

Biochemical Methane Potential of Palm Oil Mill Effluent (POME) Co-Digested with Rubber Latex Effluent (LTE): Effect of POME/LTE Ratio and Temperature

Nattawut YINGTHAVORN¹, Laddawan NOYNOO¹,
Tammathat BOONKAMNERD¹, Nirattisai RAKMAK^{1,2} and
Chairat SIRIPATANA^{1,2,*}

¹School of Engineering and Technology, Walailak University, Nakhon Si Thammarat 80160, Thailand

²Biomass and Oil-Palm Center of Excellence, Walailak University,
Nakhon Si Thammarat 80160, Thailand

(* Corresponding author's e-mail: schairat61@gmail.com)

Received: 4 March 2019, Revised: 22 October 2019, Accepted: 4 November 2019

Abstract

Single anaerobic digestion of rubber latex effluent (LTE) is known to be difficult and low yield which produces biogas containing high sulfur dioxide and ammonia. This article investigates the potential of co-digestion of palm oil mill effluent (POME) and LTE both in terms of synergistic, inhibitory effects and process stability particularly in inferring what would happen in an industrial-scale biogas plant if this type of co-digestion is to be used. The article focuses on the biochemical methane potential (BMP) of POME-LTE at different mixing ratio within the temperature range of 30 - 45 °C, the range which is used in most commercial biogas power plants in Thailand. It was found that proper co-digestion between POME and LTE provided a good opportunity to optimize the bio-methane yield because of their synergistic effect. All mixing ratios provided stable biogas production up to at least 45 days. Co-digestion of POME and LTE had a synergistic effect that when mixing 80 - 90 % of POME with 10 - 20 % of LTE, it enhanced the BMP by 25 - 35 %. It is also recommended that, in mesophilic range, 45 °C would be the best for both methane yield and high methane content in the biogas. We also have illustrated that 2-substrate models (in this case the Gompertz 2 substrate (GTS) model) is very suitable for representing and describing co-digestion data because of their inherently multiple substrate tendency. In most cases, Gompertz-type equations for single substrate did not represent the accumulated biogas/methane data adequately.

Keywords: BMP, POME: LTE ratio, Temperature, Anaerobic co-digestion, GTS modeling

Introduction

Natural rubber is a global commodity of which Thailand is the largest producer followed by Indonesia and Malaysia, respectively. In 2014, Thailand produced 4.09 million tons of natural rubber which was accounted to 32 % of total world production and valued at 5,662 million USD. Southern Thailand contributes to 69 % of total rubber plantation in the country and it is the main economic crop of the region [10]. Thus, most rubber manufacturing facilities are in Southern Thailand where rubber latex effluent is generated in large amount and require costly treatment before being released into the natural waterways. The concentrated rubber latex factories (currently over 60 factories, mainly in Southern Thailand) are notorious for air and water pollution, giving rotten egg smell and high nitrogen effluent [4].

Rubber latex effluent (LTE) is characterized by medium organic content ($10,000 < \text{COD} < 30,000$ mg/L), high nitrogen content ($500 < \text{TN} < 1,500$ mg/L), high ammonia ($300 < \text{Total NH}_3 < 1,000$ mg/L)

and high sulfate ($500 < \text{SO}_4 < 2,000 \text{ mg/L}$) [9,11]. Due to a low operating cost and high COD removal efficiency, anaerobic digestion (AD) is now widely used to treat rubber latex effluent (LTE) [9]. However, the methane yield is relatively low and cleaning the biogas for gas engine is costly due to the high sulfate concentration in LTE and high H_2S in the resulting biogas [6,7].

In concentrated rubber latex factories, sulfuric acid is added heavily to recover rubber particles in skim latex, resulting in sulfate-rich effluent which, by the work of sulfate reducing bacteria, produces H_2S , causing inhibitory effect to anaerobic microbes even at the low concentration of 0.002-003 M [3]. One way to improve the methane yield in anaerobic digestion of LTE is to substitute hydroxypropyl methylcellulose polymer (HPMC) for sulfuric acid in rubber recovery from skim latex. As illustrated by Chaiprapat *et al.* [4], HPMC substitution changed wastewater characteristics and increase the biogas yield by more than 2.5 times in batch assay as well as in continuous operation.

Co-digestion of LTE with other wastewater provides another strategy to dilute sulfate concentration as well as complement it with more balance nutrients. Kongjan *et al.* [7] studied the biochemical hydrogen and methane potential (BHP and BMP) of the co-digestion of skim latex serum (SLS: the main part of LTE) and POME at various mixing ratio under thermophilic condition ($55 \text{ }^\circ\text{C}$). They found that mixing ratio of 55 % SLS: 45 % POME gave the optimum yield which could produce hydrogen yield of $84.5 \pm 0.7 \text{ mL H}_2/\text{g-VS}_{\text{added}}$ in 1st stage and methane yield of $311.2 \pm 8 \text{ mL CH}_4/\text{g-VS}_{\text{added}}$ in the 2nd stage. Co-digestion of SLS and POME resulted in synergistic effect that potentially could improve the overall H_2 and CH_4 yields significantly. However, currently there is no practical use of this synergistic effect in an industrial scale. Furthermore, the long-term stability of this kind of continuous AD co-digestion system has not been thoroughly investigated so it is risky to come up with all positive conclusion. In fact, there was an incident occurred in 1 pair of factories in Southern Thailand where rubber latex effluent, LTE is anaerobically co-digested with POME (50 % POME: 50 % LTE) in an industrial scale biogas plant. It was found that the plant failed within 75 days of operation. The failure dynamics of the incident was not clear, but it was observed that after 60 days of co-digestion, the pH dropped sharply, and the plant started to fail irreversibly [19].

