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1 Biomethane Emissions: Measurement in Wastewater Pond at Palm Oil Mill by Using TGS2611 Methane Gas Sensor

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2 ABSTRACT

Palm oil mill effluent (POME) contains high amounts of organic matter, potentially as a source of environmental pollution. The processing of POME in anaerobic ponds is produced by biomethane, which is a greenhouse gas and also is a potential as a renewable energy source. Indonesia is the world's largest CPO producer, but POME processing is still mostly done by conventional methods without methane capture. In this system, the value of methane emitted into the atmosphere is unknown. This research focused on estimating the methane emissions in anaerobic ponds (AP) multiple feeding wastewater treatment plants (WWTPs) for land applications, with CH₄-meter systems based on TGS2611 sensors, SHT11 and microcontrollers, and using closed static chambers. The sampling of wastewater and methane gas was carried out in October–November 2018. The results showed that the methane gas emissions in combined anaerobic ponds (AP2-AP1) and AP3 were 43,704 and 35,321 mg/m²/day respectively, and a total of 405.358 and 61.812 kg/day sequential on AP2-AP1 (9,275 m²) and AP3 (1,750 m²). It was obtained from the correlation between methane emissions with removed COD as a conversion coefficient of 0.2107 kg CH₄/kg COD removed. On the basis of linear regression with R² 0.9725, it was still below the theoretical value (stoichiometry) of 0.25 kg CH₄/kg COD removed. From the conversion coefficient, COD removed, and the amount of POME in 2018, which was 104,179 m³, contributed to emitting 462 tons of methane from the entire anaerobic pond. This conversion coefficient can be used to quickly estimate the methane emissions in Indonesian palm oil mills.

Keywords: methane emissions, CH₄-meter, TGS2611 and SHT11 sensor, anaerobic pond, POME, conversion coefficient

INTRODUCTION

Indonesia is the largest palm oil producer in the world since 2006 (Djamhur, 2015). In 2016 the Indonesia's production of Crude Palm Oil (CPO) reached 33.23 million tons (Directorate General of Plantation, 2016), around 57% of world production amounted to 58.29 million tons. Indonesia is the largest exporter of palm oil, in 2016, 25.1 million tons were exported (GAPKI, 2017), with foreign exchange values reaching USD 17.8 billion and 5.9 million workers (11%).

According to Wicke et al. (2008), in the process of processing fresh fruit bunches (FFB) of palm oil into crude palm oil (CPO), around 21.5–23 percent corresponded to CPO production; around 230 kg of CPO and 55 kg of palm kernel (PK); (Buana et al., 2004), the remainder includes by-products or solid, liquid, and gas waste. Solid waste consists of empty fruit bunches (16–23%), fruit juice (11–26%), palm kernel (4%), shells (4–6%), and other solid wastes (16.5%). According to Mahajoeno (2008), each ton of processed fresh fruit bunches (FFB), produced 0.7 m³ of

wastewater. According to Yuliasari et al. (2001), Morad et al. (2008), palm oil mill effluent would produce 0.75-0.90 m³/ton FFB or 3.33 tons of POME (2.5-3 tons according to Wu et al., 2010) for every ton of CPO.

POME contains high BOD, COD, TSS, oil and grease, TS and VS, so it has the potential to be a pollutant source. Disposal of POME without treatment into the waters can pollute aquatic environment, reducing dissolved oxygen levels, deteriorating fish health and aquatic biota (Lam and Lee, 2011). The study conducted by Mahajoeno (2008) showed that POME was colloidal, thick, brown or grayish, pH 4.4-5.4 and had an average COD content of 49.0-63.6; BOD 23.5-29.3; TS 26.5-45.4 and SS 17.1-35.9 g/L, all variables exceeded the quality standard according to the Regulation of The Environment Minister 05/2014, so it had the potential to pollute the environment.

The processing of POME in Indonesia is generally carried out relatively simply, namely by flowing and decomposition in the ponding system; there are still a few who carry out methane capture to utilize biogas for energy. In this system, POME is degraded anaerobically, which causes methane emissions. Methane emissions contribute to global warming because it is a greenhouse gas (GHG) which is 20-30 times stronger than carbon dioxide (Porteous, 1998).

One of the palm oil mill wastewater treatment systems is a multiple feeding system, where the POME output from the deoiling pond and coolant is fed simultaneously to anaerobic ponds. This system is generally applied to palm oil mills that carry out land application to plantation land. The advantages of this system are reducing the organic content and increasing the pH faster, shortening waste treatment, having less number of waste ponds and WWTP land area, but having treated wastewater with BOD > 1000 mg/L. This WWTP system is not well-known and few researchers have reported the value of its methane emissions.

