The influence analysis of cow dung additional at biogas production of Palm Oil Mill Effluent (POME)

F Suryani\textsuperscript{1*}, M Madagaskar\textsuperscript{2} and S Aprilyanti\textsuperscript{1}

\textsuperscript{1}Department of Industrial Engineering, Faculty of Engineering, Universitas Tridinanti Palembang, Palembang, Sumatera Selatan, Indonesia
\textsuperscript{2}Department of Mechanical Engineering, Faculty of Engineering, Universitas Tridinanti Palembang, Palembang, Sumatera Selatan, Indonesia

*faizahsuryani@univ-tridinanti.ac.id

Abstract. Palm Oil Mill Effluent (POME) with the anaerobic fermentation method can be converted into biogas. The aim of this study was to determine the effect of adding cow dung to biogas production from POME. This study used a pure POME and mixture of POME and cow dung. The ratio used POME mixture: Cow dung 90:10, 80:20, and 70:30. This fermentation was carried out 25 days with a digester with a volume of 10 L which was equipped with a stirrer. Before fermentation, some measurements were done, initial measurements of pH, temperature, C levels, N levels, C / N ratio and total Volatile solid (TVS) POME and also a mixture of POME and cow dung to determine the chemical properties of the two materials. During the fermentation process, pH and temperature were reduced. The biogas produced was measured on the 10\textsuperscript{th}, 15\textsuperscript{th}, 20\textsuperscript{th} and 25\textsuperscript{th} day using a Gas Chromatography. From these measurements it was found that a mixture of POME and 70:30 cow manure on the 20\textsuperscript{th} day produced the greatest levels of biogas which was 300.25 ppm, whereas pure POME with the same time only produces 210.4 ppm. This means that the addition of cow dung can increase biogas production.

1. Introduction

Along with the increasing human population, the energy needs are also increasing. On the other hand, the available source of energy is getting less and less. Energy sources used by humans are still dominated by fossil fuels such as petroleum, coal and others. With these limitations, humans began to look for other energy resources, such as natural gas, geothermal, biomass energy, etc.

One of the potentially large and untapped wastes is palm oil liquid waste. This waste is the result of the process of making palm oil which still contains organic compounds and carbon, decomposition of organic compounds by anaerobic bacteria and can produce biogas [1].

POME is a waste from the process of making palm oil, POME is usually accommodated in a waste storage pond (lagoon) and deposited until the gas content contained therein evaporates. POME contains Methane (CH\textsubscript{4}) gas, which is one of the greenhouse gases that can cause climate change [2]. Besides containing Methane, POME also contains other compounds such as protein, fat, fiber and others. The content of POME can be seen in Table 1.
Table 1. Characteristics and components of POME [3].

| No. | Parameter                              | Unit | Range           |
|-----|----------------------------------------|------|-----------------|
| 1.  | Biological Oxygen Demand (BOD)         | mg/L | 20,000-30,000   |
| 2.  | Chemical Oxygen Demand (COD)           | mg/L | 40,000-60,000   |
| 3.  | Total Suspended Solid (TSS)            | mg/L | 15,000-40,000   |
| 4.  | Total Solid                            | mg/L | 30,000-70,000   |
| 5.  | Oil and Fat                            | mg/L | 5,000-7,000     |
| 6.  | NH₃-N                                 | mg/L | 30-40           |
| 7.  | Total N                                | mg/L | 500-800         |
| 8.  | Temperature                            | °C   | 90-140          |
| 9.  | pH                                     |      | 4-5             |

Because the methane content in POME reaches 40-70%, POME can be made into an alternative fuel, biogas. Biogas is a gas produced through the anaerobic fermentation process of organic materials. The general biogas content is shown in Table 2.

Table 2. Biogas contents [1].

| Component                      | Percentage |
|--------------------------------|------------|
| Methane (CH₄)                  | 55-75      |
| Carbon Dioxide (CO₂)           | 24-45      |
| Nitrogen (N₂)                  | 0-0.3      |
| Hydrogen (H₂)                  | 1-5        |
| Hydrogen Sulfide (H₂S)         | 0-3        |
| Oxygen (O₂)                    | 0.1-0.5    |

The content of methane in gas affects the quality of biogas, the higher biogas produced the better it will be. In addition, several factors also affect the biogas content produced, including:

a. Temperature
   High temperatures will usually produce good biogas. However, the ideal temperature for biogas formation is room temperature (20-40°C) with an optimum temperature of 28-30°C [4]. Since the methane-forming bacteria will thrive at this temperature.

b. Acid Level (pH)
   Methane-forming bacteria lives at an optimum pH of 6.7-7.5 [1], and 6.8-7.2 [5].

c. Stirring
   Stirring is one of the important things in producing biogas. Without stirring, the ingredients will not be homogeneous because there is still gas trapped.

d. C/N ratio
   Carbon and Nitrogen are the nutrients most needed by the methane-forming bacteria in anaerobic fermentation for the formation of enzymes that carry out metabolism. The lowest the C/N ratio, the more optimal the biogas produced [6].
   Cow dung is used in this study as a mixture ingredients in the manufacture of palm oil liquid waste. Cow dung is suitable as a source of biogas production and also as a biostarter in anaerobic fermentation process, because in cow dung contained methane gas-producing bacteria contained in the stomachs of ruminant animals [7].

