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The Influence Of Chemical Oxygen Demand (COD) And pH Of Pome As Biogas Raw Material On The CH_4 Produced

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Abstract:*POME is liquid wastewater derived from processing of palm fruit. POME contains nitrogen, phosphate, potassium, magnesium and calcium compounds, that can be used as a good fertilizer for plantations. However, before application, POME must be processed because direct use of unprocessed POME can damage the environment. PT XYZ utilizes POME as raw material for biogas through an anaerobic fermentation process to produce alternative energy for electricity generation, however, biogas production at PT XYZ produces CH_4 levels that do not meet the desired standard, namely 60%, while the value obtained is still 57%, so it can occure an incomplete combustion process in the engine. Therefore, research was carried out to analyze the influence of POME's Chemical Oygen Demand (COD) and the pH of POME as biogas raw material on the CH_4 produced. Meanwhile, based on measurements of POME pH, fluctuations are caused by environmental conditions, therefore before the feed enters the biodigester, the first treatment is increasing pH until 6-7 to adjust the optimal conditions for bacteria working to break down organic substances. The results shows that the estimated potential for a Biogas Power Plant (PLTBg) with a production capacity of fresh fruit bunches (FFB) of 60 tons/hour, the high generating capacity is influenced by the large COD value, meaning that the COD value greatly influences the CH4 produced, but must also be in accordance with Other factors that influence CH_4 production such as pH, temperature, stirring and others.*

Keywords: Biogas, COD, pH, POME

1. INTRODUCTION

Indonesia produces 59% of the world's total palm oil production or 45.5 million tons per year. In 2022, Indonesia exported 25.01 million tons of CPO and its derivative products (BPS, 2022). The results of the palm oil industry can be used as raw materials other industries such as food, cosmetics, and soap. The process of processing Fresh Fruit Bunches (FFB) of oil palm into *crude palm oil* (CPO) uses a lot of water, up to 1-2 m3 / ton of FFB.

Therefore, the TBS processing process contains by-products such as Palm Oil Liquid Waste (LCPKS), solid waste and hazardous and toxic waste. One of the by-products caused by the palm oil processing industry is LCPKS or also known as *Palm Oil Mill Effluent* (POME).

POME is one of the wastes that has the potential to have a negative impact on the environment, palm oil mill liquid waste can cause pollution, especially water bodies. Another impact caused by POME is from the degradation process by anaerobic and aerobic microorganisms in the formation of methane gas and carbon dioxide are Greenhouse Gases (GHG) which can cause global warming (Makmun and Sarto, 2018). POME contains high organic matter, namely *Chemical Oxygen Demand* (COD) 48,000 mg / L, *Biological Oxygen Demand* (BOD) 25,500 mg / L, Total Suspended Solid (TSS) 31,170 ml / L, oil and fat 3,075

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ml / L and pH 4 (Zulfahmi et al., 2017). The high COD figure exceeds the quality standards for liquid waste produced by the palm oil industry which is regulated in accordance with the Regulation of the Minister of Environment No. 5 of 2014 concerning Wastewater Quality Standards, where the quality standard for liquid waste for COD is 350 mg / L.

According to Winanti et al. (2019), the high COD numbers that are harmful to the environment require processing of COD that has a high organic content anaerobically. The anaerobic degradation process is a fermentation process of organic matter by the activity of anaerobic bacteria in conditions without free oxygen and changing from suspended to dissolved and biogas. Anaerobic fermentation in the breakdown of COD carried out by anaerobic microbes in a lagoon digester (closed reactor) through several stages, namely the hydrolysis process in the form of a complex biomass decomposition process into simple glucose produced by microorganisms. The acidogenesis process is the process of breaking down monomers and polymers into acetic acid, CO2 , and short-chain fatty acids and alcohol. The acidogenesis process that produces acetic acid, $_{CO2}$, and H_2 . The last stage of methanogenesis is the change of compounds into methane gas (CH_4) which is the biogas produced (Alkusma et al., 2016).