In this work, we further investigate the potential of co-digestion of POME and LTE both in terms of synergistic effect and process stability particularly to infer what would happen in an industrial-scale biogas plant if this type of co-digestion is to be materialized. Since normally commercial-scaled biogas plants in Thailand operate at mesophilic temperature ($30 - 35 \text{ }^\circ\text{C}$) and only biomethane production is economically feasible, we thus, focus on the biochemical methane potential (BMP) of POME-LTE at different mixing ratio within the temperature range of $30 - 45 \text{ }^\circ\text{C}$. We also use Gompertz 2-substrate (GTS) models as tools for data analysis as well as to create a preliminary prediction for the corresponding continuous AD operation. Synergistic effect and potential instability will be inferred based on these BMP data.

Materials and methods

Biochemical Methane Potential (BMP) tests for POME-LTE Co-digestion

The inoculum for BMP assays was collected from anaerobic sludge at the bottom of the most active anaerobic digester in a POME biogas plant in Phrasang district, Surat Thani province, Thailand, where POME was collected. The inoculum was tested for specific methanogenic activity (SMA) using the standard method for SMA assay and was found to be $0.0098 \text{ gCOD/gVSS}\cdot\text{d}$. The LTE was collected from the wastewater pond of rubber latex effluent in the concentrated rubber latex plant in Palian district, Trang province, Thailand. The inoculum was kept at $40 \text{ }^\circ\text{C}$ and the wastewater was kept at $0 - 4 \text{ }^\circ\text{C}$ until used in the experiments.

The co-digestion experiments were done at 3 different temperatures, namely: 30 ± 1 , 40 ± 1 and $45 \pm 1 \text{ }^\circ\text{C}$. The AD experiments were carried out in 300-ml serum bottles which their headspaces were flushed with nitrogen gas to remove oxygen residues. These were then covered by air-tight caps. All experiments were carried out in batch mode for 45 days in triplicates at different mixing ratios of POME: LTE (**Table 1**) and initial pH of each digester was estimated to 7.0 - 7.7. Biogas generation was measured daily by water displacement method as used by many authors [1,5,13,14]. The methane concentration in

the biogas was measured using Gas Chromatograph (GC-8A Shimadzu) for day 1 to day 13 and analyzed Soluble Chemical Oxygen Demand (SCOD), Total Chemical Oxygen Demand (TCOD), Total solids (TS), Volatile solids (VS), pH, Alkalinity (Alk), Volatile fatty acid (VFA) and Temperature were performed in accordance with standard methods of APHA [16].

Table 1 summarizes the design of the BMP experiments as well as the initial VS and COD of each batch. It should be noted that the COD: VS ratios are consistent with most of the previous work and it is a typical value for agro-industrial wastewater.

Table 1 BMP test design for POME: LTE Co-digestion.

Digester	Mixing ratio of POME : LTE	Wastewater (ml)		Inoculum (ml)	VS (mg/L)	COD (mg/L)	COD/VS
		POME	LTE				
D1	100:0	40	0		40,200	65,600	1.63
D2	90:10	36	4		32,620	57,600	1.77
D3	80:20	32	8		32,060	49,600	1.55
D4	70:30	28	12		37,360	60,800	1.63
D5	60:40	24	16		35,480	57,600	1.62
D6	50:50	20	20	160	31,800	52,800	1.66
D7	40:60	16	24		34,420	56,000	1.62
D8	30:70	12	28		34,400	56,000	1.62
D9	20:80	8	32		30,060	49,600	1.65
D10	10:90	4	36		27,680	44,800	1.61
D11	0:100	0	40		22,240	36,800	1.65

Mathematical modeling

In the Gompertz 2-substrate model, Noynoo *et al.* [12] postulated that the specific growth rate follows the following relation:

$$\mu = \mu_c e^{-\alpha_c t} + \dot{g}(t) \mu_s e^{-\alpha_s t}$$

Here $\dot{g}(t)$ is the derivative of switching function, describing how the microorganisms switch from 1 substrate type to another. The researchers developed 3 variants of the model based on how the switching function is represented:

Model I: set $g(t) = 1$,

$$P' = P'_c + P'_s = (P_{\infty c} + P'_{e0})\theta_c + (P_{\infty s} - P_{\infty c} + P'_{s0})\theta_s$$

$$\theta_c = \exp\left(-\exp\left(\left(\frac{R_{mc}}{P'_{\infty c}}\right)(\lambda_c - t) + 1\right)\right)$$

$$\theta_s = \exp\left(-\exp\left(\left(\frac{R_{ms}}{P'_{\infty s}}\right)(\lambda_s - t) + 1\right)\right)$$

where θ is fractional conversions of digestible substrates, $P' = P + P'_0$ is the total accumulative biogas generated, P'_0 is the amount of biogas produced by active biomass before the experiment starts and P is the observed biogas after the AD process starts. μ is specific growth rate of micro-organisms, P_{∞} is the final ($t \rightarrow \infty$) biogas accumulated and the switching time (τ_s), switch gain kappa (κ), lag-time (λ), R_m is

the maximum specific biogas production rates. e is a constant (2.7183). The subscripts e and s represent easily and slowly degradable substances respectively.

Model II: where switching/preference function $g(t)$ is chosen as,

$$P' = (P_{\infty} + P'_{e0})\theta_e + g(t)(P_{\infty} - P_{\infty} + P'_{s0})\theta_s$$

$$g(t) = (1/\pi)(\tan^{-1}(\kappa(t - \tau_s)) + (\pi/2))$$

Model III: which is essentially a subset of model II where we set $\lambda_s = 0$.

Noynoo *et al.* [12] proposed that typical ABE curves could be classified by 4 hypothetical types based on the distribution of easily and slowly degradable present in the wastewater (**Figure 1**).

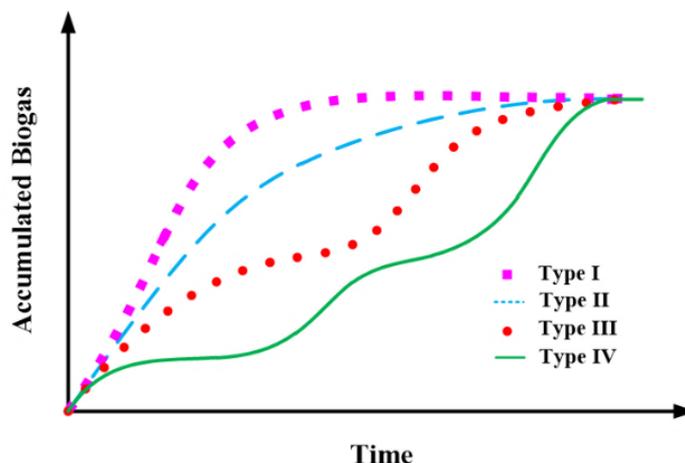


Figure 1 Types of ABE curve [12].