The measurement of biogas flow rate emission with the main content of biomethane, as well as other gas compositions, is still limited due to the requirements in equipment, the level of difficulty in gas sampling; the analysis costs are relatively expensive, also due to the changing nature of gas according to circumstances and environmental factors. Thus, a practical, fast and accurate measuring system is needed. Methane testing that is commonly carried out with Gas Chromatography and conducted in a laboratory was a costly

method. Gas measurement methods have been developed for quantification and monitoring of greenhouse gas emissions, especially methane and carbon dioxide, in waters and installation of wastewater treatment plants, namely through closed static chambers (Yacob et al., 2005; Yacob et al., 2006; Hasanudin et al., 2006; Park and Craggs, 2007; Silva et al., 2015; Paredes et al., 2015; Lorke et al., 2015; Silva, 2016). The method being developed is a sensor-based CH₄-meter and microcontroller that allows continuous real-time measurement, and automatic recording (Sugriwan and Soesanto, 2017; Sugriwan et al., 2015; Eugster and Kling, 2012). This research aimed at assessing the characteristics of wastewater and estimating methane emissions in WWTP with a multiple feeding system, using the CH₄-meter system based on TGS611 sensors, SHT11 sensors and microcontrollers, and the relationship of methane emissions to the levels of organic matter in POME.

1 MATERIAL AND METHODS

Description of processing palm oil mill wastewater

Field measurements of methane emissions and palm oil mill wastewater were conducted in Banyuasin Regency of South Sumatra Province, with a production capacity of 60 tons of FFB/hour, within ± 21 km from Palembang (-2.826S, 104.732E). The WWTP facility consists of 7 ponds, including 3 oil quotation ponds, 1 cooling pond, and 3 anaerobic ponds (Figure 1). This research focused on anaerobic ponds with anaerobic microbial activity, characterized by the presence of active bubbles of biogas (methane) production. Three anaerobic ponds (AP) were measured in terms of methane emissions. The AP dimensions can be seen in Figure 1 with a depth of ± 6 meters, and the total volume of all APs was ± 46,305 m³, with HRT > 130 days.

Following the process, the wastewater is used oil palm plantation land, located about 1 km from the WWTP outlet. The wastewater treatment process starts from the deoiling pond and the cooling pond; then it is pumped and fed to AP2 and AP3 (± 500 meters) together (multiple feeding), with a ratio of 50:50, 40:60, and 60:40 according to the quality of processing results to meet the BOD ≤ 5000 mg/L required by POME for land

applications. WWTP outlets on AP3 with rotary system pumps are applied to land as much as 300-500 m³/day.

1 Monitoring the characteristics of wastewater

Sampling of WWTP wastewater, from various types of inlet and outlet waste ponds, was carried out over two weeks period for ± 2 months (n=6) includes 6 sampling locations (Figure 1). The wastewater samples, from each wastewater sampling point, were combined from the POM operations in the morning (± 09.00) and evening (± 16.00). In addition to composite time, pond depth composites (0-2 meters) and composite locations (locations 1 and 2 in the area around the inlet or outlet of the waste pond) were also carried out. The test variables of the characteristics of wastewater included BOD, TSS, TS, VS, oil and grease with the Standard Methods for the Examination of Water and Wastewater testing method (APHA, 1998); COD using the COD-Vario Photometer-System, Lovibond; N-total with TOC/TN Analyzer, Torch, Teledyne Tekmar. In turn, the pH, Eh and temperature were taken directly in the field with Adwa AD-111 portable pH meter.

Estimated methane emissions in anaerobic ponds

Closed static chambers for biogas (methane) capture are made of transparent polypropylene (PP) material, in the form of a cylinder with the dimensions of 0.30×(0.18×0.415 m (upper diameter×lower diameter×height), containment

volume = 0.02742 m³ (27.42 liters) and with the wide-scale area of 0.07 m². The chamber volume was 15.44 liters when applied above the anaerobic pond, with 3 cm submerged below the surface of the pond (effective height of chamber = 0.385 m); (see Figure 2) and the placement of chambers could be seen in Figure 3.

The methane (biogas) concentration measuring instrument uses a sensor system, namely CH₄-meter modified from Sugriwan et al. (2015), Sugriwan and Soesanto (2017), consisting of the TGS2611 methane gas sensor, SHT11 air temperature and humidity sensor, Arduino Mega 2560 microcontroller (ATMega2560), 20x4 LCD, and data logger (micro SD) storage. The TGS2611 and SHT11 sensors from the CH₄-meter were mounted on the chambers. The CH₄-meter system is used to allow continuous, real-time, and automatic recording. The CH₄-meter calibration of standard methane gas at 100 to 10,000 ppm, has met the precision criteria of % RSD (relative standard deviation) and % RSD-Horwitz (Harmita, 2004).