PT XYZ processing fresh oil palm fruit bunches with a production capacity of approximately 60 tons/hour, with a large production volume will produce a large amount of POME. POME is used as the main raw material for biogas which produces electrical energy for factory needs. The biogas production process in PT XYZ *produces* $_{CH4}$ levels that do not meet the desired standard of 60% while the value obtained is still 57%, so that the combustion process that occurs is not perfect in the engine. Based on the background above, it is necessary to conduct research on "The Effect of COD POME and pH POME as biogas raw materials on the CH4 $_{produced}$ ".

2. MATERIALS AND METHODS

2.1 Materials and tools

The materials used in this study were POME obtained from PT XYZ , and COD reagent. The tools used in this study were pH meter, photometer with COD, COD reactor, measuring flask, beaker and sample bottle.

2.2 Analysis Procedure

a. pH

Take a POME sample at the sampling point, collect it using a sample container, turn on the pH meter then rinse the electrode using distilled water, dip the pH meter into the sample container until the number on the pH meter is stable, after finishing rinse the electrode using distilled water and dry it.

b. *Chemical Oxygen Demand* (COD)

Prepare the tools and materials to be used, take 2.5 ml of POME sample into a 25 ml measuring flask, dilute with distilled water to the meniscus limit and homogenize, add the POME solution in the measuring flask into 0.2 ml of COD 1 reagent, add 0.2 ml of distilled water into COD 2 reagent as a blank, heat all reagents in the COD reactor at a temperature of 150 °Cfor 2 hours, cool the reagents to room temperature, then calculate the COD value on the photometer with COD.

2.3 Data Analysis Techniques

Data analysis to determine the estimated potential for biogas power generation (PLTBg) from POME can be done by calculating the potential for electrical energy based on the POME to Biogas Conversion Guidebook in Rahayu et al. (2015), the calculation stages are as follows:

1. Daily Liquid Waste Flow (m^3/day)

   = Processed TBS capacity × POME to TBS ratio ....(Equation 1)

2. COD *Loading* (kg COD/day)

   $= COD \times \text{Daily Wastewater Flow} \times \frac{kg}{1.000.000\,mg} \times \frac{1000\,L}{m^3}$ ……(Equation 2)

3. $_4$ production (Nm^3 CH_4/day)

   =COD *Loading* × CODeff × CH_4/COD ....(Equation 3)

4. Generating Capacity (MWe)

   $= \frac{produksi\ CH \times CH_{4,ev} \times Gen_{eff}}{28 \times 60 \times 60}$ (Equation 4)

In the calculation above, the results of the wastewater flow, COD *loading* , $_{CH4}$ production , and its generating capacity are obtained. With the amount of CH4 production obtained , the following is an explanation of the calculation of the potential for generating energy from biogas based on the POME conversion guidebook to biogas in table 1:

Table 1 Calculating Renewable Energy Potential

No	Parameter	Unit	Information
1	Operating Hours	Hours/Days Day/Year	Average number of factory operating hours per day Average number of days the factory operates in a year

	Operation Day		
2	Annual TBS	Tons of FFB/year M3 / ton TBS	The number of TBS processed in a year .
3	POME to FFB ratio COD	Mg/L	The ratio of the volume of POME produced per FFB processed POME: FFB (M3 POME)/(ton FFB) COD of liquid waste was analyzed using a COD meter.

Source: POME to Biogas Conversion Guidebook, Rahayu et al., 2015

This calculation is based on several operating parameter assumptions based on the POME to Biogas Conversion Guide book, the assumptions are in the following table.

