



The effect of POME ultrasonication pretreatment on biogas production and reduction of greenhouse gases emissions from wastewater treatment units of palm oil mills

Thunwadee Tachapattaworakul Suksaroj^a, Sutisa Yaeed^b, Chaisri Suksaroj^{c,*}

^aASEAN Institute for Health Development, Mahidol University, Salaya, Phutthamonthon, Nakhon Pathom 73170, Thailand, Tel. +(66) 2449040-3, Ext. 33; email: thunwadee.suk@mahidol.edu (T.T. Suksaroj)

^bFaculty of Science and Technology, Hatyai University, Hatyai, Songkhla 90110, Thailand, Tel. +(66) 74200300, Ext. 326; email: sutisa@hu.ac.th (S. Yaeed)

^cDepartment of Irrigation Engineering, Faculty of Engineering at Kamphaeng Saen, Kasetsart University, Kamphaeng Saen Campus, 73140, Thailand, Tel. +(66) 34351897; email: fengcss@ku.ac.th (C. Suksaroj)

Received 13 January 2019; Accepted 21 May 2020

ABSTRACT

Palm oil mill effluent (POME) contains a high concentration of organic matter that could be produced useful biogas. Ultrasonication is a promising alternative method of POME pre-treatment with the potential to enhance biogas production from wastewater treatment systems at palm oil mills. Ultrasonication with an input power of 0.27–0.44 W mL⁻¹ for 90 min, in the batch experiment, increased oil separation efficiency by 29.0% compared with natural sedimentation. The soluble chemical oxygen demand/total chemical oxygen demand (SCOD/TCOD) ratio and reducing sugar concentration were increased under this optimal ultrasonication condition, indicating that the pre-treated POME was improved biodegradability. The pre-treated POME was fermented in a semi-continuous stirred treatment tank to determine biogas production efficiency. The ultrasonication pre-treated POME increased biogas production and also increased the proportion of methane from 40% to 63% and methane yield from 103.47 to 139.59 mL CH₄ g⁻¹ COD_{removal} compared to the control condition. The highest methane yield was obtained at a hydraulic retention time (HRT) of 16 d. However, longer HRT yielded slightly higher COD removal efficiencies. When the biogas produced is used for onsite electricity generation therefore, it is possible to diminish the electricity costs incurred to perform the ultrasonication setup and reduce greenhouse gases (GHGs) emissions to the environment. The overall GHGs emissions reduction from palm oil mill could reach up to 11% or 913.23 ton CO₂eq y⁻¹ when the optimal ultrasonication scenario from this study applied to wastewater treatment system.

Keywords: Palm oil mill effluent; Ultrasonication; Biogas; Pre-treatment; Greenhouse gases reduction

1. Introduction

Palm oil mill effluent (POME) is the wastewater generated from palm oil processing. POME is acidic and contains residual oil that is not easily separated using conventional gravity-based systems. In addition, due to its characteristics

which are dark brownish colored, high discharged temperature, high solid contents, etc., the effective treatment to treat this kind of wastewater is still a challenge. The oily mixed wastewater requires sufficient oxygen for decomposition when it has a high biochemical oxygen demand (BOD₅). Raw

* Corresponding author.

POME can have a BOD_5 up to 100 times higher than that of domestic sewage, even after treatment, a significant amount of organic matter and color remains, and still cause environmental impact if it was directly discharged. Therefore, the uses of biotechnological advances and advanced POME treatment technology to sustainably reuse and recover POME has redefined and POME from a waste to a valuable resource [1].

POME has been converted to energy through an anaerobic digestion process that produces biogas. Today, most palm oil mill factories in Thailand manage their wastewater by converting the biomass in POME to energy through a biogas system and the produced biogas is used as fuel in the production process, such as to produce steam boiler or to generate electricity. The biogas produced from anaerobic digestion of POME consists of about 65% methane, 35% carbon dioxide (CO_2), and a trace of hydrogen sulfide (H_2S). Based on a study on clean development mechanism (CDM), Ahmad et al. [2] reported that there is potential in the waste sectors to produce energy and the greatest potential exists where anaerobic degradation takes place within municipal landfills and POME ponds.

According to our previous study [3], ultrasonication has the highest efficiency for POME biodegradability improvement when compared to coalescer filtration and dissolved air flotation (DAF) processes at the batch-experimental laboratory scale. The ultrasonication process can enhance the removal efficiencies of organic impurities in POME and increase the proportion of methane produced as a result of higher microbial activity [3].

Ultrasonication uses the mechanical energy of sound waves to change the physical conditions of organic substances and facilitate better degradation [4]. The use of ultrasonication has resulted in enhanced biogas production, oil separation, and retention time reduction before sending the wastewater to the biogas system. The ultrasonication process requires electricity for operation, however, most of palm oil mills in Thailand have installed gas-engine power plants. Thus, the electricity cost will be minimal and the existing infrastructure can support this type of pre-treatment process.

The greatest portion of greenhouse gases (GHGs) emitted from palm oil mills was estimated that it was originated from POME treatment systems. The 1,000 kg of crude palm oil (CPO) can generate more than 1,000 kg CO_2 equivalent (CO_2eq), however, 20% of this volume can be reduced by the installation of biogas capturing equipment [5]. POME was normally contained discharged high temperature ($>60^\circ C$), to reduce its temperature and separate grease and oil (1%–2%) and suspended solids (2%–5%) in POME, cooling ponds were normally used as a pre-treatment before introducing POME to biogas systems. The thermophile phase, high temperature, can reduce methane production and COD removal ratio [6]. These pre-treatment ponds series can emit methane up to 200 kg CO_2eq per 1,000 kg of CPO [7]. Kaewmai et al. [8] estimated that 1,000 kg of fresh fruit bunches (FFB) processed could generate 670 kg of POME and each tonne of POME is able to produce 28 m^3 of methane. In palm oil mill, most GHGs emitted from the open ponds used before the biogas system and from the stabilization ponds used after the biogas system [7]. The overall hydraulic detention times in the

systems are proportional to the size and number of ponds which directly reflected GHGs emission from wastewater.