Chambers were positioned at three locations, each in the inlet, center and outlet of the anaerobic pond (AP2-AP1 and AP3); (Figure 3). The measurements of methane production were carried out for three days (n=3) in the combined AP2-AP1 and AP3, 11 hours per day (07:00 to 18:00), with blasting of chambers every 2 hours. The reading of the concentration of methane gas with CH₄-meter was carried out continuously per 2 hours. Further data processing and analysis at intervals of each data were taken per 5 minutes (12 data per hour). In order to detect the effect of

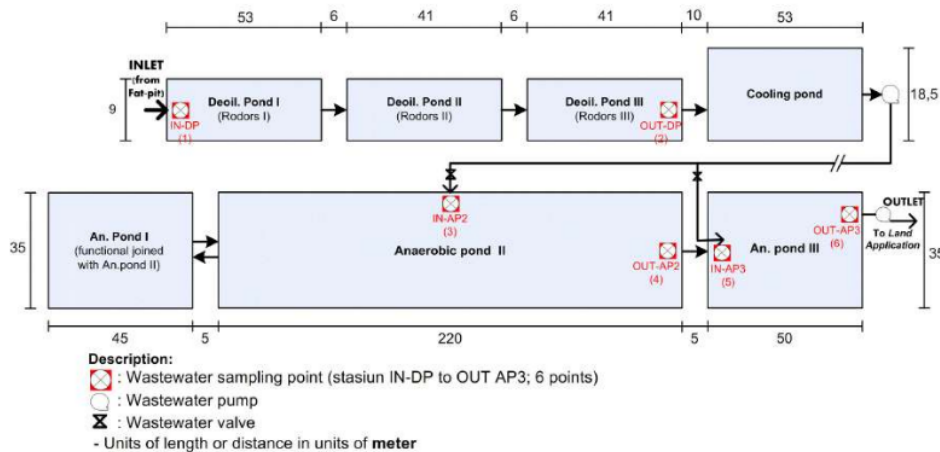


Figure 1. Plan of WWTP and location of wastewater sampling point

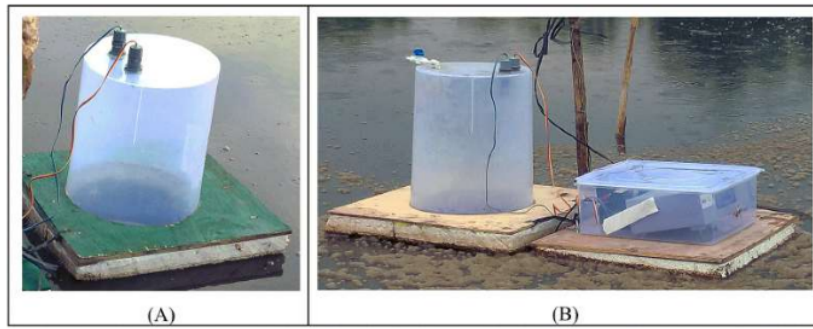


Figure 2. (A) Chamber for methane capture, (B). CH₄-meter system and chamber

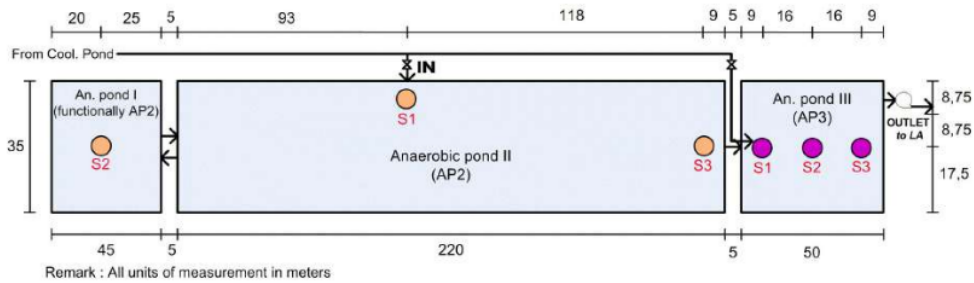


Figure 3. Placement of chambers in anaerobic ponds

rain on methane emissions, the rainfall data was used in mm/12 hours format. The data from rain-drop station involved one group of oil palm plantation companies, within ± 2,000 meters from the the WWTP outlet (-2.821S, 104.700E).

Methane emissions/fluxes were calculated as Khalil et al., 1991; IAEA, 1992; Lantin et al., 1995:

$$E = \frac{dc}{dt} \cdot \frac{Vch}{Ach} \cdot \frac{Wm}{Vm} \cdot \frac{273.2}{273.2 + T} \quad (1)$$

where: E is emission/flux CH₄ (mg/m²/minute); dc/dt is difference in CH₄ concentration per unit time (ppm/minute); Vch is containment volume (m³); Ach is cover area (m²); Wm is molecular weight CH₄ (16.04×10³ mg); Vm is the molecular volume of CH₄ (22.41×10⁻³ m³) and T is chamber air temperature on average at sampling (°C).