Table 2 Assumptions in calculating Power

No	Parameter	Symbol	Mark	Unit	Information
1	Conversion ratio of CH4 to COD	CH_4 /COD	0.35	Nm^3 CH_4 /kg COD *removed*	The volume of methane produced per kg of COD removed from wastewater is theoretically
2	COD removal efficiency	COD_{eff}	80-95	%	COD percentage to be changed
3	Energy value of methane	$CH_{4,ev}$	35.7	MJ/ ^{m3}	Methane energy content
4	Average electrical efficiency	Gen_{eff}	38-42	%	The efficiency of gas engines in converting methane energy value into electrical energy.

Source: POME Conversion Handbook into Biogas, Rahayu et al., 2015

Data analysis to determine the effect of COD and pH of POME on the methane gas produced is regression analysis. Regression analysis is a statistical analysis tool that utilizes the relationship between two or more variables with the aim of making reliable estimates (predictions) to create the value of a variable (dependent or dependent variable or response variable), if the value of the variable related to it is known (free variable or independent variable or predictor variable) (Purba and Purba, 2022). The following is a simple linear regression formula to determine how much influence the COD and pH test variables have on the production of $CH4_{produced}$.

$y=a+bx$ ……………………(equation 5)

Where :

y: Consequence variable ($CH_{4\ Production}$)

x: Causal variable (COD POME)

a: Constant

b: Regression coefficient

Table 3 Interpretation of r values

Coefficient Interval	Relationship Level
0.80-1.00	Very strong
0.60-0.70	Strong
0.40-0.599	Strong enough
0.20-0.0399	Low
0.00-0.199	Very low

Source: Purba and Purba, 2022

3. RESULTS AND DISCUSSION

3.1 Data on COD POME, pH POME, and $CH_{4\ values}$

Table 4 is the data obtained after testing.

Table 4 Data from COD, pH, and CH4 analysis $_{results}$

Day/date/year	COD Feed (ppm)	pH of Feed	CH4 (%)
06/07/2023	41,980	6.53	58.88
07/13/2023	39,390	7.44	59.12
07/22/2023	46,820	6.94	58.88

03/08/2023	42,690	6.62	57.88
10/08/2023	43,850	6.99	57.87
08/24/2023	44,730	6.39	58.48
08/31/2023	45,810	6.68	58.02

Source: Research, 2023

3.2 Discussion

1. *Chemical Oxygen Demand* (COD) Analysis

COD analysis was carried out directly in the PT XYZ laboratory , the results of the test can be seen in table 3, the fluctuation of COD values is influenced by various factors. First, the incoming TBS is different every day, fluctuations also occur due to the processing of TBS which contains more water than the substrate itself (Yasmin et al., 2022), high COD values are caused by organic substances produced from the TBS processing process.

Fluctuations also occur because the source of POME sampling taken comes from *the cooling pond* (open pond) which is the second POME processing site at PT XYZ . Before POME is flowed to *the cooling pond* , POME is collected in a fatpit tank as a temporary storage place for liquid waste produced from various sources, namely from clarification stations, sterilization, and cleaning of the factory floor area. In the *cooling pond area* , there is a process of decreasing temperature, pH, sludge sedimentation, and residence time in the pond. In the study by Viena et al. (2023) it was stated that the factors that influence the presence of COD include the volume of the reactor or water, the residence time of solids, oxygen demand, and the volume of sludge, so that it can cause the high and low COD produced by POME.

Low COD is influenced by the concentration or dilution of wastewater and processing time, the more dilute the liquid waste, the lower the COD concentration and vice versa, the higher the COD value indicates a large amount of organic matter. POME containing high organic matter produces a thick POME substrate.

Biogas is the result of fermentation of organic materials POME by anaerobic bacteria. According to Widarti et al. (2015), COD is a food material for microorganisms for the hydrolysis process in the formation of acid anaerobically, the acid formed will be utilized by microorganisms in producing biogas. The formation of biogas is highly dependent on the chemical composition of the substrate or COD which is degraded into simple compounds in the form of gas (Winanti skk, 2019).