POME contains complex organics and phenolic compounds making difficult biodegradation and some researches have reported that POME treated by biogas systems or stabilization ponds still retained high organic content [9–11]. Therefore, many works continue to investigate alternative POME pre-treatment methods in order to enhance biogas production efficiency, reduce the color in treated POME, and to minimize emissions of GHGs by biogas capture. Many pre-treatment processes reported include physical, chemical, and biological processes and some characteristics of treated POME were improved after these processes [12–17].

The objective of this paper, therefore, is to evaluate the effect of ultrasonication on biogas production in a semi-continuous stirred tank reactor (CSTR). The current work is an up-scale from our previous study [3]. The changes in POME characteristics after ultrasonication were described. The consequence in terms of GHGs emitted reduction, was also determined based on the scenario designed from results obtained. This paper provided new knowledge for possible alternative technology for palm oil mill that is challenged with high polluted wastewater and how to maximize sustainable management under their own power generation capacity.

2. Materials and methods

2.1. POME collection and characterization

POME was collected from a cooling pond of an industrial palm oil wastewater treatment plant in Trang Province, Thailand, and preserved in the laboratory at $4^\circ C$ until use. The parameters analysis including soluble chemical oxygen demand (SCOD), total chemical oxygen demand (TCOD), 5 d biological oxygen demand (BOD_5), total solids (TS), volatile solids (VS), and fat, oil, and grease (FOG) was done in according to the procedures of the Standard Methods [18]. The characteristics of the POME used are presented in Table 1.

2.2. Ultrasonication process optimization for POME pre-treatment in a batch experiment

The effect of ultrasonication power on POME treatment and biogas production was investigated in this study. An ultrasonic processor (Cole Parmer ultrasonic processor VC750, USA) was used in the experiments. Samples of POME after undergoing natural sedimentation in order to remove oil and grease on the surface, which is similar to a conventional operation in palm oil mill, were used in ultrasonication experiments. One liter of POME sample was sonicated at a specific power input and ultrasonication time using a 2.2 cm probe submerged in 2 cm of depth below the wastewater surface. The optimized sedimentation time (30, 60, 90, 120, 180, and 300 min) was studied. After sedimentation at 120 min which was an optimal condition, 250 mL POME samples were sonicated at powers varying in the range of 67.5, 77.5, 110 W with different ultrasonication times (amplitude 20%–90%, power density 0.27, 0.31, and 0.44 $W mL^{-1}$ (maximal capacity of the instrument), and

Table 1
Effect of ultrasonication on the POME characteristics

Parameter	POME***	POME**	Ultrasonication for 90 min		
		(SE)	0.27*	0.31*	0.44*
pH	4.85–5.6	5.43 ± 0.50	5.10 ± 0.50	5.12 ± 0.50	5.03 ± 0.50
TS (g L ⁻¹)	70.14 ± 0.30	42.01 ± 0.10	41.65 ± 0.10	41.66 ± 0.10	41.06 ± 0.10
VS (g L ⁻¹)	49.10 ± 0.20	29.31 ± 0.10	28.95 ± 0.10	28.78 ± 0.10	28.98 ± 0.10
SS (g L ⁻¹)	21.74 ± 0.10	12.78 ± 0.10	11.67 ± 0.10	11.1 ± 0.10	10.18 ± 0.10
VSS (g L ⁻¹)	15.22 ± 0.10	8.97 ± 0.10	7.21 ± 0.10	7.20 ± 0.10	7.10 ± 0.10
Oil and grease (g L ⁻¹)	10.16 ± 0.50	8.27 ± 0.50	7.05 ± 0.05	6.55 ± 0.05	5.01 ± 0.05
TCOD (g L ⁻¹)	98.52 ± 1.20	88.08 ± 1.20	88.06 ± 0.20	85.64 ± 0.20	86.64 ± 0.20
SCOD (g L ⁻¹)	19.53 ± 0.20	21.42 ± 0.20	21.43 ± 0.20	21.44 ± 0.20	21.45 ± 0.20
BOD ₅ (g L ⁻¹)	52.48 ± 1.20	49.02 ± 1.20	49.80 ± 0.20	49.94 ± 0.20	50.102 ± 0.20
Reducing sugar (g L ⁻¹)	4.36 ± 0.02	4.30 ± 0.02	5.00 ± 0.02	6.95 ± 0.02	8.12 ± 0.02

*Power input is in W mL⁻¹; **POME (SE) is POME after 2 h sedimentation; ***characteristics from our previous study [3]. SS, suspended solids; VSS, volatile suspended solids.

ultrasonication time 30, 60, and 90 min.). After ultrasonication, each sample was tested its SCOD, BOD₅, and reducing sugar concentration to identify the optimal ultrasonication conditions.

2.3. Biogas production by semi-continuous stirred tank reactor

A semi-continuous CSTR with 2.0 L of working volume was used (Fig. 1). The experiments were carried out in separated reactors operated as semi-continuous CSTR. The substrates performed included POME left for sedimentation at 120 min (SE) and POME pre-treated with SE plus sonication (SE+US). The one reactor was used for one duration of the reactor or one hydraulic retention time (HRT) time. An organic loading rate of 2 g VS_{substrate} g⁻¹ VS_{seed} was used for start-up and reactions were performed at 35°C ± 1°C with a temperature-controlled bath. The effect of retention time was studied with the semi-continuous feeding in and out at 8, 16, and 32 d of HRT with an organic loading rate of 0.68, 1.34, 2.68 g SCOD L⁻¹ d⁻¹. The ratio of substrate to inoculum used was 2:1 by VS as recommended in BMP tests [3]. The constant effluent volume was collected and a similar volume of new wastewater was fed every 24 h for each HRT experiment. The effluent biogas volume, percentage of methane, COD were measured daily.

2.4. Analytical methods

The dinitrosalicylic acid method (DNS) with a UV-visible spectrophotometer was used to analyze reducing sugar. The reducing sugar was detected after boiling the aqueous solution with a mixed basic solution and 3,5-dinitrosalicylic acid. The concentration of reducing sugar was obtained by comparing to a standard curve of reducing sugar at 520 nm.

