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Evaluation of the Stability of the Anaerobic Digestion Process of POME Based on the Correlation of VFA, Alkalinity and Methane Content

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ABSTRACT

Palm Oil Mill Effluent (POME) contains a high organic load and requires effective treatment to prevent environmental pollution while enabling energy recovery. Anaerobic digestion is widely applied for POME treatment due to its ability to reduce organic pollutants and produce methane-rich biogas; however, its performance is highly dependent on process stability. This study aims to evaluate the stability of the anaerobic digestion process of POME through correlation analysis among volatile fatty acids (VFA), total alkalinity (TA), suspended solids (SS), and methane content (CH_4) using field operational data. The study was conducted at an industrial-scale biogas plant treating POME, where slurry samples were collected periodically from multiple biodigester units representing different digestion stages. VFA and TA were analyzed using acid–base titration, SS by gravimetric method, and methane content using a gas analyzer. The results show that the anaerobic digestion process operated under stable mesophilic conditions (35 ± 2 °C) with reactor pH maintained in the optimal range of 6.8–7.5. VFA concentrations remained relatively low (approximately 480–510 mg/L), supported by sufficient alkalinity (about 5,600 mg/L as $CaCO_3$), resulting in a low VFA/TA ratio (~0.09), indicating stable process conditions. A significant reduction in COD from approximately 41,700 ppm in the influent to about 7,200 ppm in the effluent was achieved, corresponding to a COD removal efficiency of 83%. Methane content in the biogas remained stable at ≥55%, supporting effective energy utilization without flaring. These results demonstrate that maintaining a balanced relationship among VFA, alkalinity, suspended solids, and operating conditions is essential for ensuring stable anaerobic digestion and consistent biogas quality in industrial-scale POME treatment systems.

Keywords
Biogas, Palm Oil Mill Effluent (POME), anaerobic digestion, volatile fatty acids (VFA), total alkalinity (TA), methane

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INTRODUCTION

The palm oil industry produces large volumes of liquid waste called Palm Oil Mill Effluent (POME), which has a high organic load reflected by its elevated Chemical Oxygen Demand (COD). If unmanaged, POME can cause significant environmental pollution. Anaerobic digestion is widely used to treat POME, reducing pollutants while generating methane-rich biogas as renewable energy [1]. However, successful digestion depends not only on COD reduction but also on the stability of biological processes within the biodigester [2].

In operational practice, the main challenge in anaerobic digesters treating POME is the occurrence of imbalance between the acidogenesis and methanogenesis stages. This imbalance can lead to the accumulation of volatile fatty acids (VFA), a decrease in pH, inhibition of methanogenic microbial activity, and a decline in the quality of the biogas produced [3]. Therefore, controlling and evaluating process stability is a crucial aspect to ensure the sustainability of biodigester operation, particularly in continuously operated industrial-scale systems.

Several parameters are widely used to evaluate the stability of the anaerobic digestion process, including VFA, total alkalinity (TA), and the VFA/TA ratio, which reflects the balance between acid formation and the buffering capacity of the system. In addition to these chemical parameters, suspended solids (SS) play an important role in representing organic solids degradation, active biomass concentration, and physical dynamics within the digester, including decompaction phenomena [4]. Meanwhile, the methane (CH_4) content in biogas serves as a final performance indicator that directly reflects the success of the methanogenesis stage and the overall effectiveness of the anaerobic digestion process [5].

Although numerous studies have reported the performance of anaerobic digestion of POME, most have focused primarily on COD removal efficiency or quantitative increases in biogas production, generally based on laboratory-scale or pilot-scale experiments. Studies that specifically evaluate process stability through a correlational approach between VFA, alkalinity, and SS in relation to methane content stability, particularly using field operational data, remain relatively limited. In fact, operational data represent real system conditions influenced by variations in feed characteristics, temperature, pH, and complex biological dynamics [6].

Based on this background, this study aims to evaluate the stability of the anaerobic digestion process of POME through correlation analysis among VFA, total alkalinity, suspended solids, and methane content (CH_4) in continuously operated biodigesters. This study utilizes field operational data to relate biological stability parameters to the quality of the biogas produced, thereby providing a more comprehensive understanding of the dynamics of POME anaerobic digestion as a basis for evaluation and control of sustainable industrial-scale biogas systems.