2. pH analysis

Table 4 shows that there are variations in pH values. Fluctuations in pH values are influenced by various factors, one of which is environmental factors. When sampling, the intensity of sunlight causes the temperature of POME to increase, causing a high pH and when it rains, the pH of POME can be low. The decrease in POME pH occurs due to the adsorption process of organic compounds contained in POME (Sidebang and Syafril, 2024). Meanwhile, the increase in POME pH is caused by the hot weather on that day and stable factory production, causing the pH to increase. In line with what Trisakti et al. (2021) said, as the temperature increases, the resulting pH will be high. Fluctuations in pH are also influenced by the organic content in POME. The increase in pH occurs because it comes from organic acids in POME (Ramadhan et al., 2021).

The pH required for biogas production at PT XYZ is around 6-7, in *the cooling pond* the POME pH is still 3.5-4.5, so POME is stirred with the biodigester effluent with the aim of increasing the pH of the feed before entering the biodigester lagoon.

3. Estimated Potential of PLTBg with a TBS Production Capacity of 60 tons/hour

Table 5 Estimated Calculation of Biogas Potential with a Capacity of 60 tons/hour

Day	COD POME (ppm)	COD *loading* (kg COD/day)	$_4$ production (Nm ^{3} CH $_4$ /day)	Generating Capacity (Mwe)
(2)	39,390	20717	6163,3	1,01
(1)	41.980	27706	8242,5	1,36
(4)	42.690	28175	8382	1,3
(5)	43.850	28941	8609,9	1,42
(6)	44.730	29521	8782,4	1,45
(7)	45.810	30234	8994,6	1,48
(3)	46.820	30901	9193	1,51

Source: Research, 2023

*Mwe: Mega Watt Electrical

Based on the table above, the COD concentration value affects the power plant capacity, where the highest power plant capacity is in weeks 3 and 7. COD produced through testing for 7 weeks, obtained COD *loading* or total COD load that enters *the digester lagoon*. With COD entered into the estimation formula, the COD *loading value*, CH_4 production , and electricity generation capacity generated from COD will be obtained. The high power plant capacity is influenced by the large COD value on that day where in weeks 3 and 7 the COD concentration values were 45,810 mg/L and 46,820 mg/L with the resulting power plant capacity of 1.48 MWe and 1.51 MWe. Based on Table 5, the linear regression equation is obtained in Figure 1.

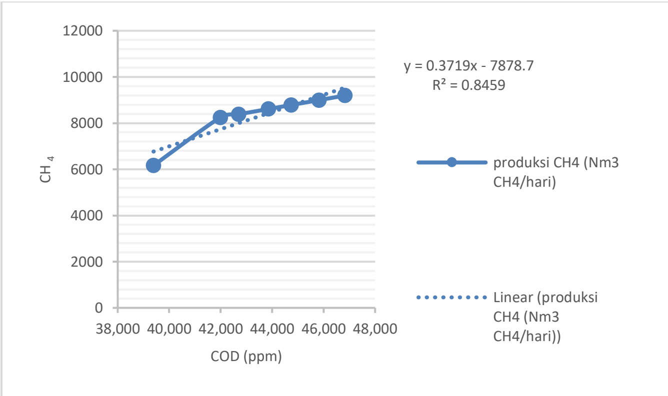

Figure 1 Linear Regression Equation of the Effect of COD on CH_4.

From Figure 1, an equation is obtained using the calculation formula in Equation 5 to determine the effect of COD on methane gas production (CH_4) at PT XYZ , along with the linear regression equation.

$$y = 0.3719x-7878.7$$

In the linear regression equation above, the R2 value is 0.8459, the R value is 0.91. So that the relationship between the linear regression equation between COD and the percentage of methane gas production (CH_4) is 0.91. According to Purba and Purba, 2022. the interpretation value of R *square* 0.8-1 is included in the very influential category, The linear regression equation can be obtained from the methane gas production (CH_4) produced from the COD obtained, so that the amount of methane gas production (CH_4) can be known by the linear regression equation. High COD concentration will affect the high production of methane gas (CH_4) produced. In the research of Sugiyono et al. (2019), high COD values will result in methane gas production (CH_4) in biogas with a large electrical capacity. To see the effect of COD on the calculation of the PLTBg potential estimate, you can see Figure 2.