The total rate of methane emissions per sampling point per day was calculated by integrating the emission values using the SimpsonNumericalMethod (Arif et al., 2015):

$$\int_a^b f(x)dx \approx \frac{b-a}{6} \left[f(a) + 4f\left(\frac{a+b}{2}\right) + f(b) \right] \quad (2)$$

where: $f(x)$ is total methane emissions (mg/m²/day); a is the initial hours of measurement of emissions and b is the final hour of measurement of emissions.

On the basis of the average emission rate per sampling point, the total methane emissions per day (mg CH₄/pond/day) were calculated with the following formula:

$$\text{Total emissions CH}_4 = \text{average CH}_4 \text{ emission rate (mg/m}^2\text{/day)} \times \text{anaerobic pond area (m}^2\text{)} \quad (3)$$

Statistical analysis was performed using IBM SPSS statistics version 25 to test the relationship between environmental variables and wastewater with methane emissions. All data from the field were tested for linearity and normal distribution. Multiple linear regression equation to achieve BLUE (best linear unbiased estimation) was carried out with regression assumption tests, namely: residual normality test (Shapiro-Wilk test), multicoleniarity test (variance inflating

factor; VIF), homoskedasticity test (Glejser test and Spearman Rho test), and non-autocorrelation (Durbin-Watson).

RESULTS AND DISCUSSION

Multiple feeding systems on palm oil mill effluent properties

The POME processed with a multiple feeding system in WWTP has the biochemical content relatively identical to the results reported by other researchers (Tong, 2011; Mahajoeno, 2008; Wu et al., 2010; Saron, 2014); (Table 1), the difference in BOD levels in this study was lower due to the quality of FFB raw materials, oil palm harvest season, and laboratory test methods. Both COD and BOD variables are references in determining the organic matter content of POME, so that estimates of the amount and rate of methane emissions can be determined (IPCC, 2006).

All test results variables do not meet BMLC (Regulation of Environment Minister 05/2014), but meet BMLA (Decree of Environment Minister 29/2003), either raw POME from fat-pit from the factory or WWTP output (effluent or AP3 outlet), which utilizes wastewater for land application (LA). This fact explains that POME with high levels of organic matter is a source of environmental pollution, and required management and improvement of technology for its processing.

The biochemical levels of POME in Table 1 with COD content of almost 45,000 mg/L – apart from being a source of pollution – also had the

potential to produce biogas containing methane gas as an energy source (Saron, 2014). The value of organic matter content on POME, as indicated by COD content, has a conversion factor with methane gas. Theoretically (stoichiometry) the degradation process of organic matter every 1 kg of COD can be produced 0.35 m³ or 0.25 kg CH₄ under STP conditions (standard temperature and pressure; 0°C and 1 atm); (IPCC, 2006), although from many field-scale studies of value had rarely been achieved (Yacob et al., 2006; Hasanudin et al., 2006; Park and Craggs, 2007; Paredes et al., 2015).

This wastewater treatment system, with simple POME processing techniques, has shorter HRT (hydraulic retention times); (< 35 days on AP3), wide area of ponds and fewer ponds (7 ponds and area < 1.4 hectares); (Figure 1). WWTP with this system is able to reduce the POME variable COD, BOD, TSS, TS, VS, N-total, and oil and grease 81.56; 86.56; 59.09; 64.25; 68.89; 17.47; 88.59 %, and increased pH 59.38% respectively. The mean value of raw POME variable COD was 44,917 mg/L and AP3 POME outlet was 8,283 mg/L. This indicated that the WWTP system was capable of removing COD in the amount of 36,633 mg/L (81.56%); (Table 2). The use of COD variables was suitable for estimating methane emissions in POME and other types of wastewater (IPCC, 2006; Yacob et al., 2006; Basri et al., 2010). The removing of COD variables in anaerobic ponds (AP1 to AP3) was able to reduce 21,050 mg/L (46.86%), and final processing wastewater with a value of COD 8.283 mg/L (18.44%) for the use of land applications and sources of nutrients for plant.