METHOD

Data collection was conducted at a biogas treatment facility based on the anaerobic digestion of Palm Oil Mill Effluent (POME), which is equipped with several biodigester units (BDT). The observations focused on evaluating the stability of the anaerobic process and the quality of the biogas using the parameters Volatile Fatty Acids (VFA), Total Alkalinity (TA), the VFA/TA ratio, Suspended Solids (SS), and methane content (CH_4). Samples were collected periodically under normal operating conditions.

Slurry samples were collected from BDT 1, BDT 3, and BDT 4, which respectively represent the initial, intermediate, and final stages of the anaerobic digestion process. Samples were taken through sampling valves, placed in airtight bottles, labeled with the sampling time and location, and immediately analyzed to minimize changes in sample characteristics.

VFA and TA analyses were performed using acid–base titration methods and expressed as mg/L as CH_3COOH and mg/L as $CaCO_3$, respectively, while the VFA/TA ratio was used as an indicator of process stability. The SS parameter was analyzed using the gravimetric method and expressed in mg/L to evaluate solids degradation. Methane content (CH_4) was measured in the biogas stream exiting the biodigester using a gas analyzer through a sampling port on the biogas pipeline after stable flow conditions were achieved. The CH_4 concentration was expressed as a percentage by volume (% v/v). All measurements were conducted with instrument calibration using standard gases prior to analysis.

Anaerobic Digestion of POME

Anaerobic digestion is a biological process in which organic matter is decomposed by microorganisms under oxygen-free conditions through several sequential and interrelated stages, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis [7]. During the hydrolysis stage, complex organic compounds such as carbohydrates, proteins, and lipids are broken down into simpler compounds that can be utilized by microorganisms in subsequent stages [8]. Palm Oil Mill Effluent (POME) contains high levels of organic matter and nutrients, particularly in the form of Chemical Oxygen Demand (COD) and biodegradable compounds, making it highly suitable for treatment using anaerobic digestion as a waste management method while simultaneously producing renewable energy in the form of biogas [9]. The success of anaerobic digestion is strongly dependent on the balance among these stages, as disturbances at any stage such as acid accumulation during acidogenesis or imbalance during methanogenesis can lead to pH reduction, inhibition of methanogenic bacterial activity, and ultimately a decline in overall system performance in terms of both process stability and methane production. The process flow is shown in Figure 1.

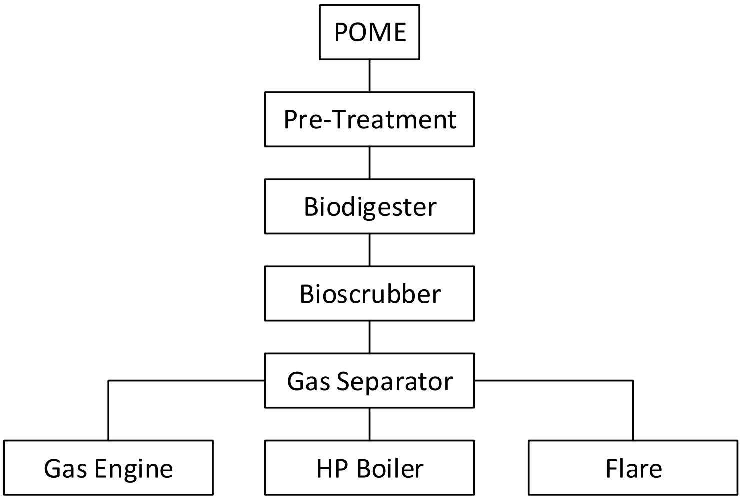

Figure 1. Process Flow Diagram of the POME-Based Biogas Production System

Volatile Fatty Acids (VFA), Total Alkalinity (TA), and VFA/TA Ratio

Volatile Fatty Acids (VFA) are intermediate products formed during the acidogenesis and acetogenesis stages of the anaerobic digestion process, whereas Total Alkalinity (TA) reflects the buffering capacity of the system to neutralize the acids produced. The balance between VFA formation and alkalinity buffering capacity plays a crucial role in maintaining digester stability and sustaining the activity of methanogenic microorganisms [10]. Therefore, the ratio of VFA to Total Alkalinity (VFA/TA) is widely used as a key indicator of anaerobic process stability, as it represents the relationship between the rate of acid formation and the system's ability to maintain conditions that are optimal for methanogenesis. A low VFA/TA ratio indicates a stable and well-balanced digester condition, while an increase in this ratio is often associated with the risk of acidification and a decline in methane production performance [11].