Type I represents ABE curves involving single substrate which is consumed of essentially single group of microorganisms. Typically, the curves can be described well by Monod kinetics or Gompertz-type equations.

Type II is for ABE curves resulted from the environment where multiple substrates were consumed in parallel or sequential by 1 or multiple groups of microorganisms. Traditional single-substrate Monod-type or Gompertz-type models cannot describe the ABE curve adequately.

Type III represents the cases where multiple substrates exist, but they can be simplified by 3 categories: readily degradable, slowly degradable substrates and intermediates.

Type IV is more complex since Type III models would not describe the ABE curve adequately.

The described Gompertz 2-substrate models were designed for type I, II and III, not for type-IV ABE curves. Fortunately, we rarely encountered Type IV curves in practice.

Results and discussion

The characteristics of wastewater/substrate were analyzed and shown in **Table 2**.

Table 2 Characteristics of POME and LTE used in the experiments.

Characteristics	POME	LTE	Inoculum
SCOD (mg/L)	28,799	5,008	-
TCOD (mg/L)	96,000	36,800	48,000
Volatile solids (mg/L)	57,440	22,440	29,820
pH	7.6	7.3	-
Alkalinity (mg/L)	6,000	2,500	-
Volatile fatty acid (mg/L)	750	750	-
Temperature (°C)	27.6	28.6	-

It was noticed that LTE used in this work had rather high volatile solid (24,460 mg/L) in comparison with those published data (10,000 - 23,000 mg/L) [11]. The fraction of SCOD for POME and LTE was 0.30 and 0.14, respectively, which implies that POME is easier for microorganisms to digest. The VFA/ALK ratio of POME and LTE were 0.125 - 0.3 which is considered as within a stable range. The ratio of COD: VS for POME, LTE and the inoculum were 1.67, 1.47 and 1.61 which is consistent with other previous works. We did not measure ammonia nitrogen and sulfate content in LTE and POME. However, many previous works confirm that while in POME ammonia nitrogen and sulfate content is moderate and does not pose significant inhibitory effects at least in short term, ammonia nitrogen and sulfate content in LTE is typically very high (in the range of 300 - 1,000 and 500 - 2,000 mg/L respectively [9,11]).

Accumulated biogas evolution (ABE) curve

The ABE curves obtained from the batch AD experiments are shown in **Figures 2 - 4** and the corresponding methane potentials are summarized in **Table 3**. The BMP results given in **Table 3** clearly show that the temperature close to 45 °C was required in order to make the potential of mixed wastewaters approached their maximum value. (Approximately 550 - 650 mL CH₄ /gVS or 440 - 470 mL CH₄/gCOD depending on the component of wastewater) [2,18]. This can be explained that when the temperature got higher from 30 to 45 °C, the mesophilic methane producing microorganisms can utilize the larger percentage of VS due to temperature effect on microbial activities in all reaction steps of anaerobic digestion.

Biogas yields and biochemical methane potentials (BMP)

The BMP results show that at 30 °C the digestibility of POME, thus also the BMP, was not different from that of LTE significantly (315 mL CH₄/gVS for POME and 334 mL CH₄/gVS for LTE). Co-digestion of POME and LTE had a synergistic effect that when mixing 80 - 90 % of POME with 10 - 20 % of LTE, it enhanced the BMP by 25 - 35 % which could be due to more nutrient balance. However, adding more LTE (> 20 % LTE) diminished the synergistic effects; thus, suppressed the enhanced feature of co-digestion. This behavior could be a result of inhibitors present in LTE which started to show up when its concentration exceeded the threshold limit.

As the temperature got higher from 30 to 45 °C, and the synergistic effects started to lose its momentum, the inhibitory effect associated with LTE could be dominated and could reduce the BMP. At 45 °C, for example, adding 10 % of LTE could enhance the BMP by 11 % (509 mL CH₄/gVS for 100 % POME and 565 mL CH₄/gVS for 90 % POME). However, further increase in % LTE resulted in the decrease of BMP performance. It seemed that the microorganisms were more susceptible to the presence of inhibitory effects as the temperature got higher while the increased of temperature can enhance the

substrate biodegradability. Thus, the best result from our experimental set (45 °C, 90 % POME: 10 % LTE) occurred when the combined effects of inhibitors, nutrient balance, and other synergistic effects were at its proportionally optimal state. **Figure 6** also illustrates the synergistic and inhibitory effects at different temperatures and mixing-ratios for this co-digestion graphically.

Table 3 BMP and biogas yield of AD co-digestion between POME and LTE at different mixing ratio and mesophilic temperatures.

Digester	POME: LTE	BMP (mL CH ₄ /gVS)			BMP (mLCH ₄ /gCOD)			Biogas yield (mLBiogas/gVS)		
		30 °C	40 °C	45 °C	30 °C	40 °C	45 °C	30 °C	40 °C	45 °C
1	100:0	315	412	509	193	253	312	626	728	964
2	90:10	422	441	565	239	250	319	788	818	1,009
3	80:20	396	426	430	256	276	278	742	788	787
4	70:30	332	350	390	204	215	240	625	654	716
5	60:40	321	373	401	198	230	247	619	694	772
6	50:50	334	390	410	201	235	247	641	752	805
7	40:60	300	347	405	185	213	249	596	688	805
8	30:70	330	309	396	203	190	244	615	614	770
9	20:80	333	340	508	202	206	308	662	721	957
10	10:90	324	352	506	200	217	312	692	772	945
11	0:100	304	360	479	184	217	290	659	789	984