Methane concentration in the biogas was measured using a gas chromatograph equipped with a thermal conductivity detector and helium serving as the carrier gas. The injector, detector, and oven temperature were 150°C, 200°C, and 120°C, respectively.

Fourier transform infrared spectroscopy (FTIR) was used to analyze the functional group of molecules in the samples with a spectrometer (EQUINOX 55, BRUKER, USA) equipped with a KBr beam splitter and a deuterated triglycine sulfate detector. This technique was used to monitor the change of molecules in the samples after treatment process. Spectra were recorded from 500 to 4,000 cm⁻¹ at a resolution of 4 cm⁻¹. A zero-filling factor was applied to give a final resolution of one point per wavenumber.

2.5. Determination of greenhouse gases emission

The impact of the ultrasonication process on POME in terms of GHGs emission was reported as a percentage of overall emission reduction. Although palm oil mills can produce electricity themselves, the ultrasonication process requires high energy input. Therefore, the impact of its application should be evaluated. The impact was determined in terms of GHGs reductions. Existing GHGs emission calculation methodologies based on the Intergovernmental Panel on Climate Change [19], Thailand Greenhouse Gas Management Organization (Public Organization) (TGO) [20], and those developed by Kaewmai et al. [8] were used. Primary and secondary data were used to calculate GHGs emission in terms of CO₂eq. The treatment system scenario used to calculation was set as no discharging treated water (as occurring in the real situation by effluent quality control in Thailand), no sludge treatment, and no biomass treatment. The COD of wastewater samples were determined to calculate GHGs emissions according to the methodologies mentioned above. The average GHGs emission was calculated based on the annual CPO production.

3. Results and discussion

3.1. Effect of ultrasonication power and duration on POME in batch experiments

The results of experiments with a variation of ultrasonication duration ($P = 0.06\text{--}0.44$ W mL⁻¹ and $t = 0\text{--}180$ min)

showed that the concentrations of reducing sugar, BOD₅, and COD slightly increased after the first 30 min of operation (Fig. 2). However, it was almost twice the time for the reducing sugar when compared with the initial value (from 4.30 to 7.90 g L⁻¹ at an input power of 0.44 W mL⁻¹ and ultrasonication time of 30 min). These were caused by the bond destruction of lignocellulose and the release of sugar monomer molecules [21].

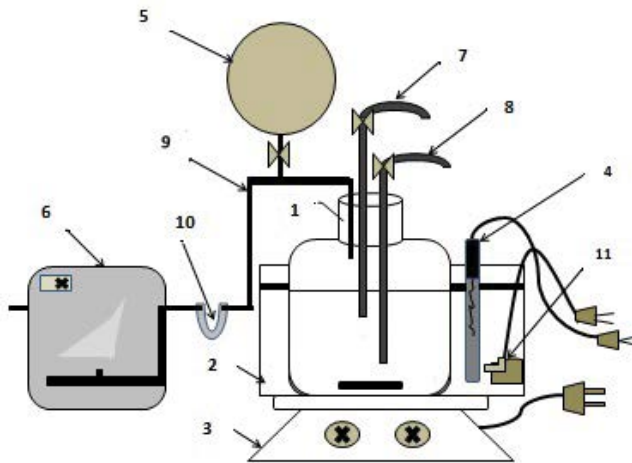


Fig. 1. Semi-continuous stirred digester. The labels are: (1) 2.5 L reactor, (2) water bath, (3) stirrer, (4) heater (35°C), (5) gas collection balloon, (6) gas counter, (7) feed port, (8) sampling port, (9) gas port, (10) septum and U-tube, and (11) submerge pump.

If the effect of different power input was considered, for example at the longest process duration, 90 min, the different power input did not alter pH, TS, VS, VSS, or TCOD as shown in Table 1. However, the increased power input, 0.27, 0.31, and 0.44 W mL⁻¹, can enhance oil separation to 14.75%, 20.80%, and 39.42%, respectively, yielded lower oil and grease content (Fig. 3). The preliminary experiments indicated that the natural sedimentation time required 120 min as the maximum oil and grease removal efficiency but was still lower than 20%. The longer sedimentation time than this point had no effect on oil and grease removal from POME (Fig. 4a). It was caused by POME characteristics that contained small oil droplets, 0.01–0.1 mm (Fig. 4b), which were rather stable and were very difficult to separate by natural sedimentation. Therefore, the application of ultrasonication was not only beneficial to oil and grease removal efficiency but it could reduce the operation time of oil and grease trap units that may affect its number and size reduction.

Oil and grease can be used as a substrate for microorganisms' activity in biogas systems. However, during the degradation of oil and grease, the by-products such as fatty acids can be increased, then inhibit methane production [22,23]. Normally, oil and grease in POME are found in concentrations greater than 10 g L⁻¹ (10.2 ± 0.5 g L⁻¹ in this study). Concentrations of oil and grease over 10 g L⁻¹ may reduce the efficiency of anaerobic digestion systems [24]. Treatment with ultrasonication can reduce the concentration of oil and grease and TCOD of raw POME, which were originally inappropriate ranges for the anaerobic digestion (<5.1 g L⁻¹ and 50–80 g L⁻¹, respectively). Furthermore, it may be an