There are several stages in processing palm oil liquid waste into biogas in the anaerobic fermentation process these stages are [8]:

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a. Hydrolysis
   At this stage complex compounds are broken down into simpler compounds. Complex compounds include proteins with the help of bacteria [1]. Bacteria that can be used in this stage are *Pseudomonas*, *Escherichia*, *Flavobacterium*, and *Alcaligenes* [9].

b. Acidogenic
   At this stage short-chain organic acids produced from fermentation and fatty acids obtained from fat hydrolysis will be fermented into acetic acid, H2, and CO2 by acetogenic bacteria [10].

c. Methanogenic
   Methanogenic stage is the final stage in the formation of biogas, where at this stage methane gas has begun to be formed as below:

   The general mechanisms of biogas formation is:

   $\text{Organic material} \xrightarrow{\text{Aerob Microorganism}} \text{CH}_4 + \text{CO}_2 + \text{H}_2 \text{NH}_3 [12]$ (1) 

   In making biogas, there are two types of digesters commonly used [11]. The two types of digesters are continuous feeding and batch Feeding.

2. Research methodology
   There are two types of fermentation in producing biogas, they are aerobic and anaerobic fermentation. Aerobic fermentation is fermentation which occurs by using oxygen, while anaerobic fermentation does not use oxygen [12].

2.1. Materials and research utilities
   The material used in this study was Palm Oil Mill Effluent (POME), a mixture of Palm Oil Liquid Waste (POME) and cow dung with a ratio of 90:10, 80:20, 70:30. NaOH as a pH regulator. The digester used was a stirred batch type digester with a volume of 10 L.

2.2. Research procedures
   This experiment was conducted by varying the fermentation time 10, 15, 20, and 30 days. Preparations made were SOME slurry mixed with cow dung according to predetermined ratios, then added NaOH to adjust the pH to match and then stirred until it was stirred homogeneous. Initial analysis was done to determine temperature, pH, Total Volatile Solid (TVS), organic C, N organic, and C/N ratio homogeneous raw materials were put into the digester that was given a stirrer. Stirring would be executed periodically to keep the mixture homogeneous. In this study periodically things affecting biogas production, they are:

   a. Temperature measurements
      Temperature measurements will be conducted on the day of service using a thermometer. Before the measurement was carried out stirring so that the substrate was evenly distributed.

   b. pH Measurement
      This measurement would be carried out on the day of observing the biogas content. Before measuring sludge in the digester, it would be stirred so that the measurements obtained were more even. The appropriate pH range to produce biogas-forming bacteria for life was 5-7. Over time, the pH value would continue to decline, it showed the levels of acetic acid in the material increases and could inhibit the formation of biogas [13]. Therefore, the longer the production of biogas would decrease.

3. Results and discussions

3.1. Pre-treatment analysis
   Before the mixture of POME and cow dung was put into the digester, initial measurements were made to find out the chemical composition in POME and the mixture of POME + cow dung. Initial analysis of POME is shown in Table 3 below.
Table 3. Chemical composition of POME.

| Parameter     | Value       |
|---------------|-------------|
| TVS           | 1.9%        |
| Carbon (mg/l) | 23,000      |
| Nitrogen (mg/l) | 737.12   |
| pH            | 6           |
| C/N Ratio     | 31.2        |

The above table showed that the C/N POME ratio was quite high, it would affect the lack of Nitrogen in the substrate. Nitrogen deficiency inhibits the formation of proteins needed by bacteria to grow [1].

To reduce the C/N ratio in POME, additional ingredients were needed, which in this study used cow dung. Cow dung was chosen because besides having a low C/N ratio also contained three important components in the formation of biogas; carbohydrates, proteins and fats which could be converted into Volatile Fatty Acid (VFA) to produce Methane (CH₄) gas.

In this study, an initial analysis was executed on the composition of the organic material included in the digester, this was done to determine the change in the C/N ratio of the mixture between POME and cow dung.