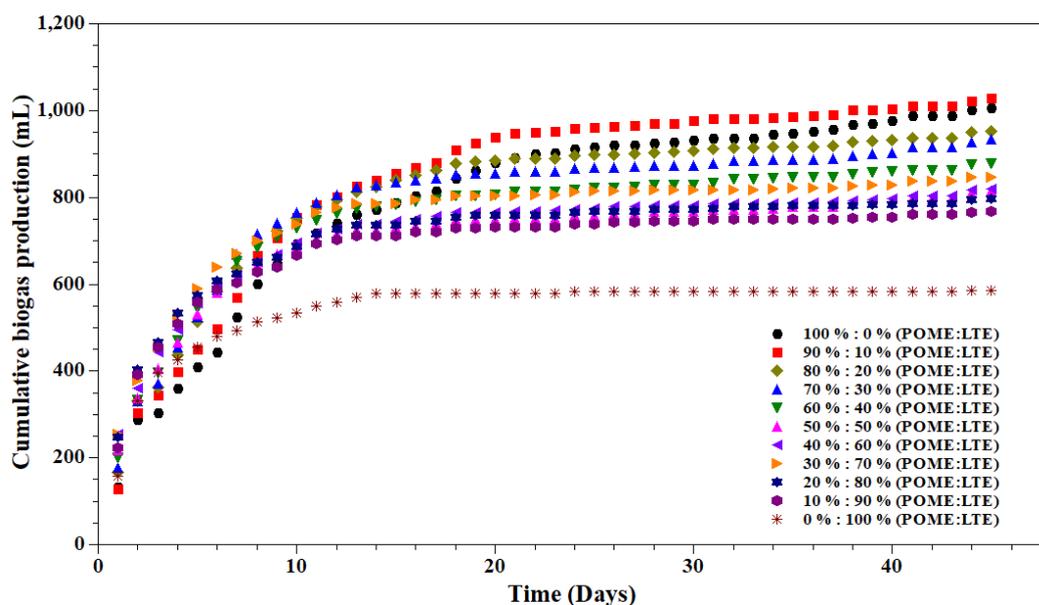


Figure 2 Cumulative biogas production from anaerobic co-digestion of inoculum with POME and LTE at 30 °C.

As summarized in **Table 3**, in the mesophilic temperature range (30 - 45 °C), higher biogas yield and BMP was associated with higher temperatures. Co-digestion results showed synergistic effect when mixing POME: LTE ratio is higher than 50 : 50 %. Thus the best POME: LTE ratio was 90 : 10 % as this gives highest biogas yield and a BMP of 1,009 and 565 mL/gVS respectively. This yield is comparable to that of Kongjan *et al.* [7] in which they found that mixing ratio of 55 % LTE: 45 % POME gave the optimum yield which could produce hydrogen yield of 84.5 ± 0.7 mL H₂/g-VS_{added} in 1st stage and methane yield of 311.2 ± 8 mL CH₄/g-VS_{added} in the 2nd stage. This is only a rough comparison because they did the experiment at different temperature (55 °C) and the substrate was not identical.

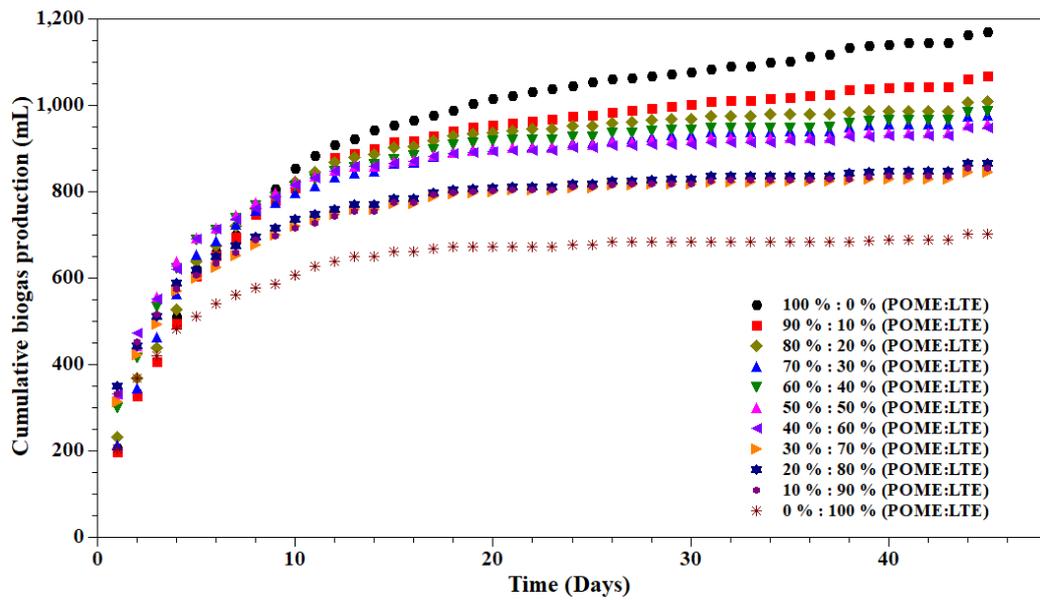


Figure 3 Cumulative biogas production from anaerobic co-digestion of inoculum with POME and LTE at 40 °C