Table 1. Characteristics of POME from the waste pond tested

Variable ^a	Unit	Inlet WWTP (Raw POME)		Outlet WWTP (AP3)		Removed	
		Mean	Interval	Mean	Interval	Value	%
COD	mg/L	44,917 ± 11,889	33,500 - 66,000	8,283 ± 4,846	2,200 - 16,000	36,633	81.56
BOD	mg/L	9,567 ± 2,551	6,060 - 11,961	1,285 ± 203	1,007 - 1,546	8,281	86.56
TSS	mg/L	52,610 ± 20,390	31,530 - 90,350	21,522 ± 9,664	11,850 - 31,720	31,088	59.09
TS	mg/L	54,053 ± 13,912	37,920 - 71,620	19,327 ± 5,116	13,720 - 27,220	34,727	64.25
VS	mg/L	46,813 ± 13,835	29,840 - 65,640	14,565 ± 5,352	7,980 - 20,940	32,248	68.89
N-total	mg/L	1,789 ± 719	1,234 - 3,046	1,476 ± 357	1,083 - 1,997	313	17.47
Oil and grease	mg/L	18,083 ± 10,456	5,570 - 32,860	2,063 ± 1,492	780 - 4200	16,020	88.59
pH	--	4.59 ± 0.08	4.46 - 4.69	7.31 ± 0.11	7.22 - 7.50	-2.72	-59.38 ^b
Eh	mV	157 ± 7	147 - 169	(-20) ± 7	(-33) - (-14)	177	112.61 ^c
Suhu	°C	67.5 ± 3.0	62.4 - 70.4	33.4 ± 1.6	32.4 - 36.8	34	50.51

^a TSS=total suspended solid; TS=total solid; VS=volatil solid; Eh=redox potential.

^b Negative percentage means an increase.

^c Eh value percentage is from positive (157 mV; low reduction) to negative (-20 mV; moderate reduction), so > 100%.

Table 2. Decreasing COD variables in WWTP with multiple feeding system

Characteristics of COD variables	Deoiling-Cooling pond		Anaerobic pond			
	IN-DP	OUT-DP	IN-AP2	OUT-AP2	IN-AP3	OUT-AP3
COD (mg/L)	44,917	41,000	29,333	12,967	16,963	8,283
Decreasing of COD (mg/L); (%)	0 (0.00)	3,917 (8.72)	15,583 (34.69)	31,950 (71.13)	27,953 (62.23)	36,633 (81.56)
Decreasing of COD and final outlet:						
a. Inlet deoiling pond to Inlet AP2 (mg/L); (%)	15,583 (34.69)					
b. Inlet AP2 to outlet AP3 (mg/L); (%)			21,050 (46.86)			
c. Outlet final IPAL (Outlet); (mg/L); (%)			8,283 (18.44)			

Decreasing the COD variable was 81.56% higher than obtained by Yacob et al., 2005 (80.7%), but smaller than in Yacob et al., 2006 (97.8%) based on field-scale research results; smaller than the results of Faisal and Unno, 2001, Najafpour et al., 2006, and Saron, 2014, amounting to 95.3, 97 and 86.86% respectively, in laboratory-scale research. The decrease in COD variable occurred in anaerobic ponds and non-anaerobic ponds (deoiling-cooling ponds) was 46.86 and 34.60% (or 21,050 and 15,583 mg / L), respectively (Table 2), which showed that the AP performance was still not optimal, due to siltation of ponds by sludge (digestate). As a result, the process of reforming organic matter by micro-organisms became shorter and the process of forming biogas (methane) was not completed.

The negative Eh values indicated a moderate-strong reduction reaction, in the formation of methane (methanogenesis), as in the measurement results of the average variable value of Eh-20 mV (Table 1) and -26 mV (moderate reduction) at AP3 outlets and AP2 outlets, respectively. Meanwhile, positive Eh (low reduction) occurred on AP3 and AP2 inlets, reaching 27 and 154 mV, respectively. Medium-strong reduction with negative values is a condition for the formation of methane gas. According to Drapcho et al. (2008), anaerobic conditions must be maintained for the production of methane gas in the Eh-300 mV for the growth of methanogenic bacteria.

The rate of methane emissions

Measuring the rate of methane emissions by using chambers and the TGS2611 sensor-based CH_4 -meter system in anaerobic ponds of multiple feeding system palm oil mills has not been widely reported. Determination of the sampling points location was based on consideration of microbial activity, high, low and medium rate of biogas (methane) emissions and previous research,

namely inlet, middle and outlets pond (Yacob et al., 2006; Park and Craggs, 2007; Mahajoeno, 2008; Paredes et al., 2015). The TGS2611 and SHT11 sensors mounted on the chamber were capable of detecting and presenting data on methane gas concentrations and chamber temperatures according to the manufacturer's technical data (Figaro, 2012). Some data with methane gas values > 1.5% were still able to read well.

Methane emissions in combined anaerobic ponds (AP2-AP1) and AP3 reached 43,704 and 35,321 mg/m²/day, respectively, with a total of 405.358 kg/9,275 m²/day at AP2-AP1 and 61.812 kg/1,750 m²/day on AP3 (Table 3). The highest value of methane emissions was at the sampling point near the inlet and the lowest was at the location of sampling the middle of the pond both on AP2-AP1 and AP3. The high value of methane emissions was caused by the location of the inlet, i.e. the point of entry for the wastewater with the highest organic matter content compared to the other two sampling points. At this location, the rate of biogas production (methane) was highest, but the lowest methane content was lowest (Yacob et al., 2006; Mahajoeno, 2008).

