Effect of recycle ratio on methanogenic anaerobic digestion of palm oil mill effluent (POME) in a stirred tank reactor assisted by ultrafiltration membrane into biogas in transition conditions

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Abstract. The purpose of this study is to increase the conversion of biogas production using digester type CSTR by recycling the effluent through ultrafiltration membrane at transition conditions (45°C). In this research was investigated the effect of recycle ratio on the pH profile, alkalinity, production, and biogas composition produced. Initially, the suitable loading up was determined by varying HRT at 25, 15, 10, and 6 days in 2 L CSTR with agitation rate 250 rpm, pH 7 ± 0.2, and at temperature of 45°C. Furthermore, the effect of the recycle ratio was determined by varying the recycle ratio, i.e. 0, 15, and 25%. Analysis of total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), and chemical oxygen demand (COD) were carried out to study the changes of organic compounds that were converted into biogas. Gas analysis is also carried out by measuring the volume and composition of the biogas produced. The highest total biogas production was achieved at 25% recycle ratio of 33.15 x 10² L/g.VS.day, with the composition of methane (CH₄), carbon dioxide (CO₂), and hydrogen sulfide (H₂S) were 79; 19; and 0.006% respectively.

1. Introduction

The palm oil industry is one of the major industries in Indonesia [1][2]. As the world's largest producer of crude palm oil (CPO), with total production reached around 41.5 million tons/year produced from oil palm plantations with an area of 11.6 million hectares in 2018. For each ton of fresh fruit bunch (FFB) produced, will produce an average of 120-200 kg CPO, 230-250 kg of empty bunches, 130-150 kg of fiber, 60-65 kg of shells, 55-60 kg of kernels, and 0.7 m³ of palm oil mill effluent (POME) [3]. To process one ton of FFB, usually takes around 5-7 tons of water. From the amount of water, 50-79% will end up as POME [4]. That means, for every ton of CPO produced will produce 2.4-3.7 tons of POME [5]. Therefore, POME is produced in large quantities where in 2018 it is estimated that POME production is around 97-153.5 million tons.

Fresh POME are brownish, thick, and colloidal, contains 95-96% water, 4-5% total solids (TS), 2-4% suspended solids (SS), and 0.6-0.7% oil and fat at 80-90°C [6]. POME includes in acid groups that contains a number of strong amino acids, inorganic nutrients, short fibers, nitrogen, free organic acids and carbohydrates [7]. POME has a low pH, contains high suspended solids (SS), nitrogen, chemical oxygen demand (COD) and biological oxygen demand (BOD) [8] so it is called as high strength organic pollutant. Therefore, the POME is processed to reduce COD value by converting into biogas through a methanogenic anaerobic digestion process [9].

In multi-stage anaerobic digestion (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) the degradation of organic matter and the formation of CH₄ and CO₂ occur through the activity of microorganisms. Fresh POME is first converted to volatile fatty acids (VFAs) by acid-forming
bacteria and then converted to CH\textsubscript{4} and CO\textsubscript{2} in the anaerobic digestion process. This process produces biogas such as biomethane and biohydrogen through rapid degradation of organic compounds from POME [10][11]. In anaerobic digestion of POME, one of the most recommended digesters is the continuous stirred tank reactor (CSTR) [12]. CSTR is a stirred tank containing immobilized biomass. The substrate is pumped into the reactor continuously, and effluent are produced at the same time. In POME processing, Trisakti et al (2016) have successfully used CSTR with a COD removal efficiency of 81% and maximum methane production in biogas of 76.6% [13].

Along with the era development, the use of CSTR reactors has increasingly innovated. One of them is the use of membranes to help maintain biomass residence time in CSTR. The biomass residence time in CSTR increases because the membrane output i.e retentate will be recycled to CSTR. According to Ferguson the benefit of waste recycling is to reduce the addition of bases needed so that it will minimize the total operational costs of the process due to the reduction in the addition of bicarbonate salt [14]. Biogas production using an anaerobic reactor assisted by ultrafiltration membrane (UF membrane) is aimed to increase the conversion of biogas produced [12]. Research conducted by Abdurrahman et al (2011) was the use of membranes to recycle retentate from effluent of stirred reactors made from POME in biogas production. The results showed that increasing the recycle feed will increase the value of microbial growth, VS decomposition, COD decomposition, and the amount of biogas production. However, the best methane composition was obtained at the lowest recycle ratio and then decreases with increasing recycle ratio [15].