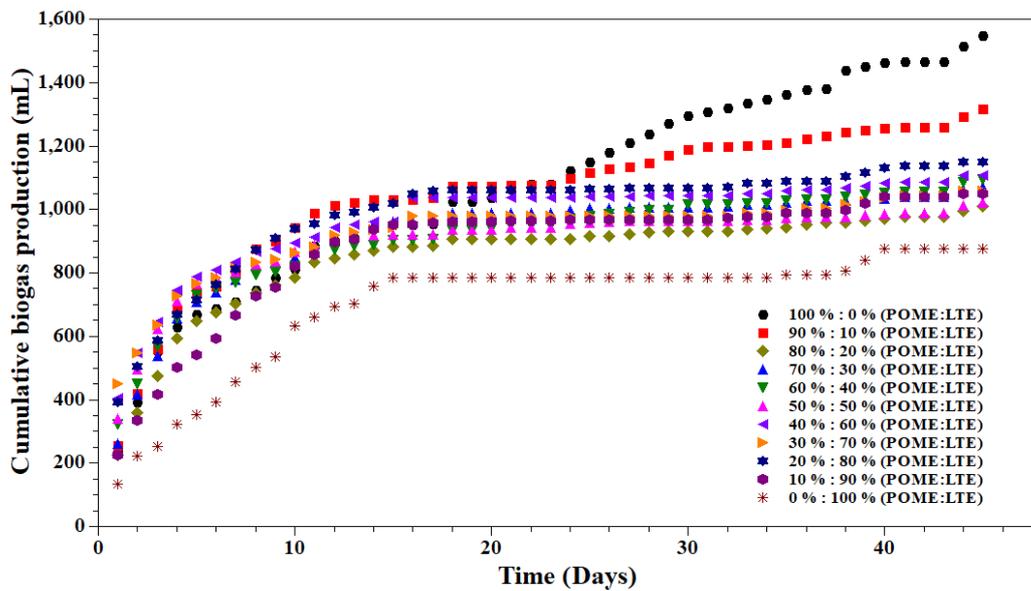


Figure 4 Cumulative biogas production from anaerobic co-digestion of inoculum with POME and LTE at 45 °C.

Methane production

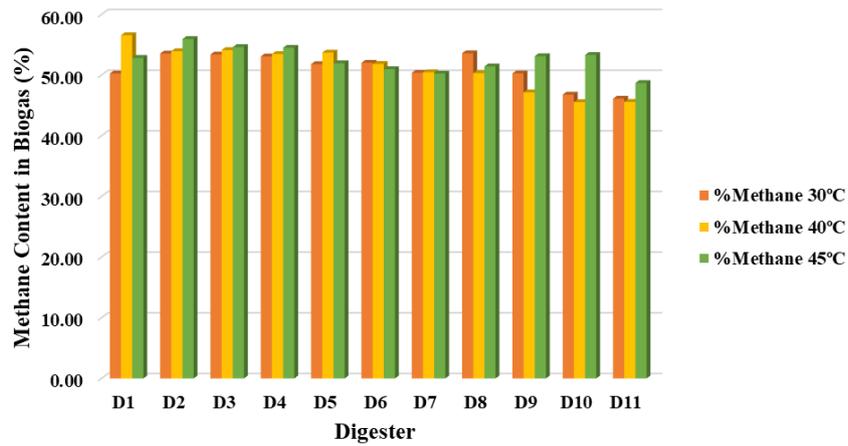


Figure 5 Methane content in biogas from anaerobic co-digestion of POME-LTE at difference mixing ratio and temperature.

The effect of temperature and % LTE

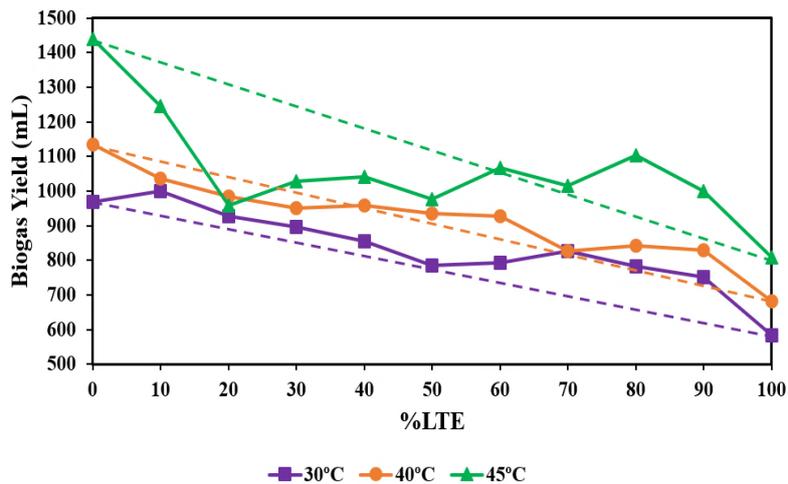


Figure 6 Cumulative biogas yield versus % LTE at all temperature. (Dashed lines are hypothetically linear trends)

On average, the best methane (53 - 55 % methane) was obtained when the synergistic effects were dominated. As shown in **Figure 5**, for the temperature range of 30 - 40 °C, the synergistic effects were optimal when LTE was less than 30 %. Except for 45 °C, higher proportion of LTE (> 30 %) reduced the percentage of methane in biogas gradually. Pure LTE gave lowest methane content for all temperature in the current experimental range (30 - 45 °C). Surprisingly, at 45 °C, there was a synergistic effect occurred when 10 - 20 % POME was co-digested with 80 - 90 % LTE. The increased of methane content (as well as BMP) was significant as it was raised above 50 % threshold (suitable for generating electricity by gas

engines). These did not happen for 30 and 40 °C. Overall, temperature of 45 °C did not give the highest methane yields and higher methane percentage.

Modeling and model fitting

In order to obtain another level of insight from this set of experimental data, we used the Gompertz approach to describe the whole set of ABE data. The preliminary conclusions are presented below:

1. While it is acceptable to use members of traditional Gompertz-type model such as Gompertz, logistic, Richards, exponential or Schnute equations to describe or represent some ABE curves obtained from our set of experiments, they did not fit well, and the error seemed systematic one. That is if one tries to fit the initial and final periods of the ABE curves, the middle period would be overestimated/predicted. Likewise, if the weight is placed on the middle period (5 - 20 days), the prediction for both initial and final periods was systematically off the model trend.

2. We tried to fit the data with a simple single-substrate Monod kinetics and the same preliminary results were similar to that of traditional Gompertz-family models.

3. Furthermore, some ABE curves exhibited 2 plateaus one at the initial-to-middle period (10 - 20 days) and another one occurred in the final period (> 25 days).

4. The observation in (1) to (3) suggested that the ABE curves should be better described by the co-existence of multiple substrates. However, to simplify the model, we proposed that 2 groups of substrates would be enough for model development for this type of co-digestion. So, the so-called “Gompertz 2-substrate (GTS) model” was developed by Noynoo *et al.* [12] and used in our analysis in this article.