The value of methane emissions was near the highest inlet in the presence of gas bubbles, then increased near the outlet, and the lowest in the middle of the pond. The micro-organism activity was seen to increase along with surface temperatures leading to daylight (Park and Craggs, 2007), but when the rainfall occurred, the emissions decreased, and a scum/solid organic matter was formed which could be seen on the ponds. These conditions could be seen on AP2 and AP3; however, it was less on AP1. This was because the AP1 pond was just an additional water reservoir, with the AP1 pond outlet returning to AP2 (Figure 3).

In this study, the methane emissions were still lower than the ones obtained by previous researchers. Yacob et al., 2006 produced methane

Table 3. Methane emissions in anaerobic ponds

Sampling location	Anaerobic Pond AP2-AP1		Anaerobic Pond AP3	
	Emission CH ₄ (mg/m ² /day)	n	Emission CH ₄ (mg/m ² /day)	n
Inlet	97,534 ± 45,223	3	49,715 ± 1,963	3
Middle	11,631 ± 11,546	3	27,499 ± 18,461	3
Outlet	21,948 ± 15,546	3	28,750 ± 4,978	3
Mean	43,704 ± 38,295		35,321 ± 12,481	

Remark: Methane emissions AP2-AP1 405.358 kg/day with an area of 9,275 m² and AP3 61.812 kg/day with an area of 1,750 m², a total of 467.170 kg/hr (11,025 m²).

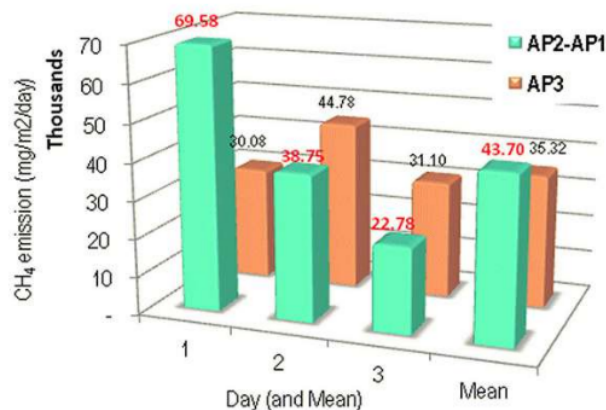
emissions of 1,043.1 kg/pond (1,373 m²)/day and Mahajoeno, 2008 reported 1,935.6 kg/pond (10,800 m²)/day, or each equivalent to 759,723 and 179,222 mg/m²/day, while this research is 43,704 and 35,321 mg/m²/day for AP2-AP1 and AP3, respectively. This is due to the condition and performance of the AP which is not optimal in the degradation of organic matter in POME, owing to siltation of ponds, which results in shorter HRT, so that the performance of microorganisms in degradation of organic matter is not optimal. HRT that is too short causes the process of overhauling organic matter to be incomplete or pushes bacteria out of the digester (Rahayu et al., 2015).

The methane emissions on AP2-AP1 were higher than AP3, this is highly related to HRT and the load of organic matter (OLR) of waste entering the AP2-AP1 was higher in the organic content. In the multiple feeding system, AP3 received the same wastewater and even higher volumes (AP3 – 60% volume and AP2-AP1 – 40% when the study was conducted), but at the same time, AP3 received flow from AP2 with wastewater degraded, while AP2 was directly fed from the cooling pond with higher levels of organic matter.

Another finding obtained from this study was that methane emissions on AP were strongly influenced by the presence of rain that increased the liquid volume and reduced the temperature of anaerobic ponds, this phenomenon was seen in AP2-AP1 and AP3 (Figure 4). In AP2-AP1 on day 3, there was a volume of 85 mm/12 hours (14.45-16.00) of rain, causing the rate of methane emissions to decline by 22.78 g/m²/day, but on the contrary when the sun was clear without rain on day 1, the highest emission rate was obtained (69.58 g/m²/day). Likewise, in the AP3, the first day of rainfall with a volume of 16 mm/12 hours (15.35-16.20) caused the lowest methane emission rate of 30.08 g/m²/day and day 2 with bright sun resulted in the highest rate of methane emissions (44.78 g/m²/day).