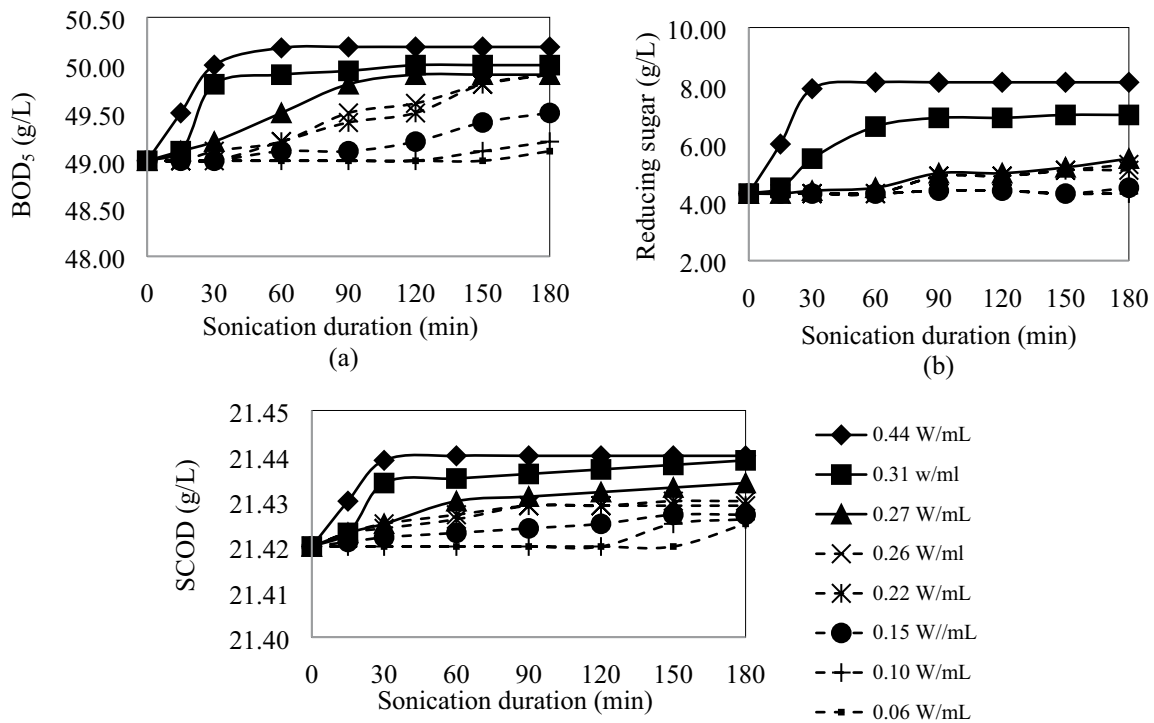


Fig. 2. (a) BOD₅, (b) reducing sugar concentrations, and (c) COD in POME samples after natural sedimentation (SE), plus with ultrasonication for different time and power input.

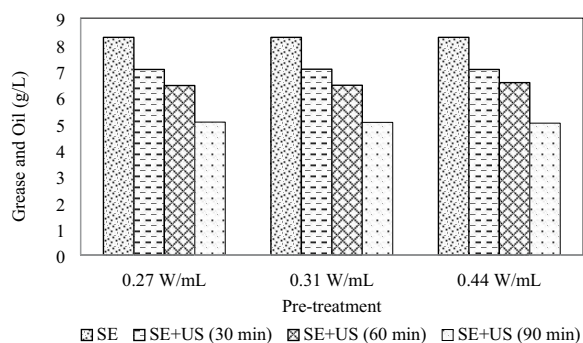


Fig. 3. Oil and grease content in POME treated with ultrasonication after sedimentation.

additional benefit from separated oil since it could be sold as a low-grade CPO or returned to the purification process.

The $BOD_5/TCOD$ ratio of POME, which was used as a biodegradability indicator, were also increased (Table 1) after ultrasonication (from 0.53 of raw POME to 0.56 of SE and then 0.60 when treated by SE+ultrasonication). For biodegradable organics, this ratio should be in the range of 0.3–0.6, and if it is beyond this point then the substrate is easily degraded by biological mechanisms [25–27]. The soluble organic to a total organic ratio (SCOD/TCOD) also increased after ultrasonication and was related to the increased concentration of reducing sugar. It may state that the organic substance was more soluble or less complex which would affect the substrate digestibility in the biogas system.

According to the assumption for the molecule changing after ultrasonication, the FTIR technique was used to analyze the species of the organic molecule. The functional groups found in POME sonicated at 0.44 W mL^{-1} were those identified in samples of lignin, polysaccharides, plant proteins, and hemicellulose which could be the cause of the often-observed colored water [28,29]. Functional groups detected were O–H, C=O, C–H, and C–O (Fig. 5), which correspond to the wavenumbers of 3,410; 1,615; 1,419; and 1,114 which confirm the presence of organics such as carbohydrates, hemicellulose, oil, and protein. The functional

group O–H represents glucose, galactose, and ribose, while C–O and O–H can both represent fructose. The peak change at position $1,000\text{--}2,000 \text{ cm}^{-1}$ (C–O stretch) [30] could be a broken bond of lignin, hemicellulose, and oil that yielded the increased reducing sugar concentration. Therefore, ultrasonication can enhance oil separation efficiency and improved the biodegradability of POME. Meanwhile, the volume of POME storage pond prior to the biogas system should decrease in response to the decreasing of sedimentation time.

Base on all results from batch experiments, 0.44 W mL^{-1} for 30 min was the optimal condition to be used for POME pre-treatment operating in the next experiments with semi-CSTR.

3.2. Semi-CSTR of POME after ultrasonication

The variation of HRT was investigated in this part. The study of methane yields obtained from different HRT experiments revealed that the increase in HRT could benefit the methane yield. The highest methane yield was obtained at 16 d of HRT for reactor fed with pre-treated POME with 0.44 W mL^{-1} (Fig. 6), $139.59 \text{ mL CH}_4 \text{ g}^{-1} \text{ COD}_{\text{removal}}$. Ultrasonication could improve both the efficiency of biogas systems and the quality of biogas produced in terms of the total proportion of methane (40%–63%). This could impact to an application for an electrical generator gas engine that was normally installed in palm oil mill factory and it was then possible to increase the income of the proprietor by using and selling electricity.

Ultrasonication increased the removal efficiencies of BOD_5 and SCOD from 52.0% to 82.20% and 63.85% to 90.50% for non-treated and pre-treated POME at 0.44 W mL^{-1} of ultrasonication, respectively. The removal efficiencies of other organic substances that are difficult to digest, such as phenols and lignin, also increased, hence the ultrasonication also contributed to a reduction of POME color (Fig. 7).