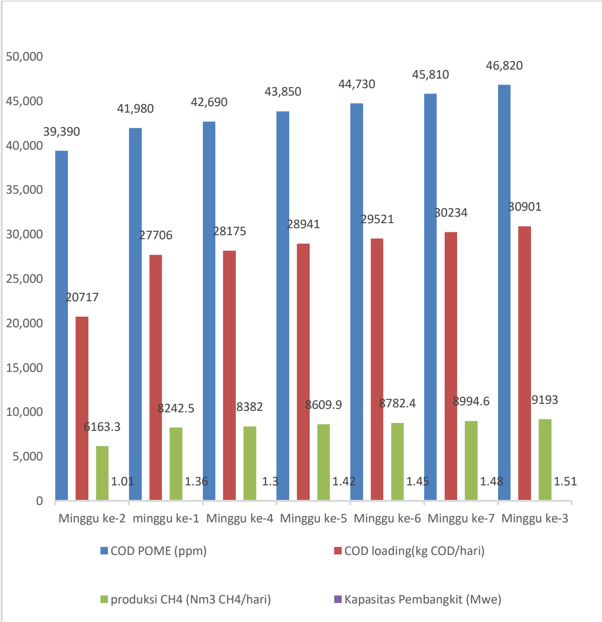

Figure 2 Estimation of Biogas Potential with a Capacity of 60 tons/hour

In Figure 2, it can be seen that the high COD concentration will affect COD *loading* , CH4 production , and generator capacity. The formation of biogas is highly dependent on the chemical composition of the substrate or COD produced in POME. High COD will affect the production of CH4 produced . In this study, it can be seen in the figure above that the higher the COD concentration, the higher the CH4 produced . high. The high CH4 produced will affect the amount of biogas energy produced. This means that the higher the CH4 content will affect the amount of energy content in the biogas and vice versa if the CH4 is small then the smaller the value of the biogas energy produced.

In addition to COD, other factors that affect biogas production include temperature, pH, and stirring in POME. According to Aprizal and Siregar (2019), factors that affect biogas production are substrate concentration (COD), organic fatty acid content, pH, carbon and nitrogen ratio, and temperature. If seen in Table 3, the potential for methane gas content in biogas at PT AMP *Plantation* is more than 50% of the methane gas produced. According to Ibrahim et al. (2018), if the methane gas content (CH4) in biogas is more than 50%, the biogas is suitable for use as fuel.

4. CONCLUSION

the Chemical Oxygen Demand (COD) parameter in POME, the highest concentration value was 46,820 ppm and the lowest concentration was 39,390 ppm. The factor that influences the fluctuation of the decrease in COD concentration in POME is the process of diluting wastewater in *the cooling pond* . The more dilute the liquid waste, the lower the COD concentration will be, indicating that organic substances are contained in small amounts. Meanwhile, based on the measurement of POME pH, fluctuations are caused by environmental conditions, but before the feed is put into the biodigester, *treatment* is carried out first with the aim of increasing the pH to 6-7 to match the optimal conditions of bacteria that work to decompose organic substances.

Based on the calculation results of the estimated potential of the Biogas Power Plant (PLTBg) with a production capacity of fresh fruit bunches (FFB) of 60 tons/hour, the high capacity of the plant is influenced by the large COD value, where the high COD value at a COD concentration of 46,820 ppm so that the large capacity of the plant is 1.51 Mwe. With the linear regression calculation formula to determine the effect of COD on methane gas (CH4) production at PT XYZ, namely Y = 0.3719x-7878.7 with an R value of 0.91, meaning that the COD value greatly affects the CH4 produced , but must also be in accordance with other factors that affect CH4 production such as pH, temperature, stirring and others.

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