2. Materials and methods

2.1. Characteristics of POME
Fresh POME as the main raw material is obtained from the Rambutan palm oil mill (POM), PTPN III located in North Sumatra, Indonesia. The POME was taken from the fat-pit at a wastewater treatment plant and stored in a 20 L plastic container. The raw material was taken to the laboratory, stirred evenly, then put into a 1 L plastic bottle, and stored in a refrigerator at 4°C.

Starter as a source of microbes taken from anaerobic methanogenic digester 3,000 L at the Biogas Pilot Plant, Universitas Sumatera Utara, Medan, Indonesia. Sodium bicarbonate (NaHCO\textsubscript{3}) was used to adjust the pH and chemicals for analysis used were hydrochloric acid (HCl), potassium dichromate (K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}), mercury (II) sulfate (HgSO\textsubscript{4}), silver sulfate (Ag\textsubscript{2}SO\textsubscript{4}), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), ammonium sulfate (FAS), and ferroin. Before being used as feed into CSTR, POME was analyzed first as presented in Table 1.

| Parameter                                | Unit   | Results     | Methods     |
|------------------------------------------|--------|-------------|-------------|
| **pH**                                   | -      | 3.90-4.50   | APHA 4500-H |
| Chemical Oxygen Demand (COD)             | mg/L   | 40.288      | APHA 5220B  |
| Total Solid (TS)                         | mg/L   | 14,000-28,000 | APHA 2540B  |
| Volatile Solid (VS)                      | mg/L   | 10,000-26,000 | APHA 2540E  |
| Total Suspended Solid (TSS)              | mg/L   | 21,040-25,160 | APHA 2540D  |
| Volatile Suspended Solid (VSS)           | mg/L   | 9,040-17,160 | APHA 2540E  |
| Soluble Chemical Oxygen Demand (SCOD)    | mg/L   | 19,424      | APHA 5220B  |

2.2. Experiments
The experimental setup used in this research is shown in Figure 1. The CSTR type was EYELA model MBF 300ME with working volume is 2 L. The fermenter was equipped with an integrated on-line temperature and pH data storage system. 80% fresh POME and 20% starter from the pilot plant were put into 2 L CSTR. PH was adjusted at 7.0 ± 0.2, agitation 250 rpm, and transition condition (45°C).
First, the experiment was conducted to determine the suitable loading up to obtain an HRT target, which is 6 days. Next, the experiment continued with variation of the recycle ratio which was first passed through the ultrafiltration membrane i.e. 0, 15, and 25%. Data collected from liquids every day were pH, M-Alkalinity, TS, VS, TSS, and VSS, while COD and SCOD were analyzed every 3 days according to the APHA (1999) standard method for water and wastewater [16]. Measurement of biogas volume and composition (CH$_4$, CO$_2$, and H$_2$S content) were carried out every 3 days by using the SAZQ Biogas Analyzer.

The membrane used is a membrane ultrafiltration (UF) roll type was placed in a cartridge as shown in Figure 2. This membrane has a cross flow, with ability to filter particles from 0.1 to 0.001 microns. In this type of flow there are two outflows namely permeate and retentate. In this study, retentate or effluent that does not pass through the membrane will be recycled back to CSTR, while permeate will be discharged as effluent with low waste parameter values.

![Experimental setup of biogas production assisted by UF membrane](image1.png)

**Figure 1.** Experimental setup of biogas production assisted by UF membrane

![Membrane ultrafiltration](image2.png)

**Figure 2.** Membrane ultrafiltration

2.3. Data collection
Data collected during the experiment were pH, M-alkalinity, TS, VS, TSS, VSS, COD, and SCOD based on the American Public Health and Association standard methods (APHA) for water and wastewater as presented in Table 2. While the biogas composition data was measured using a portable biogas detector type SAZQ Biogas Analyzer, manufactured by Beijing Shi’an Technology Instrument Ltd., China.
Table 2. Analysis methods of data collection

| Parameter                        | Unit  | Methods          |
|----------------------------------|-------|------------------|
| pH                               | -     | APHA 4500-H      |
| Chemical Oxygen Demand (COD)     | mg/L  | APHA 5220B       |
| Total Solid (TS)                 | mg/L  | APHA 2540B       |
| Volatile Solid (VS)              | mg/L  | APHA 2540E       |
| Total Suspended Solid (TSS)      | mg/L  | APHA 2540D       |
| Volatile Suspended Solid (VSS)   | mg/L  | APHA 2540E       |
| Soluble Chemical Oxygen Demand (SCOD) | mg/L | APHA 5220B |