The results of model fitting are depicted and summarized in **Figure 7 - 9** and **Table 4 - 6** respectively.

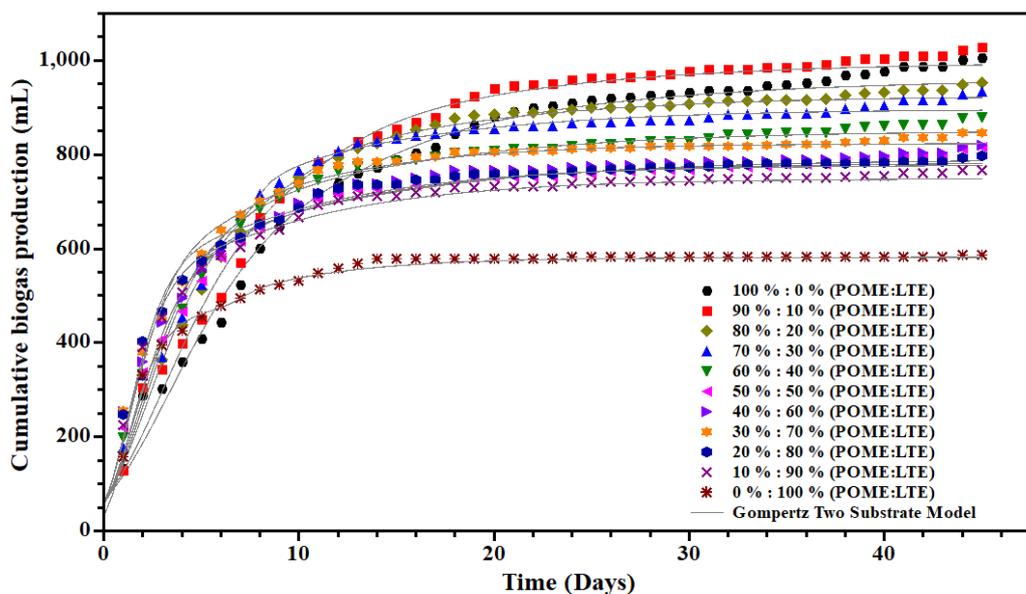


Figure 7 Cumulative biogas production of inoculum with POME: LTE at 30 °C for GTS model.

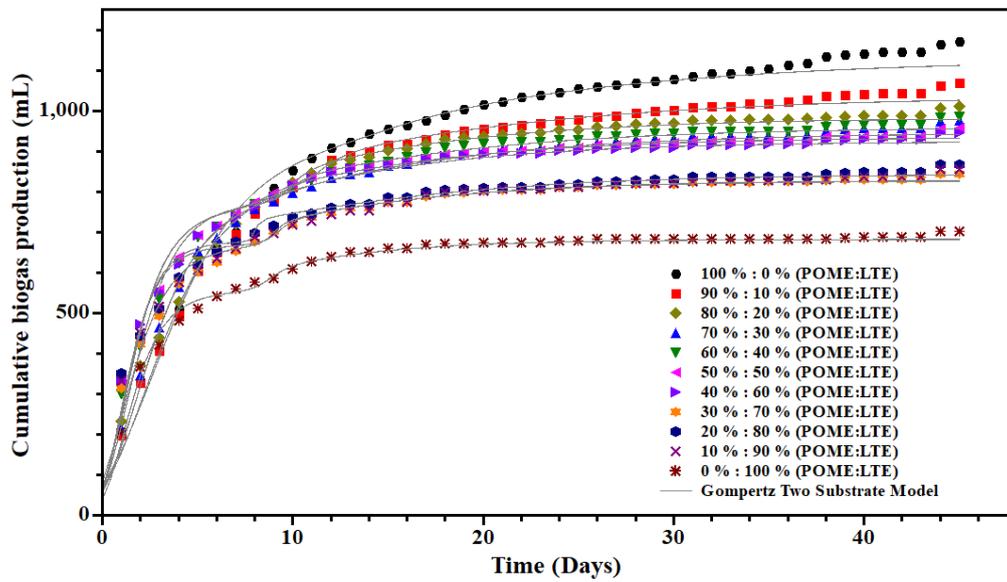


Figure 8 Cumulative biogas production of inoculum with POME: LTE at 40 °C for GTS model.

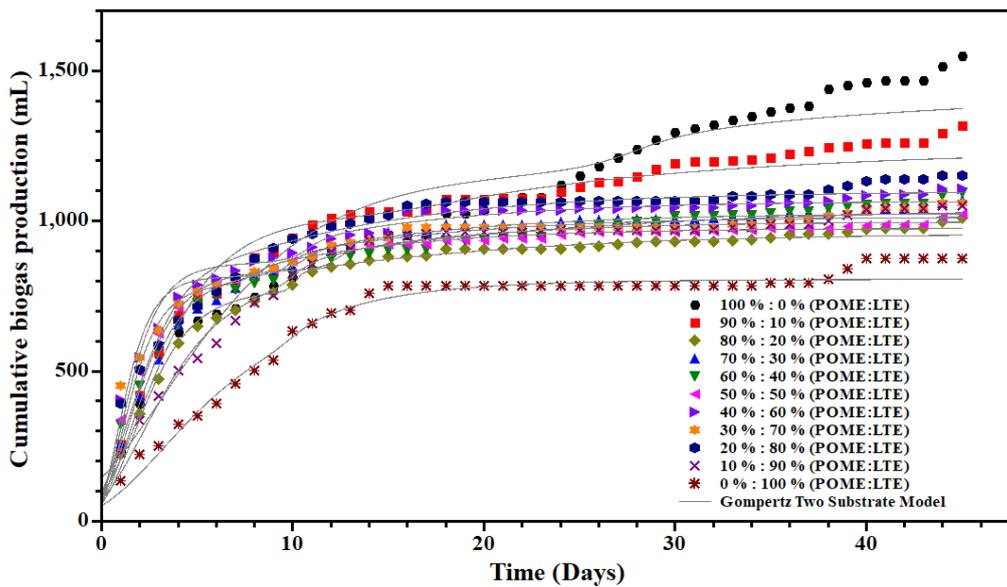


Figure 9 Cumulative biogas production of inoculum with POME: LTE at 45 °C for GTS model.