Table 4. Composition of mixture POME and cow dung.

| Parameter     | 1    | 2    | 3    | 4    |
|---------------|------|------|------|------|
| TVS           | 1.9% | 2.4% | 2.9% | 3.3% |
| pH            | 6    | 5.9  | 6    | 6.3  |
| Carbon (mg/l) | 23,000| 17,100| 19,080| 18,200|
| Nitrogen (mg/l) | 737.12| 650.12| 670.45| 700.25|
| C/N Ratio     | 31.2 | 26.30| 28.45| 25.99|

**Information:**
1. POME100%;
2. Mixture 90% POME, 10% Cow Dung;
3. Mixture 80% POME, 20% Cow Dung;
4. Mixture 7% POME, 30% Cow Dung

Table 4 shows that POME had been mixed with the addition of cow dung, the C/N ratio decreases. Since cow dung waste had a low C/N ratio, which was around 18. Waste that came from animal dung usually contained C levels which were lower than N levels. So, when mixed with palm oil waste would produce a C/N ratio which was more suitable for biogas formation [14]. Levels of carbon (C) and nitrogen (N) of the material were measured at the beginning of the study using fresh substrate material.

Total Volatile solid (TVS) was an organic solid contained in POME that could be converted into biogas. The higher the value of TVS, the more biogas production would be. TVS levels had increased when POME was mixed with cow dung. Pure TVS POME was only 1.9% while with cow dung mixture 10% TVS increased to 2.4%. The increasing value of TVS was caused by cow dung having a TVS value of 75.85% [15]. The pH value in pure POME and a mixture of POME and cow dung was still in the pH range suitable for making biogas.

### 3.2. Biogas measurement

Figure 1 shows concentration of biogas after the biogas content was measured using a Gas Chromatograph. It was found that the highest gas content was obtained from the mixing ratio of POME with cow dung 70:30 on the 20th day. This is because the C/N ratio was the lowest among other mixes, which was 25.99. The optimal ratio for biogas formation was 20: 1 or 30: 1.

In the first 4 days, biogas had not formed yet, since the gas storage balloon that still looks flat. Gas began to form on the 5th day and slowly continued to increase along with the 20th day at 300, 35 ppm, and decrease at day 25th. In addition, the pH C/N ratio also affected the formation of biogas. The expected optimal ratio was 20: 1. While the lowest biogas levels were obtained in pure POME without being mixed with cow dung on the 10th day of observation that was equal to 180.6 ppm. This
indicated that POME has a large C/N ratio so that the biogas produced was not as much as POME mixture with cow dung.

One of the influential factors in the formation of biogas was stirring. Stirring was done to make the material evenly mixed so that it became homogeneous. Homogeneous material would make the fermentation process take place more optimally [13]. In addition stirring was done to avoid the accumulation of material so that methanogenic bacteria could not break down organic compounds, thus inhibiting the anaerobic fermentation process. Methanogenic bacteria were bacteria which had a role in the formation of biogas. These methanogen bacteria used the results of acidogenic processes such as carbon dioxide (CO$_2$), hydrogen (H$_2$) and format acetate as raw materials to produce methane gas [16]. On the other hand, cow dung contained cellulose and lignin which was difficult to degrade so that the hydrolysis stage lasted for quite a long time.

3.3. Temperature measurement
Temperature (temperature) was measured on the day of observation, namely the 10, 15, 20, 25 days using a thermometer mounted on the digester. Since the conditions inside the digester were known with certainty. In anaerobic fermentation, normally has two types temperature range, namely mesophilic level with temperature range of 25-40°C and thermophilic level for temperature range over 40°C [17]. The optimum temperature for methanogenic bacteria was room temperature. The data during the study the temperature obtained from measurements ranging from 24-28°C was still ideal because it is still below 30°C. Pure POME sludge has a temperature range between 24.5-26°C. The mixture of POME and cow dung with a ratio of 9:10 had a temperature range of 24.7-28°C. The 80:20 ratio has a temperature range of 25-29°C. The 70:30 ratio has a temperature range of 25-29°C. The 70:30 ratio has a temperature range of 25-29°C.

3.4. pH measurement
Measurement of pH. Similar to temperature (temperature), the acidity or pH was also measured on the day of observation. The pH level measured during the study ranged 5.5-7 still qualifying for bacteria because the ideal pH range was 5-7. pH is one of the supporting factors in the growth of microbes to produce biogas [18]. This pH condition is influential on the growth of anaerobic microbes in producing biogas, especially methane gas. By observing changes in pH level, the growth of microorganism in the digester takes optimally [19].

4. Conclusion
The highest level of biogas was obtained from the mixing ratio of POME and cow dung 70%: 30% on the 20th day that was 300.25 ppm. In addition to this mixing ratio, the C/N ratio decreased, so that it approached the optimal conditions to produce good biogas. While the lowest biogas levels were obtained from pure POME fermentation on the 10th day. It was 180.16 ppm. This means that the addition of cow dung can increase biogas production. The results of substrate temperature analysis show temperatures of 25 - 29°C where the optimal temperature for microorganisms is below 3°C. pH
measurement results during the process show the pH is in the range of 5.5-7. This is in accordance with the pH range of microorganisms to grow and develop is 5-7.

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