Conversion coefficient of methane emissions

By plotting the data between COD removed and the rate of production of methane in the AP-AP1 and AP3 anaerobic ponds, the conversion coefficient or conversion factor was obtained. In the AP2-AP1 and AP3 ponds based on this study,

**Figure 4.** Effect of rain on the rate of methane emissions

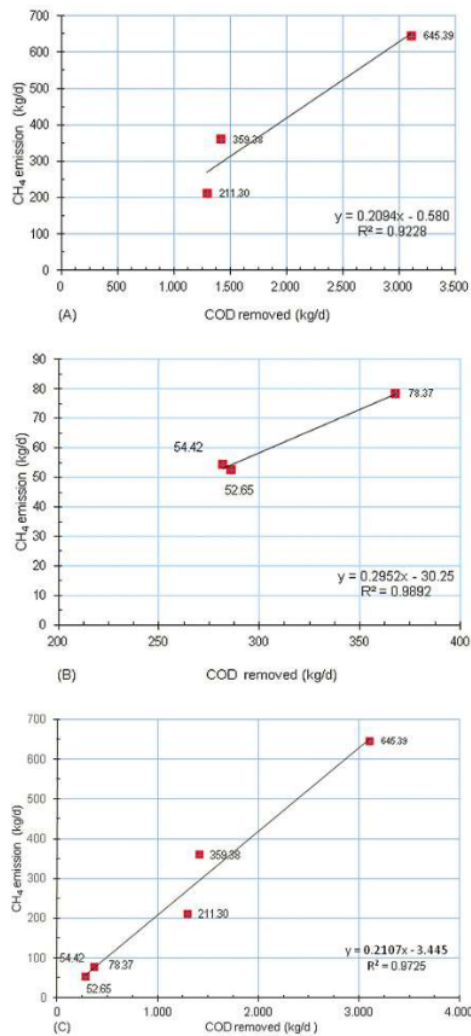


Figure 5. Relationship between methane emissions and COD removed: A) AP2-AP1 pond, B) AP3 pond, C) combined pond AP-AP1 and AP3

0.2094 and 0.2952 kg CH₄/kg COD removal was obtained, respectively, while using all data, 0.2107 kg CH₄/kg COD was removed (Figure 5). This value was based on linear regression with a significant coefficient of determination (R²), 0.9228; 0.9892 and 0.9725, respectively. The high R² value stated that the independent variable (COD removed) was able to explain the dependent variable (CH₄ emissions) significantly, while the rest (1-R²) was the influence of other variables. Compared to the research of Yacob et al., 2006, the results of this study had better

distribution of data and were very close to linear line with high R² (> 0.92).

The conversion coefficient value obtained in this study was 0.2107 kg CH₄/kg COD removed, smaller than Yacob et al., 2006 (0.238) in the WWTP anaerobic pond of palm oil mills in Malaysia, but higher than in the research of Hasanudin et al., 2006 (equivalent to 0.105) in the AP tapioca factory in Lampung, Indonesia. This difference was very dependent on harvesting and factory activities (Yacob et al., 2006), environmental factors, and wastewater treatment systems. From the previous research mentioned above and the results of this study, the obtained conversion coefficient was below the theoretical value (stoichiometry) 0.25 kg CH₄/kg COD removed. This conversion coefficient could be used in the rapid estimation of methane emissions in Indonesian palm oil mills, especially for conversion to energy sources and control of greenhouse gases in oil palm agro industry.

From the anaerobic ponds of all WWTPs, the average AP2-AP1 COD inlets and AP3 outlets (IPAL outlets) were 29,333 and 8,283 mg/L, respectively, so the COD removed was distributed across all anaerobic ponds of 21,050 mg/L (21.05 kg/m³). Using the conversion coefficient, COD removed and the number of production POME, 104,179 m³ of methane gas would be emitted in 2018 throughout the anaerobic ponds of 462 tons.

Relation of methane emissions and wastewater characteristic

The multiple linear regression equation was built to determine the relationship of the biochemical variables of wastewater with methane emissions. The resulting regression equations fulfilled the regression assumptions. Methane emissions were influenced by the levels of COD, VS, oil and grease, N-total, in the form of a logarithmic linear regression equation, as follows:

$$\ln(\text{CH}_4) = 3.139 + 0.245 \cdot \ln(\text{COD-R}) + 0.620 \cdot \ln(\text{VS-R}) - 0.012 \cdot (\text{COD}/\text{Ntot-R}) + 0.002 \cdot (\text{ML-R}/\text{Ntot-R}); (R^2=0.585) \quad (4)$$

Where: CH₄ is emissions of methane emission rate (mg/m²/day), COD-R is chemical oxygen demand, VS-R is volatile solid, Ntot-R is total nitrogen, and ML-R is oil and grease removed (mg/L).

