilize rice husk as a secondary co-substrate for AD process although it could provide extra stability for the co-digestion system, helping balancing the carbon source by prolonged hydrolysis of cellulosic components [9].

In this article to further explore a fuller coverage of TRW co-digested with three animal manures (chicken, cow and quail manure) which provide better C/N ratio and nutrient balance, and rice husk for prolonged carbon source. In addition, ash from biomass power plants (fly ash) was supplemented for trace elements and initial pH adjustment. The main objectives of this work are to improve the biochemical methane potential (BMP) of the co-digestion, understand how the accumulated biogas evolution curve (ABE curves, in turn, the microbial consortium) responded to complex mixture in AD co-digestion process. The Gompertz two-substrate model will be used to characterize the ABE curves and interpret the results.

2. Material and Method

2.1. Materials

Three types of co-substrate were used in the experiments, namely Thai rice noodle wastewater (TRW), animal manures and rice husk (RH). TRW samples were collected from a community in Yala province and kept at 0-4 °C until used in the experiments. The rice husk (RH) used in this study was obtain from rice mills. The animal manures, including chicken manure (ChM), cow manure (CM) and quail manure (QM) were collected from the farm (chicken, cow and quail) of Yala Rajabhat University Mae Lan Campus. Ash (fly ash) used as a supplement was collected from the biomass power plants in Yala province. The samples were stored at room temperature prior to physico-chemical analysis and performing experiments. The characteristic of materials used in this study are shown in Table 1.

2.2. Experimental set-up and procedure:

The experiments were conducted at the room temperature (28-30 °C). The anaerobic digesters having a total volume of 300 ml and a working volume of 200 ml were used in all experiments. Whenever codigestion was applied, 10 g of animal manure and/or 10 g of rice husk was added to the 200 ml of TRW. Five different amounts of ashes (0, 2, 4, 6, 8 and 10 g) were supplemented. They were sealed with the rubber plug and cover with aluminum cap. The Biogas production was measured daily by water displacement method as used by other authors [10-11]. The methane content measured by gas chromatography (GC) (Agilent technologies 7890B). The experimental setup is shown in Figure 1. In all experiments, to analyzed pH, Chemical Oxygen Demand (COD), Total Solids (TS), Volatile Solids (VS), Alkalinity, Volatile Fatty Acids (VFA), moisture, and C/N ratio. All analytical procedures are performed in accordance with standard methods [12]. The biochemical methane potential was calculated from maximum cumulative methane divided by grams VS added/removed [13]. The experiments were operated in batch mode. The experiments were triplicated in all digesters.



Digester Solution Dottle Deaker

Figure 1. Schematic diagram of experiment

Table 1. Characteristic of materials (Thai rice noodle wastewater, rice husk, ash, and animal manures)

Parameter	Materials										
T ur uniteter	TRW	ChM	СМ	QM	RH	Ash					
pН	4.20 ± 0.09	$7.60\ \pm 0.05$	$7.52\ \pm 0.08$	$7.40\ \pm 0.09$	10.20 ± 0.18	12.00 ± 0.50					
TS (g/L or g/Kg)	109.5±8.0	883.4 ± 80.5	885.3±98.2	899.1±89.0	514.0±60.2	-					
VS (g/L or g/Kg)	71.20 ± 5.2	504.2±46.0	512.6±56.8	367.7±35.6	102.8 ± 15.0	-					
COD (g/L or g/Kg)	112.5±20.2	802.1 ±95.2	810.2±120.1	601.2±62.8	150.8±30.3	-					
Alkalinity (mg/LasCaCO ₃)	$490~{\pm}35$	$1,700 \pm 150$	$1,500 \pm 100$	$2,\!800 \pm 200$	2,600 ±180	-					
VFA (mg/LasCH ₃ COOH)	309 ±20	1,363 ±137	978 ±72	$\begin{array}{r} 1,875 \\ 125 \end{array}$	147 ±13	-					
Moisture (%)	89.10	10.66	10.47	10.09	48.57	9.90					
C/N	30.5	8.45	19.72	7.14	61.40	68.47					
%C	-	24.86	35.78	26.63	38.57	12.38					

3. Gompertz two-substrate (GTS) model

Most simple substrate growth models (both Gompertz- and Monod-type) oversimplify the substrate complexity by assuming that the reaction rate is limited by a single substrate (or a substrate entity). In other words, most wastes/waste-waters contain a complex mixture of substrates of which the microbial consortium has different preference when available at the same time. The data set used in this article (Table 2) illustrates this fact as it appears that there are second bumping curves after the preferable substrate is exhausted. In fact, most co-digestion ABE data exhibit similar patterns, causing large variation if the single-substrate models are used to represent the process.