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is used as a primary parameter to represent the organic matter content in Palm Oil Mill Effluent (POME) that can potentially be degraded during the anaerobic digestion process. A decrease in COD values and the magnitude of COD removal indicate the degradation of complex organic compounds into simpler compounds, which are subsequently converted into biogas through the stages of hydrolysis, acidogenesis, acetogenesis, and methanogenesis [12]. The COD removal value can also be used as an indicator of process performance, where percentages below 70% indicate that the process has not yet operated optimally, while values in the range of 70–85% suggest that the anaerobic digestion process is stable and effective. High COD removal reflects efficient utilization of the biodegradable organic fraction by microorganisms, supported by favorable operating conditions, particularly temperature and pH maintained within their optimum ranges [13].

$$COD\ removal = \frac{COD\ in - COD\ out}{COD\ in} x\ 100\% \quad (1)$$

Methanogenesis and Methane Content (CH_4)

Methanogenesis is the final stage of anaerobic digestion in which methane is produced as the main product. The methane (CH_4) content in biogas indicates the success of organic matter conversion into energy. The stability of methanogenesis is strongly influenced by the digester's environmental conditions, including the balance of volatile fatty acids (VFA), the alkalinity buffering capacity, and substrate availability as reflected by suspended solids (SS) levels. Therefore, the CH_4 content is commonly used as an indicator of the overall performance of the anaerobic digestion system.

RESULT AND DISCUSSION

The results of this study indicate that the anaerobic digestion process of Palm Oil Mill Effluent (POME) operated in a stable and well-controlled manner throughout the observation period, as evidenced by the maintenance of key operational and chemical parameters. These parameters include temperature, pH, Chemical Oxygen Demand (COD), volatile fatty acids (VFA), total alkalinity (TA), suspended solids (SS), and methane (CH_4) content in the biogas. The interrelationship among these parameters reflects a balanced microbial activity across all stages of anaerobic digestion, from hydrolysis to methanogenesis.

During operation, the reactor temperature was maintained within a relatively stable mesophilic range of 35 ± 2 °C. This condition is highly favorable for anaerobic microorganisms, particularly methanogenic microorganisms, which exhibit optimal activity under mesophilic conditions. In addition, the reactor pH was maintained within the range of 6.8–7.5, which is considered optimal for the growth and activity of methanogens. The stability of temperature and pH indicates that the system possesses sufficient buffering capacity to withstand operational fluctuations, thereby allowing the biological processes to proceed continuously without significant disturbances [14]. The summary of anaerobic digestion process parameters is shown in Table 1.

Table 1. Summary of Anaerobic Digestion Process Parameters

Parameter	Role in the Process	Indication of Stable Condition
Temperature	Controls microbial activity	Stable mesophilic (35 ± 2 °C)
pH	Determines methanogen viability	6,8 – 7,5
COD	Indicator of organic loading	41.700-7.200 mg/L
VFA	Intermediate product of acid fermentation	No excessive accumulation
TA	pH buffering capacity	Sufficient to neutralize volatile acids
VFA/TA Ratio	Stability indicator	< 0,4
CH_4	Performance indicator	≥ 55%

The effectiveness of organic matter degradation during the anaerobic digestion process is indicated by a significant reduction in COD values from the influent to the effluent of the biodigester. The decrease in COD demonstrates that complex organic compounds in POME were successfully broken down into simpler compounds, which were subsequently utilized as substrates for biogas production. A high COD removal efficiency indicates that the biodegradable organic fraction was optimally utilized by anaerobic microorganisms .