Even though the methane yield obtained from the experiments was rather low, $154 \text{ mL CH}_4 \text{ g}^{-1} \text{ COD}$ removal, when compared with theoretical yield. However, the methane yield from POME can vary in a certain range, 150–300 $\text{mL CH}_4 \text{ g}^{-1} \text{ COD}$ removal [7], which may affect from their

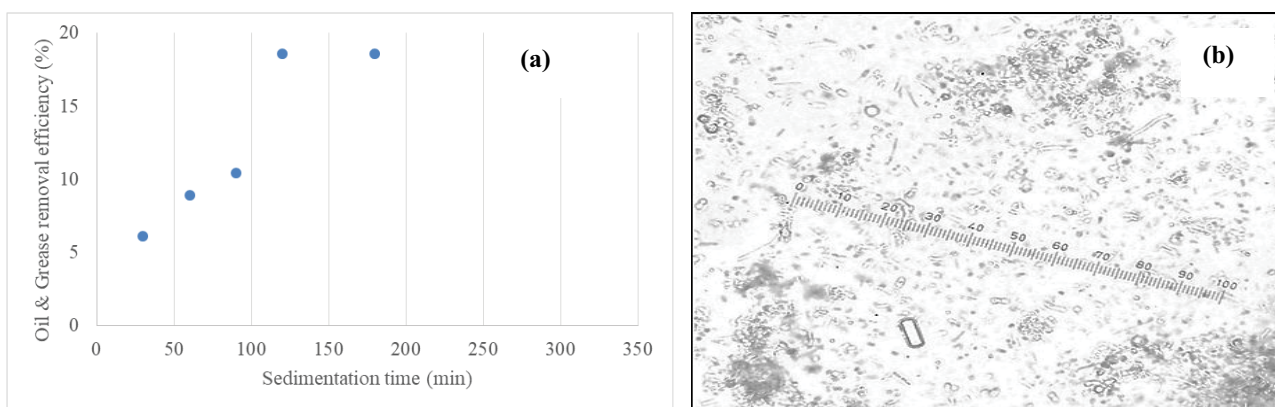


Fig. 4. (a) Oil and grease removal efficiency by natural sedimentation and (b) oil droplets suspended in POME after natural sedimentation for 120 min (scale is in millimeter) viewed under the microscope.

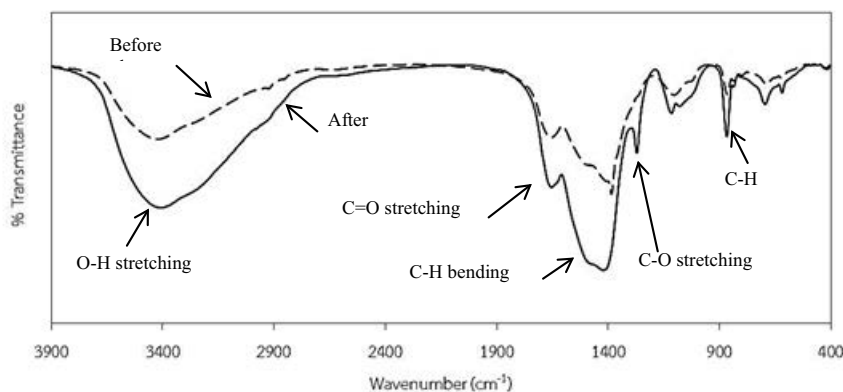


Fig. 5. Fourier transform infrared spectroscopy (FTIR) of POME before (dashed line) and after (solid line) ultrasonication at 0.44 W mL^{-1} for 90 min.

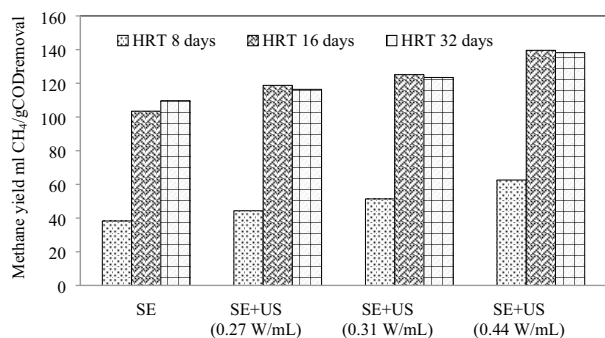


Fig. 6. Methane yield from POME with sedimentation (SE) and with SE plus ultrasonication pre-treatment (SE+US) operated in semi-CSTR with different HRT and ultrasonic power applied.

different characteristics due to the complex substances and low biodegradability ($\text{BOD}/\text{COD} < 0.6$).

3.3. Condition and impact of ultrasonication application in a POME biogas system

Open ponds are normally used to reduce POME temperature and homogenize its characteristics prior to feeding into a biogas system. The number and hydraulic retention time of these ponds vary from one pond to many and 1 d to a week, respectively [5,6]. This system is widely used because its operation cost is low. However, it requires a large area for ponds construction and is also the source of GHGs emissions that contribute to global warming.

The GHGs emissions from CPO production comes from many steps in the palm oil life cycle, for example, oil palm plantation, transportation of FFB to a factory, and from wastewater treatment ponds at palm oil mill [8]. However, the plantation and wastewater treatment sectors were reported as the major sources of GHGs emissions [8,31]. This paper attempts to discuss GHGs emissions from the wastewater treatment system in the palm oil mill based on the COD of wastewater and treatment method reported from previous work by our research team [5]. Previous work demonstrated that the cause of GHGs emissions from palm

oil mill was primarily from the POME treatment process, the ponds system where the overall hydraulic retention time can be varied from 12 to 90 d. These ponds can release the direct and fugitive GHGs into the ambient air. However, when the biogas system is installed, these gases contained in the biogas were captured to be used as a fuel to generate electricity. Even though a biogas recovery system could reduce GHGs emissions up to 77%, palm oil mills still emit significant amounts of GHGs into the atmosphere ($>1,000 \text{ kg CO}_2\text{eq } 1,000 \text{ kg}^{-1}$ of CPO) [5,8]. Therefore, the investigation options for mitigating this situation is needed. To maintain high efficiency in covered ponds or biogas production systems, the high concentration of oil and grease in raw POME must be reduced prior to feeding into a biogas system. Hence an oil trap unit is also installed to remove oil and grease. However, the long hydraulic retention time would also result in a higher volume or number of oil trap unit. The aim of this section, therefore, is to provide suggestions for reducing oil trap tank volume, or the number of units, and to evaluate GHGs emissions from POME wastewater treatment. The annual averaged value of CPO, wastewater volume, and COD of POME characteristics obtained from a case study factory with a capacity of $45,000 \text{ kgCPO h}^{-1}$ were presented in Table 2 and used to calculate annual GHGs emission with or without ultrasonication pre-treatment.