This section attempts to address this complexity by extending Gompertz model for two-coupling substrates, namely: easily and slowly degradable substrates. A switching function is also introduced to tackle the substrate preference as seen by the microorganisms. The formulation is a follow [14].

$$\mathbf{P}' = \mathbf{P}'_{e} + \mathbf{P}'_{s} = \left(\mathbf{P}_{e\infty} + \mathbf{P}'_{e0}\right)\boldsymbol{\theta}_{e} + \mathbf{g}(t)\left(\mathbf{P}_{\infty} - \mathbf{P}_{e\infty} + \mathbf{P}'_{s0}\right)\boldsymbol{\theta}_{s}$$
(1)

Where subscripts e and s are referred to easily and slowly degradable substrates respectively.

$$P' = P + P'_0, P'_e = P_e + P'_{e0}, P'_s = P_s + P'_{s0}$$
 (2)

g(t) was proposed as follows and its graphical representation is depicted in Figure 2.

$$g(t) = 1/\left(1 + e^{-\kappa(t-\tau_s)}\right)$$
(3)

4. Result and Discussion

The chemical analysis of Thai rice noodle wastewater (TRW) gave an average of COD 112,500 mg/L, which was high, but within a normal range of substrate for anaerobic digestion (AD) [15]. It also had a high C/N ratio of 30.5 which was slightly off the suitable range. However, the initial pH of TRW (pH = 4.2) rendered it unsuitable for the AD process unless been modified by some means: i.e.

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co-digestion with non-acidic substrate or by ash supplement. Therefore, the AD process must be adjusted for the pH to be in the range of 6.8 -7.2 [16]. As shown in Table 2, the co-digestion of Thai rice noodle wastewater with the other substrate helped to adjust the initial pH and the initial pH will vary according to the amount of ash supplement. In addition, co-digestion changed the C/N ratio, although the C/N ratio of all co-substrates were still within an acceptable range (10 < C/N < 30). At the end of experiment period, the digester 7 gave the highest of the cumulative of methane production and methane production potential (BMP). As shown in Table 2, for the best ACoD of TRW, digester 7 which exhibited the pH of 7.0 initially, high buffer capacity (VFA/ALK = 0.4), optimal C/N ratio 22.6 in the range of criterion. As a result, it is the environment of digester 7 (TRW 200 mL: RH 10 g: ChM 10 g: ash 6 g) was more suitable than other digesters for the microorganism in anaerobic digestion, thus for the production biogas. This confirms some previous work which reported the benefits suitable C/N ratio for improving the methane methane yield from anaerobic digestion of multi-component substrates, based on optimized feeding composition and C/N ratio [22]. Other work found that C/N ratios of 25:1 and 30:1 had similar highest cumulative biogas production, about threefold higher than that from a material with a C/N ratio of 15:1 [23].

The final of pH in all digesters with ash supplement. In most cases, pH after digestion was less than their initial values in all digesters without pH adjustment by ash supplement, 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. When ash was supplemented, the final pHs were consistently higher than the corresponding initial values. Our results were an agreement with the study of Esposito, Frunzo, Panico, & Pirozzi (2012); Rabii, Aldin, Dahman, & Elbeshbishy (2019) and Zhang, Zhang, Li, Li, & Xu (2016) [17-19]. The parameter of pH is an important factor in the biogas production process. Therefore, the co-digestion in the ratio of Thai rice noodle wastewater of 200 mL with rice husk 10 grams, chicken manure 10 grams and adding an ash supplement in the amount of 6 grams per total of working volume 200 mL gave the highest of biogas production and the bio-methane potential. The codigestion process with the suitability of co-fermentation materials and the system environment [20-21]. Typically, the chemicals used to adjust pH in the biogas process commonly used bicarbonate. It is the most commonly used chemicals in the pH control of the system. However, it is still expensive. Therefore, from this research, it can be concluded that ash the residue from the production process of biomass power plant, which is waste material, can be used to adjust the pH in the anaerobic digestion system. It can be reducing the cost and environmentally friendly. The result of kinetic models is shown in Table 2. One of the most widely-used for the kinetic study of biogas production in the modified Gompertz equation. The kinetic constant was determined by using nonlinear regression. This article compared the The Gompertz two-substrate (GTS) model with experimental data set. The results showed that two-substrate model fitted the experimental data well. The model provides much more flexibility, thus this model is empirical model can result the biogas production in more insightful explanation of co-digestion in batch anaerobic digestion corresponding the study of Noynoo et al. [14].



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Figure 2. Biogas accumulation for Gompertz two substrate model

Table 2. The results of experiment, methane yield, parameters and the coefficient of determination (R²) obtained from fitting cumulative biogas production data to Gompertz two substrate model