Table 4 Parameters and the best-fit parameter (R^2) of cumulative biogas production at 30 °C.

Model	Digester	Parameter								
		P_{∞}	$P_{e\infty}$	R_{ms}	R_{me}	κ	λ_e	λ_s	t_r	R^2
Gompertz 2 Substrate	D1	968.3	774.6	6.99	79.5	0.2049	-0.2831	0	14.34	0.9876
	D2	1,000.8	800.6	7.91	91.2	0.3205	-0.2219	0	11.82	0.9904
	D3	926.9	741.5	7.95	113.0	0.5461	-0.1740	0	11.02	0.9918
	D4	897.0	717.6	8.03	124.7	2.2971	-0.1126	0	7.90	0.9903
	D5	854.1	683.2	7.48	128.5	0.3269	-0.1482	0	7.76	0.9907
	D6	785.5	628.4	7.51	137.1	0.3832	-0.1651	0	7.74	0.9874
	D7	793.3	634.6	6.97	136.1	0.2793	-0.1646	0	7.59	0.9872
	D8	827.4	661.9	9.75	164.8	0.5168	-0.1462	0	7.47	0.9885
	D9	781.4	625.1	8.54	178.3	0.3218	-0.1073	0	7.77	0.9869
	D10	752.6	602.0	8.44	171.1	0.3371	-0.1244	0	7.72	0.9881
	D11	582.7	466.1	8.52	159.9	0.9307	0.0138	0	6.98	0.9943

Table 5 Parameters and the best-fit parameter (R^2) of cumulative biogas production at 40 °C.

Model	Digester	Parameter								
		P_{∞}	$P_{e\infty}$	R_{ms}	R_{me}	κ	λ_e	λ_s	t_r	R^2
Gompertz 2 Substrate	D1	1,134.2	907.3	7.09	120.1	0.2341	-0.2234	0	14.56	0.9894
	D2	1,036.7	829.3	6.94	128.5	0.9956	-0.1378	0	11.46	0.9931
	D3	983.2	786.5	8.44	149.5	1.3568	-0.1306	0	9.97	0.9923
	D4	950.3	760.2	8.12	151.9	0.2783	-0.0804	0	8.75	0.9938
	D5	959.3	767.4	7.94	197.3	1.4168	-0.1169	0	9.84	0.9895
	D6	935.6	748.4	8.50	218.4	0.8411	-0.1225	0	8.41	0.9878
	D7	927.2	741.7	9.04	218.8	0.3859	-0.1390	0	8.30	0.9842
	D8	827.4	661.9	8.15	176.5	1.8952	-0.3687	0	8.95	0.9859
	D9	843.1	674.4	7.38	232.6	7.4069	-0.1305	0	8.06	0.9788
	D10	828.6	662.8	8.13	234.4	1.5816	-0.1079	0	9.22	0.9803
	D11	683.1	546.4	8.79	176.2	1.2441	-0.0276	0	8.76	0.9924

Table 6 Parameters and the best-fit parameter (R^2) of cumulative biogas production at 45 °C.

Model	Digester	Parameter								
		P_{∞}	$P_{e\infty}$	R_{ms}	R_{me}	κ	λ_e	λ_s	t_r	R^2
Gompertz 2 Substrate	D1	1,439.0	1151.2	6.07	93.5	0.3795	-1.2185	0	27.69	0.9337
	D2	1,245.6	996.4	6.87	159.1	0.1869	-0.2480	0	17.76	0.9738
	D3	957.8	766.2	7.30	163.9	4.4465	-0.0742	0	10.12	0.9910
	D4	1,027.3	821.8	9.30	190.5	1.1851	-0.0784	0	10.51	0.9920
	D5	1,041.3	833.0	6.38	205.1	1.6889	-0.1482	0	12.22	0.9782
	D6	976.8	781.4	10.28	264.5	1.2286	-0.0403	0	7.91	0.9895
	D7	1,067.9	854.3	9.82	276.1	1.1801	-0.1143	0	10.78	0.9797
	D8	1,014.7	811.7	9.36	306.9	1.5961	-0.1178	0	9.87	0.9698
	D9	1,103.9	883.1	10.14	194.9	0.2671	-0.3210	0	9.38	0.9674
	D10	999.0	799.2	9.43	121.3	1.2475	-0.2670	0	10.01	0.9838
	D11	807.5	646.0	9.59	69.4	0.8367	-0.2470	0	9.85	0.9763

In fitting the ABE data to Gompertz 2-substrate model, we firstly evaluated the best percentage of easily degradable by non-constrained least square model fitting. We found that the best estimated fraction of easily degradable was in the range of 15 - 25 %. Thus, taking the average value 20 %, all parameter estimations in **Tables 4 - 6** were based on this assumption.

It should be noticed that the biogas production rate for easily digestible substrate (R_{me}) is about 10 - 20 times that of slowly digestible substrate (R_{ms}). The initial lag-time has a negative sign for all experiments. This indicated that, in the experimental setup, the amount of active microbial biomass was in excess and for a short period of digestion, the microbes started to be deprived of limiting substrate, causing the appearance of negative lag-time. It was also observed that kappa tended to increase as temperature got higher, indicating more preference on the easily digestible. Whereas the digestion of slowly degradable substrate was more independent on the easily degradable one. Lastly, it is obvious that as the percentage of POME decreased so did t_r , indicating later switching to the slowly (less preferable) degradable substrate.