3. Results and discussions

3.1. pH and alkalinity profile during the loading up process

The pH and alkalinity profile during the loading up process was presented in Figure 3. The loading up process is very dependent on the pH conditions. The pH is adjusted according to the conditions desired by methanogenic bacteria so that the anaerobic digestion process can run optimally. The optimum pH conditions for produced the best biogas with a range 6.6 - 7.6 [17]. Figure 3 showed that the pH profile during the loading up process is relatively stable with a range 6.9 - 7.6. The average pH values of HRT 25, 15, 10, and 6 were 7.35 ± 0.03; 67.04 ± 0.22; 7.06 ± 0.14; and 7.12 ± 0.06 respectively.

The pH of the feed was maintained constant by addition of NaHCO₃, so that a stable pH profile is obtained, which is 7 ± 0.2 as desired. As a result, the alkalinity value fluctuated along with the addition of NaHCO₃ into the fermenter due to provision of new feed with a lower pH of 4.9 [18]. Although the alkalinity profile fluctuates during the process, it is still within a reasonable range of 2500-5000 mg/L [19]. The average alkalinity values of HRT 25, 15, 10, and 6 were 3,550.00 ± 183.14; 3,185.71 ± 328.61; 3,250.00 ± 378.02; and 3,286.67 ± 411.60 mg/L respectively.

![Figure 3. The pH and alkalinity profile during the loading up process](image)

3.2. Effect of recycle ratio on alkalinity

In the methanogenic anaerobic digestion process, alkalinity is to show the stability of process in the digester such as the breakdown of organic compounds by microbes into biogas [20]. The effect of recycle ratio on alkalinity and average alkalinity were presented in Figures 4 and 5. During the process, the pH of the feed was maintained at 7 ± 0.2 by addition of NaHCO₃ to the feed so that alkalinity profile during the process at recycle ratio of 0, 15, and 25% tend to be stable and the
alkalinity value is still within a reasonable range of the methanogenic anaerobic digestion process of 2500-5000 mg/L [21][22]. Meanwhile, the average alkalinity at recycle ratio of 0, 15, and 25% were 3,286.67 ± 202; 3,093.33 ± 187; and 3,073.33 ± 235 mg/L respectively.

![Figure 4. Effect of recycle ratio on alkalinity](image1)

![Figure 5. Effect of recycle ratio on average alkalinity](image2)

### 3.3. Effect of recycle ratio on production and composition of biogas

The effect of the recycle ratio on biogas production expressed in liters divided by grams of volatile solid decomposed during the process was shown in Figure 6. The average biogas production at recycle ratios of 0, 15, and 25% were $14.33 \times 10^{-2}$, $20.61 \times 10^{-2}$, and $33.15 \times 10^{-2}$ L/g.VS.day. The 25% recycle ratio shows the highest amount of biogas production. According to Abdurrahman et al (2017) biogas production using ultrafiltration membranes has increased along increasing of recycle feed from membrane, where biogas production has increased from 280.5 L/day to 540 L/day on increasing recycle from 0% to 25% [23].
Figure 6. Effect of recycle ratio on total biogas production

The composition of CH$_4$, CO$_2$, and H$_2$S contained in the total biogas produced during the process was presented in Figure 7. The average composition of CH$_4$ at recycle ratio of 0, 15, and 25% were 81, 85, and 79%, respectively. The average composition of CO$_2$ at recycle ratio of 0, 15, and 25% were 18, 14, and 19%, respectively. While the average composition of H$_2$S is relatively small, where at recycle ratio of 0, 15, and 25% were 0.02, 0.007, and 0.104% respectively. While in previous studies of biogas production through the methanogenesis using CSTR with agitation of 100 rpm at thermophilic conditions produced biogas with the composition of CH$_4$, CO$_2$, and H$_2$S were 62.25, 37.75, and 0% respectively [24].

Figure 7. Effect of recycle ratio on biogas composition

4. Conclusions
The results showed that the pH and alkalinity were still within the range of methanogenic anaerobic digestion process. The pH value during the process was still within in the range of 7 ± 0.2 where the alkalinity was in the range of 3,000-4,500 mg/L. The highest total biogas production was achieved at 25% recycle ratio of 33.15 x 10$^2$ L/g.VS.day, with the composition of methane (CH$_4$), carbon dioxide (CO$_2$) and hydrogen sulfide (H$_2$S) were 79; 19; and 0.006% respectively.
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