No	Co-digestion	pH initial	pH _{final}	C/N	yield (ml/gVS _{added})	yield (ml/gVS removal)	P∞ (mL)	Pe∞ (mL)	Rm _s (mL/d)	Rm _e (mL/d)	κ	λ_{e} (d)	λ_{s} (d)	τ_{s}	R^2
1	TRW+ChM	5.3	5.8	16.36	21.26	70.61	427	217	84	7	198	0	0.30	1	0.992
2	TRW+ChM+ Ash (2)	5.3	5.8	16.80	30.47	99.70	577	404	16	416	140	1.23	0.05	1.46	0.997
3	TRW+ChM+ Ash (4)	5.6	5.9	16.09	13.16	47.35	273	101	20	24	110	1.47	-5.4	1.06	0.997
4	TRW+ChM+ RH+Ash (0)	5.9	5.9	17.93	42.44	93.37	635	200	9	53	0.57	-1.0	-1.2	35.5	0.968
5	TRW+ChM+ RH+Ash (2)	6.1	7.4	18.19	60.64	130.49	1530	296	11	20	7.64	30.4	-2.6	0.40	0.989
6	TRW+ChM+ RH+Ash (4)	6.4	7.3	22.47	161.60	278.28	1520	1146	1647	45	5.29	26.4	-0.6	1.09	0.999
7	TRW+ChM+ RH+Ash (6)	7.0	7.4	22.56	168.78	311.15	2164	1236	58	32	49	0	31.3	8.91	0.987
8	TRW+ChM+ RH+Ash (8)	7.0	7.5	22.77	132.66	203.83	2365	996	21	38	128	38.9	0.67	0.04	0.996
9	RH+Ash	7.7	7.3	22.80	77.46	194.19	2272	436	52	14	28	-4.6	26.5	22.0	0.996
10	TRW+CM	4.4	4.4	18.20	30.64	127.06	607	157	26	44	4.54	10.0	-7.1	1.02	0.996
11	TRW+CM+ Ash (2)	5.4	5.4	23.75	44.42	246.40	937	217	275	36	130	4.5	- 0.08	1.00	0.999
12	TRW+CM+ Ash (4)	6.0	7.2	24.77	56.09	128.19	1935	497	19	25	6.94	27.2	1.21	1.27	0.990
13	TRW+CM+ RH+Ash (0)	5.0	5.3	22.34	7.01	23.44	194	44	140	5	2.91	0.22	0.43	0	0.993
14	TRW+CM+ RH+Ash (2)	5.9	6.6	22.37	48.30	154.47	1302	424	51	284	14	0	25	21.9	0.996
15	TRW+CM+ RH+Ash (4)	6.4	7.1	25.58	55.79	113.59	1620	835	437	32	77	21.3	0.08	0.01	0.990
16	TRW+CM+ RH+Ash (6)	6.3	7.5	29.91	42.69	104.04	1333	626	58	12	34	1.52	31.4	26.4	0.979
17	TRW+CM+ RH+Ash (8)	6.5	7.4	32.73	54.70	177.36	1700	111	67	6	34	-4.2	21.2	17.9	0.984
18	TRW+CM+ RH+Ash	6.6	7.3	34.38	68.51	222.76	1455	572	31	10	0.77	12.5	17.0	20.9	0.996
19	TRW+OM	5.9	5.4	13.47	43.78	78.36	968	907	19	117	0.10	0.45	5.22	0.01	0.996
20	TRW+QM+ Ash (2)	6.8	5.6	13.49	13.01	45.43	293	296	12	37	10	0.69	0	4.37	0.978
21	TRW+QM+ Ash (4)	7.0	5.7	14.50	4.33	7.96	134	50	13	47	70	0.20	3.31	0.36	0.992
22	TRW+QM+ RH+Ash (0)	6.3	5.7	18.80	29.52	61.18	390	371	34	170	10	0.05	33	0.01	0.979
23	TRW+ChM+	6.0	5.8	23.38	36.35	76.01	546	472	399	434	0.50	0.69	0.99	37.4	0.980

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24	RH+Ash (2) TRW+QM+ PH+Ash (4)	6.3	7.0	23.39	35.48	75.85	487	216	14	92	41	0.76	25.7	13.5	0.968
	TRW+OM+												_		
25	RH+Ash (6)	7.0	7.3	23.38	29.96	73.65	526	366	61	11	173	5.85	0.12	0.17	0.995
26	TRW+QM+	6.8	63	23.29	40.36	81.56	464	244	3	9	15	-	0	1.28	0 993
20	RH+Ash (8)	0.0	0.0	2012)	10120	01100		2	U	-	10	2.17	0	1.20	0.770
27	RH+Ash	69	61	24 10	25 41	54 44	349	66	6	13	10	26.6	85	1 91	0 998
27	(10)	0.9	0.1	21.10	20.41	5 1.11	547	00	5	15	10	20.0	0.5	1.71	0.770

Note: TRW is the Thai rice noodle wastewater, ChM is Chicken Manure, CM is Cow Manure, QM is Quail Manure, RH is Rice husk, and (x) is amount of gram of ash supplement

5. Conclusion

The co-digestion of Thai rice noodle wastewater with rice husk and different type of manure (chicken manure, cow manure, and quail manure), with and without ash supplement by anaerobic digestion (AD) process. The digester used Thai rice noodle wastewater, chicken manure, rice husk, and 6 grams of ash supplement gave the highest methane yield. Because this co-digestion gave the balance pH (6.6-7.2) pH after the experiment did not decrease. In addition, in most cases all models traditional Gompertz-type and Monod type models fit the data well. That was used for single substrate digestion could not describe the biogas evolution curve satisfactory. In this study the co-digestion, two-substrate models were used instead and able to describe the experimental data very well.

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