The dynamics of intermediate compound formation and consumption during anaerobic digestion are reflected in changes in volatile fatty acid (VFA) concentrations and total alkalinity (TA) values. In the early stage of the process, VFA formation occurred due to the dominance of acidogenic bacterial activity. However, this increase in VFA was not accompanied by a significant decrease in pH because it was supported by adequate buffering capacity of the system, as indicated by relatively stable TA values. This balance between acid formation and alkalinity buffering capacity plays a crucial role in maintaining digester stability and preventing acidification.

The stability of the relationship between VFA and TA was evaluated using the VFA/TA ratio, which remained below the threshold value of 0.4 throughout the observation period. This ratio indicates that the anaerobic digestion process operated under safe conditions and supported the sustainability of the methanogenesis stage. Under these conditions, organic acids produced during fermentation could be effectively converted into methane and carbon dioxide by methanogenic microorganisms.

The success of the methanogenesis stage is reflected by the methane (CH_4) content in the biogas, which reached values of ≥55%. The relatively high and stable methane content indicates that the conversion of intermediate compounds into methane occurred efficiently. In addition, stable suspended solids (SS) values indicate that active biomass within the reactor was well maintained, allowing microbial populations, particularly methanogens, to support long-term process stability. From an energy utilization perspective, total biogas production during the operating period was recorded at 23,358 Nm^3, equivalent to 24,450 m^3 under actual conditions. All of the biogas produced was fully utilized without flaring, either for gas engine operation or for a high-pressure (HP) boiler. Biogas utilization in the gas engine generated 40,022 kWh of electrical energy, while the remaining biogas was used as boiler fuel to support plant utility demands. This condition indicates that a good balance between biogas production and utilization was achieved.

Overall, the results of this study demonstrate that the stability of process parameters including temperature, pH, VFA, alkalinity, SS, and COD plays a critical role in sustaining methanogenesis and ensuring the quality of the biogas produced. Proper management of these parameters is therefore essential for maintaining the stability of the anaerobic digestion process of POME [15].

Feeding POME

Biogas formation from Palm Oil Mill Effluent (POME) through the stages of hydrolysis, acidogenesis, acetogenesis, and methanogenesis is highly dependent on the balance between the formation and consumption of volatile fatty acids.