Natural sedimentation took a long time to separate oil and exhibited difficulty separating small oil droplets from POME. Application of ultrasonication to pre-treat POME could enhance oil separation in a shorter time. The effect of the ultrasonication application is not the only reduction in HRT for the oil separation and volume of oil trap unit but it increased the oil reduction efficiency and biogas production. GHGs emissions after treated by the biogas system, hence, should decrease because remained COD concentration was decreased. If natural sedimentation is operated, retention time has to be up to 120 min or more but can remove less than 20% of the oil (Fig. 3a). According to the excess concentration of oil and grease (more than 8 g L^{-1}) in raw POME, therefore it affects the biogas system [24] and results need more oil trap units to increase the efficiency of oil and grease reduction. Ultrasonication could increase oil and grease recovery and yielded lower oil and grease content in POME than a critical point since the first 30 min of sonication time

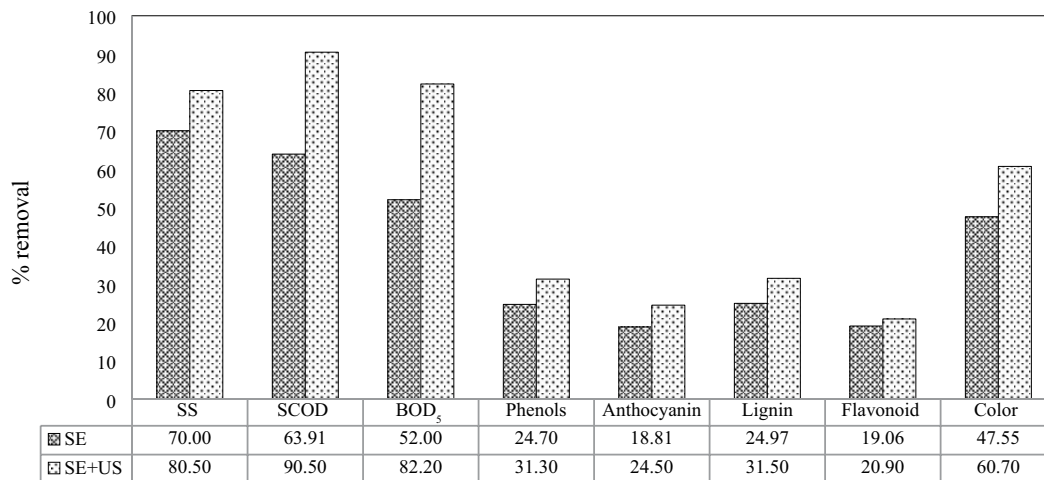


Fig. 7. Organics and color removal efficiencies of semi-continuous CSTR experiment with (SE+US) and without ultrasonication pre-treated POME (SE) at 30 min of duration, 0.44 W mL^{-1} of power input and 16 d of HRT.

but the removal efficiency can reach up to 39.42% if using 0.44 W mL^{-1} input power for 90 min. The oil recovered would have a higher oil grade quality due to the lower fatty acid content and, therefore, it could sell for a low-grade product and oil refineries will have lower operating costs.

Ultrasonication can also enhance COD removal by up to 15% (90% from 64% of COD removal efficiency) compared with the non-ultrasonicated. However, increasing biogas production efficiency also depended on other factors. Therefore, the proposed scenario for increasing COD removal efficiency with a 5% interval that effects the GHGs emission reduction (based on biogas system only) was given in Table 2.

The effects of ultrasonication in GHGs emissions reduction for the overall wastewater system are considered and demonstrated in Fig. 8. It could be noted that the ratio of GHGs emissions was changed because the pre-treated POME could affect the increase of biogas in the biogas system. After the biogas system, the ratio of GHGs emissions should be decreased due to lower COD discharged from the biogas system that results in a bit increase of contributed GHGs emissions ratio in the biogas system and a

cooling pond. The overall GHGs emissions reduction after the application of ultrasonication was 11%. This reduction was calculated based on the greater efficiency of the biogas system (up to 90% of COD removal) from the experiments. This GHGs emitted reduced was equal to $55.6 \text{ kg CO}_2\text{eq t}^{-1}$ CPO or $913.23 \text{ ton CO}_2\text{eq y}^{-1}$. In a real situation, a high-efficiency biogas system with larger quantities of biogas and a greater methane composition from POME was found using an anaerobic sequencing batch reactor (ASBR), up-flow anaerobic sludge-fixed film, modified anaerobic baffled bioreactor that could achieve over 93% efficiency [7,8].