Conclusions

Proper co-digestion between POME and LTE provided a good opportunity to optimize the biogas yield because of their synergistic effect. The mixing POME: LTE ratio of more than 0.5 showed synergistic effect for all temperatures in the experimental range (30 - 45 °C). It is also recommended that, in mesophilic range, 45 °C would be the best for both methane yield and high methane content in the biogas. We also have illustrated that 2-substrate models (in this case the GTS model) are very suitable for representing and describing co-digestion data because of their inherently multiple substrate tendency. It is recommended that, for most batch co-digestion experiments appeared in the literature, Gompertz/Logistic 2-substrate models should be used to describe the accumulated methane/biogas data instead of the traditional, single-substrate, Gompertz type models. This can be anticipated by considering the fact that one of the advantages of co-digestion is the presence of at least 2 types of substrates (which is traditionally classified as easily and slowly digestible substrates). They have different degrees of digestibility which help to release the carbon sources in such a way that the growth between acidogens and methanogens is balanced and synchronized, keeping pH and VFA/ALK at the optimal range for methane production. This will ensure high methane yield and good process stability [15].

Furthermore, as mentioned earlier, there was an incident occurred in an industrial-scale biogas plant where LTE is anaerobically co-digested with POME (50 % POME: 50 % LTE) in an industrial scale biogas plant. It was found that the plant failed within 75 days of operation. It was observed that after 60 days of co-digestion, the pH dropped sharply, and the plant started to fail irreversibly [19]. Thus, it is anticipated that the optimum/synergistic POME: LTE ratio (> 0.5) found in this work may not be applied directly to the continuous system with prolonged operation. In these cases, the accumulation of toxic substances including free ammonia and hydrogen sulfide must be suppressed to a minimum level to ensure stable operation. This problem needs further investigation.

Acknowledgements

The authors would like to thank Walailak University Fund and Biomass and Oil-Palm Excellence Center, Walailak University grant for financial support.

References

- [1] MA Abdel-Hadi. A simple apparatus for biogas quality determination. *J. Agric. Eng.* 2008; **25**, 1055-66.
- [2] S Achinas and GJ Euverink. Theoretical analysis of biogas potential prediction from agricultural waste. *Resource Efficient Technol.* 2016; **2**, 143-7.
- [3] D Batstone, J Keller, I Angelidaki, S Kalyuzhnyi, S Pavlostathis, A Rozzi and V Vavilin. Anaerobic digestion model No 1 (ADM1). *Water Sci. Technol.* 2002; **45**, 65-73.

- [4] S Chaiprapat, S Wongchana, S Loykulnant, C Kongkaew and B Charnnok. Evaluating sulfuric acid reduction, substitution, and recovery to improve environmental performance and biogas productivity in rubber latex industry. *Process Saf. Environ. Prot.* 2014; **94**, 420-9.
- [5] S Dechruga, D Kantachote and S Chaiprapat. Effects of inoculum to substrate ratio, substrate mix ratio and inoculum source on batch co-digestion of grass and pig manure. *Bioresour. Technol.* 2013; **146**, 101-8.
- [6] R Jariyaboon, S O-Thong and P Kongjan. Bio-hydrogen and bio-methane potentials of skim latex serum in batch thermophilic 2-stage anaerobic digestion. *Bioresour. Technol.* 2015; **198**, 198-206.
- [7] P Kongjan, R Jariyaboon and S O-Thong. Anaerobic digestion of skim latex serum (SLS) for hydrogen and methane production using a 2-stage process in a series of up-flow anaerobic sludgeblanket (UASB) reactor. *Int. J. Hydrog. Energ.* 2014; **39**, 19343-8.
- [8] P Kongjan, K Sama, K Sani, R Jariyaboon and A Reungsang. Feasibility of bio-hythane production by co-digesting skim latex serum (SLS) with palm oil mill effluent (POME) through 2-phase anaerobic process. *Int. J. Hydrog. Energ.* 2018; **43**, 9577-90.
- [9] M Mohammadi, HC Man, M Hassan and P Yee. Treatment of wastewater from rubber industry in Malaysia. *Afr. J. Biotechnol.* 2010; **9**, 6233-43.
- [10] C Musikavong and S Gheewala. Assessing ecological footprints of products from the rubber industry and palm oil mills in Thailand. *J. Clean. Prod.* 2016; **142**, 1148-57.
- [11] H Nguyen and T Luong. Situation of wastewater treatment of natural rubber latex processing in the Southeastern region. *J. Viet. Environ.* 2012; **2**, 58-64.
- [12] L Noynoo, S Jijai, K Phayungphan, N Rakmak and C Siripatana. *Gompertz-Type 2-Substrate Models for Batch Anaerobic Co-Digestion*. Lecture Notes in Applied Mathematics and Applied Science in Engineering. Malaysia Technical Scientist Association, Malaysia, 2019, p. 21-30.
- [13] WF Owen, D Stuckey, JB Healy, L Young and PL McCarty. Bioassay for monitoring biochemical methane potential and anaerobic toxicity. *J. Water Res.* 1978; **13**, 485-92.
- [14] J Patil, M Lourdu, A Raj, S Vinaykumar, H Manjunath and A Srinidhi. Biomethanation of water hyacinth, poultry litter, cow manure and primary sludge: A comparative analysis. *Res. J. Chem. Sci.* 2011; **1**, 22-6.
- [15] T Rachadaporn, H Thongpan, N Rakmak and C Siripatana. Modeling of anaerobic co-digestion of pig manure and domestic organic waste. *J. Teknol.* 2016; **78**, 117-24.
- [16] E Rice and A Association. *Standard Method for the Examination of Water and Wastewater*. In: RH Strauss (Ed.). American Public Health Association. 23rd ed. Washington DC, 2017.
- [17] C Siripatana, S Jijai and P Kongjan. Analysis and extension of Gompertz-type and monod-type equations for estimation of design parameters from batch anaerobic digestion experiments. *AIP Conf. Proc.* 2016; **1775**, 030079.
- [18] J Triolo, SG Sommer, H Møller, M Weisbjerg and X Jiang. A new algorithm to characterize biodegradability of biomass during anaerobic digestion: Influence of lignin concentration on methane production potential. *Bioresour. Technol.* 2011; **102**, 9395-402.
- [19] N Yingthavorn, N Rakmak, P Kongjan and C Siripatana. Mathematical modeling of existing 2-stage anaerobic digestion process for palm oil mill wastewater. *J. Teknol.* 2016; **78**, 21-6.