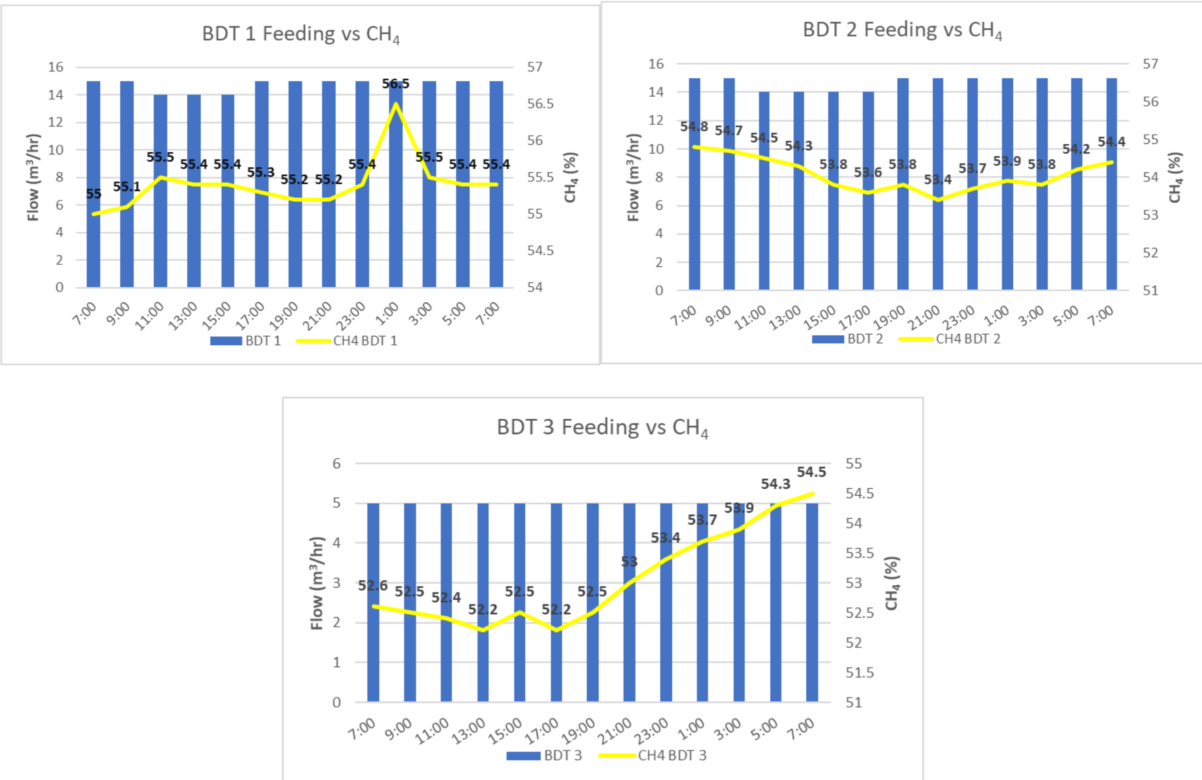

Figure 2. Process Flow Diagram of the POME-Based Biogas Production System

The POME feeding data shown in Figure 2 indicate that the feed rates at BDT 1 and BDT 2 were in the range of 14–15 (units according to operational conditions), while BDT 3 received a lower and relatively constant feed rate. The POME fed into the system had a Chemical Oxygen Demand (COD) concentration of approximately 41,700 ppm, indicating a high organic content and substantial potential as a substrate for biogas production. The relatively small variation in feeding rates suggests stable and well-controlled operating conditions throughout the observation period.

After undergoing the anaerobic digestion process, the COD of the biodigester effluent was recorded at approximately 7,200 ppm, indicating a significant reduction in COD. This decrease demonstrates that the majority of organic compounds in POME were degraded by anaerobic microbial activity. Quantitatively, this condition reflects a high COD removal efficiency, which is directly associated with the conversion of organic matter into gaseous products, primarily methane (CH_4) and carbon dioxide (CO_2) [16].

The reduction in COD was consistent with the formation of biogas with relatively stable methane content in each biodigester. The CH_4 content in BDT 1 ranged from 55–56.5%, while in BDT 2 and BDT 3 it ranged from 53–54.5% and 52–54.5%, respectively. Differences in methane content among the biodigester units reflect variations in the stages of the anaerobic digestion process and the degree of organic matter conversion, where units at earlier stages tend to exhibit higher methanogenic activity compared to downstream units.

Biogas formation during anaerobic digestion represents the final outcome of a series of biological reactions that convert COD-contributing organic compounds into methane. The significant decrease in COD from influent to effluent indicates that complex organic compounds and volatile fatty acids were successfully converted through the acetogenesis and methanogenesis stages. Therefore, the stability of POME feeding rates with high COD, followed by substantial COD reduction in the biodigester effluent, is directly correlated with the production of high-quality biogas and confirms that the anaerobic digestion system operated effectively and stably.

Volatile Fatty Acids (VFA) and Total Alkalinity (TA)

The concentration of Volatile Fatty Acids (VFA) was in the range of ±480–510 mg/L, with an average value of 501 mg/L, indicating that the rate of acid formation during the acidogenesis stage remained balanced with the system's capacity to convert these acids in subsequent stages. The relatively low and stable VFA levels suggest that no accumulation of intermediate products occurred that could potentially disrupt the stability of the anaerobic digestion process [17].

This balance in acid formation was supported by relatively high Total Alkalinity (TA) values, which ranged from ±5,580–5,630 mg/L with an average of 5,612 mg/L. The high alkalinity reflects sufficient buffering capacity to neutralize the volatile acids produced, thereby maintaining the digester environment under conditions optimal for methanogenic microbial activity. This is further evidenced by a VFA/TA ratio of approximately ±0.09, which is well below the critical threshold and indicates excellent anaerobic process stability without any tendency toward acidification.