Regression equation had fulfilled the residual normality test (Shapiro-Wilk test; significance > 0.05), multicollinearity test (variance

inflating factor (VIF) <10), homoskedasticity test (Glejser test and Spearman Rho test; significance > 0.05), and non-autocorrelation (Durbin-Watson). However, the ANOVA results of the regression equation were not significant with the coefficient of determination (R^2) 0.585. On the basis of the R^2 value, all predictors of VS-R, COD-R, N-total, and oil and grease together were able to determine the value of methane emissions by 0.585, and the remaining 0.415 were influenced by other factors. R^2 also explains how reliably the model formed is able to explain the condition of the independent variables measured in the field and the use of appropriate regression methods.

Logarithmic data transformation aims at normalizing data so that it can meet regression assumptions. Natural logarithms (ln) were for CH_4 , COD-R, and VS-R emission variables, and transformation ratios in COD-R and ML-R with N-total. The significance value of the model obtained was strongly influenced by the amount of data used in building the regression model, even though the value of R^2 was able to show the effect of COD, VS, ML and N-total variables simultaneously on methane gas emissions in organic change activities in anaerobic ponds.

VS variable was related to volatility and fixed solid. The anaerobic microbial activity in the decomposition of organic matter produces biogas (methane), highly determined from COD variables (IPCC, 2006) and solid volatile (VS); (Drapcho et al., 2008; Park and Craggs, 2007). Furthermore, Drapcho et al. (2008), reported that every kg of VS was degraded in the anaerobic process of urban domestic wastewater would result in 0.7 m³ CH₄. Besides using COD variables, based on this study, the use of VS variables was possible for a conversion coefficient (kg CH₄/kg VS). However, further studies need to be conducted.

The value of C/N ratio also affected the microbial productivity in methane formation. The C/N ratio could be approached with total COD/N-total and ML/N-total ratios which were linearly related to methane gas production. This is a new finding, but this needs further study. The change in organic content in the anaerobic process requires a balance of COD:N:P ratio of 800:5:1 in the wine industry wastewater (Molletta, 2005). COD:N:P ratio of 333:4:1 for pear waste and 500:9:1 from melons, but the anaerobic performance of the digester is adequate at a ratio of 300:5:1 (Drapcho et al., 2008).

The COD variable showed the amount of chemical oxygen demand in reforming POME organic matter, which reflected the amount of carbon (C-organic) contained in the substrate of palm oil waste water. The COD/N-total ratio could be directly obtained by mathematical comparison of COD and Ntotal, which has become a mandatory test variable in the operational compliance of WWTPs in oil palm plant. The above-mentioned facts indicate that the variables COD and / or VS were strong enough to be used in determining methane gas emissions quickly.

The process of anaerobically changing organic matter required nutrients to grow and multiply. Too low substrating with a C/N ratio would result in an increase in ammonia levels which could inhibit the methane production. Conversely, if the C/N ratio is too high, indicating a lack of nitrogen on the substrate, this has a negative impact on the formation of proteins needed by microbes to grow. Therefore, it was necessary to balance the C/N ratio so that methane gas production was more optimal (Deublein and Steinhäuser, 2008). He further said that the optimal C/N was 16:1 – 25:1; and 20:1 – 30:1, according to Stafford et al. (1980).

The oil and grease content could be seen from the ML/N-total ratio, grease is a very slowly hydrolyzed complex organic compound. Grease is a limiting factor for the rate of hydrolysis, in the anaerobic decomposition of organic matter. This compound had excessive amounts of long chain fatty acids and could inhibit the microbial work in the formation of biogas (Adrianto et al., 2001).

CONCLUSION

Fresh POME (influent) had variable levels of COD, BOD, TSS, TS, VS, N-total, oil and grease, and pH 44,917; 9,567; 52,610; 54,053; 46,813; 1,789; 18,083 mg/L and 4.59, respectively. Wastewater treatment with a multiple feeding system was able to reduce the above-mentioned variables in a row 81.56; 86.56; 59.09; 64.25; 68.89; 17.47; 88.29%, respectively, and increased pH by 59.38%. Methane gas emissions in combined anaerobic ponds (AP2-AP1) and AP3 were 43,704 and 35,321 mg/m²/day, respectively, and a total of 405.358 and 61.812 kg/day were obtained in AP2-AP1 (9,275 m²) and AP3 (1,750 m²), respectively. The correlation between the methane gas emissions with COD removed was obtained, as the conversion coefficient of 0.2107 kg CH₄/kg

COD removed. These values were based on linear regression with the coefficient of determination (R^2) equal to 0.9725. The average value of COD in the whole anaerobic pond was 21,050 mg/L, using the conversion coefficient obtained, and the production of POME in 2018 equalled 104,179 m³, which had emitted 462 tons of methane gas. Variable wastewater COD, VS, N-total, oil and grease, together had an effect on methane emissions in anaerobic ponds, in the form of logarithmic linear regression with R^2 0.585 and had met the regression assumptions.

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