Therefore, in order to minimize overall GHGs emissions, it should consider the GHGs emissions reduction of the open cooling pond prior to the biogas system, and the series of oxidation ponds after the biogas system. Ultrasonication can reduce the hydraulic retention time for oil separation, but was less effective to reduce the temperature in POME. Thus, a dispersed unit or stripping tower might be applied instead of the open pond. These units can reduce hydraulic retention times and lowering the temperature faster than open ponds. Moreover, it can avoid anaerobic conditions that cause GHGs emissions. Aerators apparatus may also be

Table 2

Total annual amounts of CPO, wastewater, and characteristics of raw and treated POME wastewater from a case study factory and the calculated GHGs emissions reductions from ultrasonication pre-treatment

	Average value	Biogas efficiency (%)	GHG emissions reduction ($\text{kg CO}_2\text{eq t}^{-1}$ CPO)
Total yearly amount of CPO (t)	16,425	–	–
Wastewater volume ($\text{m}^3 \text{ y}^{-1}$)	113,535	–	–
COD of influent wastewater (g L^{-1})	98.5	–	–
COD of influent into biogas system (g L^{-1})	58.9	–	–
COD of effluent from biogas system (g L^{-1})	14.7	75	Base line
Change in COD of effluent from biogas when increasing biogas efficiency with ultrasonication pre-treatment (g L^{-1})	11.8	80	9.0
	8.8	85	32.7
	5.9	90	55.6

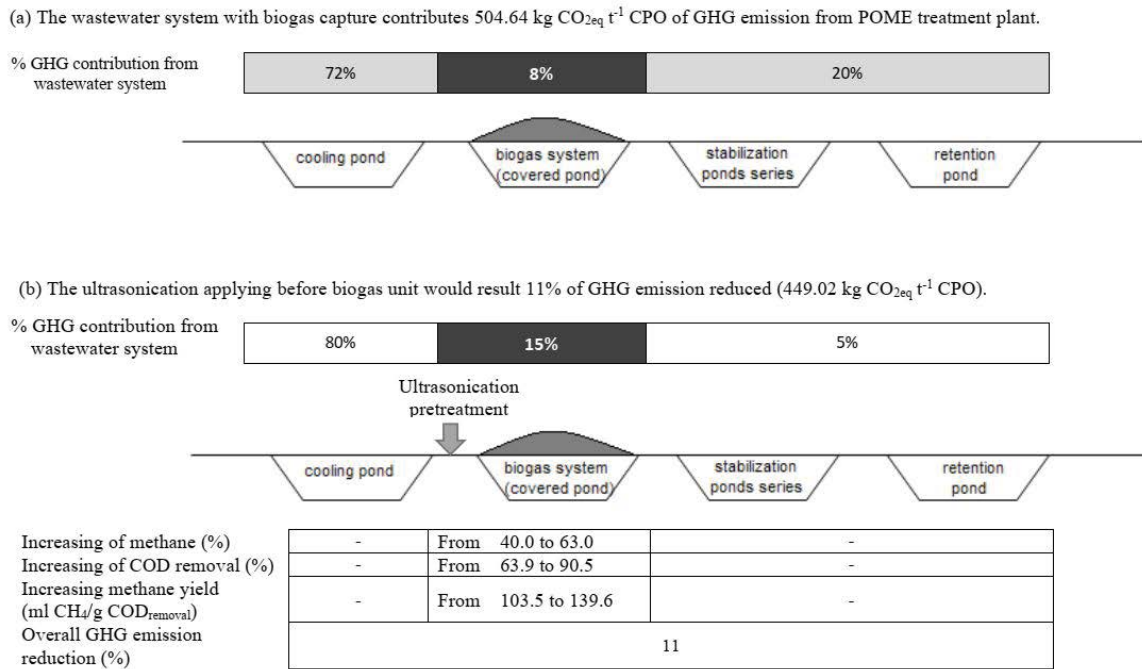


Fig. 8. GHGs emissions from a palm oil mill wastewater system at (a) baseline and (b) the scenario to apply ultrasonication as a pre-treatment.

installed in the series of oxidation ponds to convert some ponds to aerated lagoons that inhibit anaerobic degradation.

4. Conclusion

Ultrasonication improved the biodegradability of POME and enhanced the efficiencies of oil and grease recovery, with higher efficiency achieved in a shorter time period compared to the POME treatment without ultrasonication. The POME with ultrasonication increased the efficiency of the biogas system and yielded greater removal of organics in terms of COD, BOD₅, and VS. The biogas produced had a greater methane yield and methane percentage.

These results suggest that ultrasonication should be applied to POME as the first step of POME wastewater treatment (i.e., as a pre-treatment). Ultrasonication pre-treatment would reduce the hydraulic retention time for oil separation unit and biogas system. As a conclusion, expected benefits include:

- reducing the volume of oil separation units (or the number of units),
- increasing the efficiency of the biogas system, and
- reducing the overall GHGs emissions of the POME treatment plant.

Acknowledgments

The authors are grateful to the National Research Council of Thailand (NRCT; Grant No. ENG560087s), and Agricultural Research Development Agency (ARDA; Grant No. CRP5605021160) for their financial support.

References

- [1] S. Yahaya, S. Madaki, L. Seng, Palm oil mill effluent (POME) from Malaysia palm oil mills: waste or resource, *Int. J. Environ. Sci. Technol.*, 2 (2013) 1138–1155.
- [2] M.N. Ahmad, M.N. Mokhtar, A.S. Baharuddin, L.S. Hock, S.R.A. Ali, S.A. Aziz, N.A. Rahman, M.A. Hassan, Changes in physiochemical and microbial community during co-composting of oil palm frond with palm oil mill effluent anaerobic sludge, *Bioresour. Technol.*, 6 (2011) 4762–4780.
- [3] S. Yaeed, T.T. Suksaroj, C. Suksaroj, Mechanical pretreatment for enhancement of biogas production from palm oil mill effluent (POME), *Desal. Water Treat.*, 67 (2017) 133–139.
- [4] N. Saifuddin, S.A. Fazlili, Effect of microwave and ultrasonic pretreatments on biogas production from anaerobic digestion of palm oil mill effluent, *Am. J. Eng. Appl. Sci.*, 2 (2009) 139–146.
- [5] R. Kaewmai, A. H-Kittikun, C. Suksaroj, C. Musikavong, Alternative technologies for the reduction of greenhouse gas emissions from palm oil mills in Thailand, *Environ. Sci. Technol.*, 47 (2013) 12417–12425.
- [6] S.E. Hosseini, M.A. Wahid, Pollutant palm oil production process, *J. Air Waste Manage. Assoc.*, 65 (2015) 773–781.
- [7] S.E. Hosseini, M.A. Wahid, Feasibility study of biogas production and utilization as a source of renewable energy in Malaysia, *Renewable Sustainable Energy Rev.*, 19 (2013) 454–462.
- [8] R. Kaewmai, A. H-Kittikun, C. Musikavong, Greenhouse gas emissions of palm oil mills in Thailand, *Int. J. Greenhouse Gas Control*, 11 (2012) 141–151.
- [9] T.Y. Wu, A.W. Mohammad, J.M. Jahim, N. Anuar, Palm oil mill effluent (POME) treatment and bio resources recovery using ultrafiltration membrane: effect of pressure on membrane fouling, *Biochem. Eng.*, 35 (2007) 309–317.
- [10] T.Y. Wu, A.W. Mohammad, J.M. Jahim, N. Anuar, A holistic approach to managing palm oil mill effluent (POME): biotechnological advances in the sustainable reuse of POME, *Biotechnol. Adv.*, 27 (2009) 40–52.
- [11] S. Chaiprapat, T. Laklam, Enhancing digestion efficiency of POME in anaerobic sequencing batch reactor with ozonation