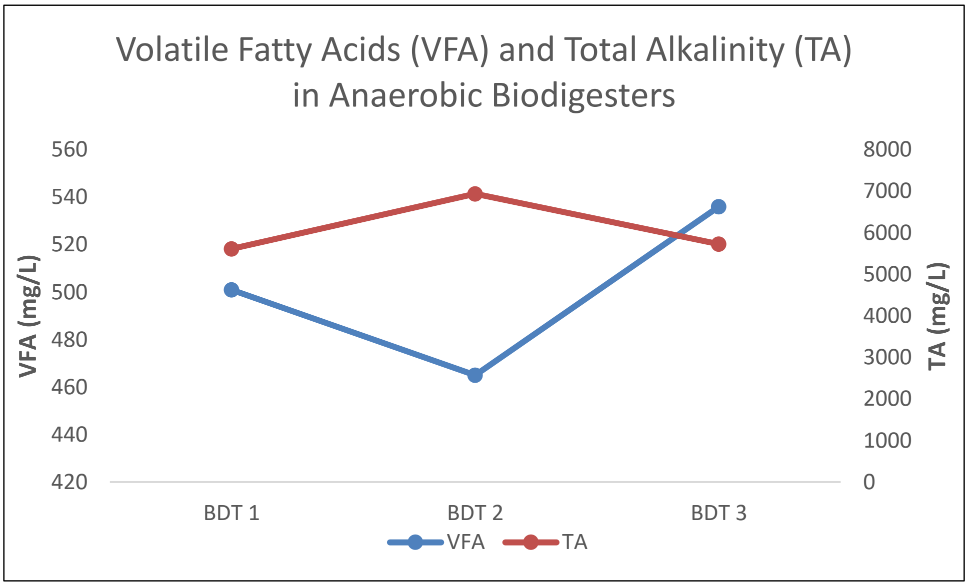

Figure 3. Volatile Fatty Acids (VFA) and Total Alkalinity (TA) in Anaerobic Biodigesters

The stability of acid formation and control stages shown in Figure 3 has a direct implication for the success of the methanogenesis stage. Stable process conditions enable the effective conversion of acetic acid as well as hydrogen and carbon dioxide into methane [18], as evidenced by the stable utilization of biogas in the gas engine and high-pressure (HP) boiler units without any gas disposal to the flare. The balance between volatile fatty acids (VFA) and alkalinity buffering capacity is therefore a key factor in maintaining stable methane (CH_4) production during the anaerobic digestion of POME and in supporting the optimization of biogas utilization.

Furthermore, Figure 3 presents the values of Volatile Fatty Acids (VFA) and Total Alkalinity (TA) in biodigester units BDT 1 to BDT 3 as indicators of anaerobic digestion process stability. In general, VFA concentrations in all three biodigesters were within the range of 465–536 mg/L, indicating that no excessive accumulation of volatile fatty acids occurred during operation. This condition suggests that the rate of acid formation during the acidogenesis stage remained balanced with the rate of acid consumption by methanogenic microorganisms.

Relatively high Total Alkalinity (TA) values were observed across all biodigester units, ranging from 5,612–6,937 mg/L as $CaCO_3$, indicating sufficient buffering capacity to maintain reactor pH stability. BDT 2 exhibited the highest TA value compared to the other units, suggesting a better buffering ability against fluctuations in acid formation. The combination of moderate VFA concentrations and high TA values resulted in a low VFA/TA ratio, reflecting stable digester operating conditions.

Differences in VFA and TA values among the biodigester units reflect the biological process dynamics at each stage of anaerobic digestion. BDT 1 and BDT 3 showed slightly higher VFA values than BDT 2, which may be attributed to variations in microbial activity and substrate characteristics in each unit. Nevertheless, all biodigester units remained under stable operating conditions, thereby supporting sustained methanogenesis and the production of biogas with optimal methane content.

Slurry Temperature

The temperature profiles of biodigesters BDT 1 to BDT 3 shown in Figure 4 indicate relatively stable operating conditions throughout the observation period. The temperatures in BDT 1 and BDT 2 were in the range of 38–39 °C, while BDT 3 exhibited a slightly lower temperature of approximately 37 °C. These temperature ranges fall within the mesophilic operating regime, which is recognized as the optimum condition for microbial activity in the anaerobic digestion process of Palm Oil Mill Effluent (POME).