- pretreatment and cycle time reduction, *Bioresour. Technol.*, 102 (2011) 4061–4068.
- [12] P. Kianmehr, W. Parker, P. Seto, An evaluation of protocols for characterization of ozone impacts on WAS properties and digestibility, *Bioresour. Technol.*, 101 (2010) 8565–8572.
- [13] T. Sattaphai, N. Pisutpaisal, C. Phalakornkule, Thermophilic methane production from palm oil mill effluent, *J. Eng. Technol. Res.*, 7 (2010) 85–93.
- [14] G. Xu, S. Chen, J. Shi, S. Wang, G. Zhu, Combination treatment of ultrasound and ozone for improving solubilization and anaerobic biodegradability of waste activated sludge, *J. Hazard. Mater.*, 180 (2010) 340–346.
- [15] A. Bernal-Martinez, H. Carrre, D. Patureau, J.P. Delgens, Ozone pretreatment as improver of PAH removal during anaerobic digestion of urban sludge, *Chemosphere*, 68 (2007) 1013–1019.
- [16] A.B.C. Alvares, C. Diaper, S.A. Parsons, Partial oxidation of hydrolysed and unhydrolysed textile azo dyes by ozone and the effect on biodegradability, *Process Saf. Environ.*, 79 (2001) 103–108.
- [17] M. Weemaes, H. Grootaerd, F. Simoens, A. Huymans, W. Verstraete, Ozonation of sewage sludge prior to anaerobic digestion, *Water Sci. Technol.*, 42 (2000) 175–178.
- [18] E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri, *Standard Methods for the Examination of Water and Wastewater*, 22nd ed., American Public Health Association, American Water Works Association, Water Environment Federation, 2012.
- [19] Intergovernmental Panel on Climate Change (IPCC), Vol. 5, *Waste*, 2006 IPCC Guidelines for National Greenhouse Gas Inventories, S. Eggleston, L. Buendia, K. Miwa, T. Ngara, K. Tanabe, Eds., The National Greenhouse Gas Inventories Programme, The Institute for Global Environmental Strategies (IGES), Hayama, Japan, 2006.
- [20] *Guidelines for Assessment of the Carbon Footprint of Products, Thailand Greenhouse Gas Management Organization (Public Organization) (TGO)*, Bangkok, 2011. Available at: http://www.tgo.or.th/download/publication/CFP_Guideline_TH_Edition3.pdf
- [21] M.D.C. Aguilar-Luzón, J.M.Á. Garcia-Martinez, A. Calvo-Salguero, J.M. Salinas, Comparative study between the theory of planned behavior and the value belief norm model regarding the environment, on Spanish housewives' recycling behavior, *J. Appl. Soc. Psychol.*, 42 (2012) 2797–2833.
- [22] C.M. Ji, P.P. Eong, T.B. Ti, C.E. Seng, C.K. Ling, Biogas from palm oil mill effluent (POME): opportunities and challenges from Malaysia's perspective, *Renewable Sustainable Energy Rev.*, 26 (2013) 717–726.
- [23] M.F. Li, S.N. Sun, F. Xu, R.C. Sun, Ultrasound-enhanced extraction of lignin from bamboo (*Neosinocalamus affinis*): characterization of the ethanol-soluble fractions, *Ultrason. Sonochem.*, 19 (2012) 243–249.
- [24] M.K. Lam, K.T. Lee, Renewable and sustainable bioenergies production from palm oil mill effluent (POME): win-win strategies toward better environmental protection, *Biotechnol. Adv.*, 29 (2011) 124–141.
- [25] G. Samudro, S. Mangkoedihardjo, Review on BOD, COD and BOD/COD ratio: a triangle zone for toxic, biodegradable and stable level, *Int. J. Acad. Res.*, 2 (2010) 235–239.
- [26] W. Choorit, P. Wisarnwan, Effect of temperature on the anaerobic digestion of palm oil mill effluent, *Electron. J. Biotechnol.*, 10 (2007) 376–385.
- [27] A.C. Larson, L.E. Gentry, M.B. David, R.A. Cooke, D.A. Kovacic, The role of seepage in constructed wet lands receiving agricultural tile drainage, *Ecol. Eng.*, 15 (2000) 91–104.
- [28] V. Limkhuansuwan, P. Chaiprasert, Decolorization of molasses melanoidins and palm oil mill effluent phenolic compounds by fermentative lactic acid bacteria, *J. Environ. Sci.*, 22 (2010) 1209–1217.
- [29] M.G. Alriols, A. Tejado, M. Blanco, I. Mondragon, J. Labidi, Agricultural palm oil tree residues as raw material for cellulose, lignin and hemicelluloses production by ethylene glycol pulping process, *Chem. Eng. J.*, 148 (2009) 106–114.
- [30] G.A. Bernabe, S. Almeida, C.A. Ribeiro, M.S. Crespi, Evaluation of organic molecules originated during composting process, *J. Therm. Anal. Calorim.*, 106 (2011) 773–778.
- [31] S.E. Hosseini, M.A. Wahid, N. Aghili, The scenario of greenhouse gases reduction in Malaysia, *Renewable Sustainable Energy Rev.*, 28 (2013) 400–409.