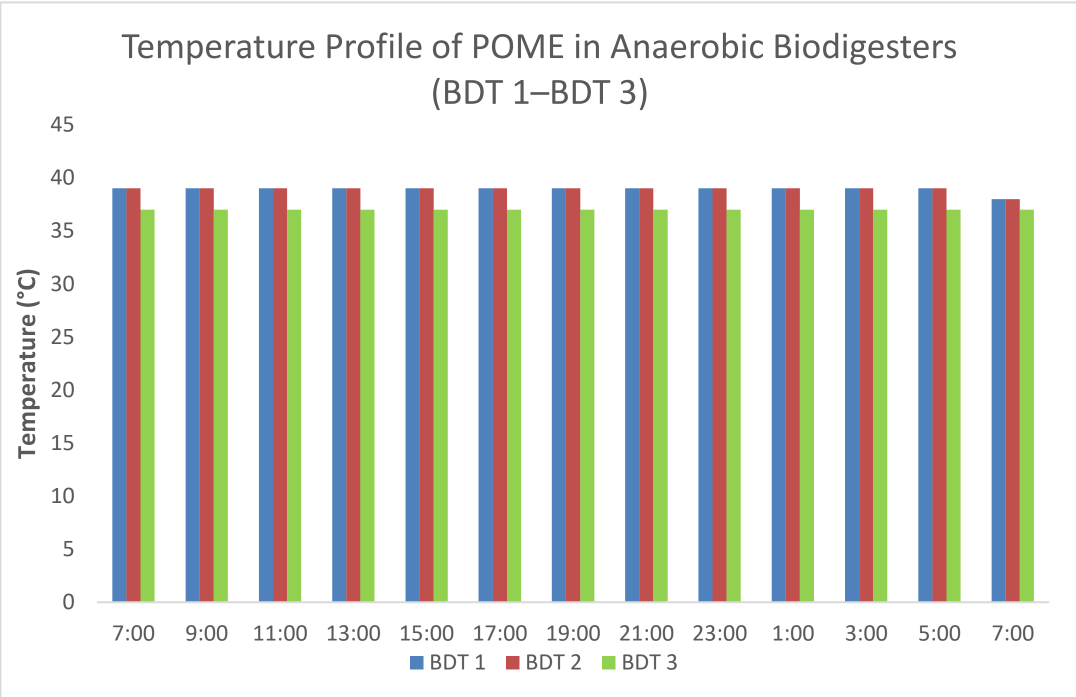

Figure 4. Temperature Profile of POME in Anaerobic Biodigesters (BDT 1–BDT 3)

Temperature stability in each biodigester unit plays a crucial role in maintaining the balance of the anaerobic digestion reaction stages, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis. During the hydrolysis and acidogenesis stages, mesophilic temperatures support enzymatic activity in breaking down complex organic compounds into volatile fatty acids (VFA). Subsequently, during the acetogenesis and methanogenesis stages, stable temperature conditions enable methanogenic microorganisms to efficiently convert acetic acid, hydrogen, and carbon dioxide into methane [19].

The relatively small temperature differences among the biodigester units reflect the biological process dynamics along the anaerobic digestion sequence [20]. The slightly higher temperatures observed in BDT 1 and BDT 2 support balanced rates of acid formation and acid consumption, while the relatively lower temperature in BDT 3 potentially enhances the stability of the methanogenesis stage. This condition is consistent with the concept that methanogenic microorganisms are more sensitive to temperature fluctuations than acidogenic microorganisms, making temperature stability a key factor in maintaining the final performance of biogas production.

The stable mesophilic temperature profile across all three biodigesters indicates that the thermal control system has effectively supported the continuous progression of biogas-forming reactions. This condition contributes to the stability of other process parameters, such as pH and the VFA-to-alkalinity ratio, and has a positive impact on the methane content of the biogas produced. Therefore, temperature control is a fundamental factor in ensuring the stability of the anaerobic digestion process of POME and in optimizing methane production [21].

pH Slurry

The pH profile shows a clear distinction between POME as the influent and the conditions inside the biodigesters. The pH of POME was in the acidic range, approximately 3.9–4.0, reflecting the high concentration of organic acids resulting from the initial degradation of organic matter in the palm oil mill. After entering the biodigesters, the pH increased significantly and stabilized within a neutral range, approximately 7.17–7.28 in BDT 1 to BDT 3, as shown in Figure 5. This shift indicates that the anaerobic digestion system was able to condition the reactor environment to levels suitable for subsequent biological processes.

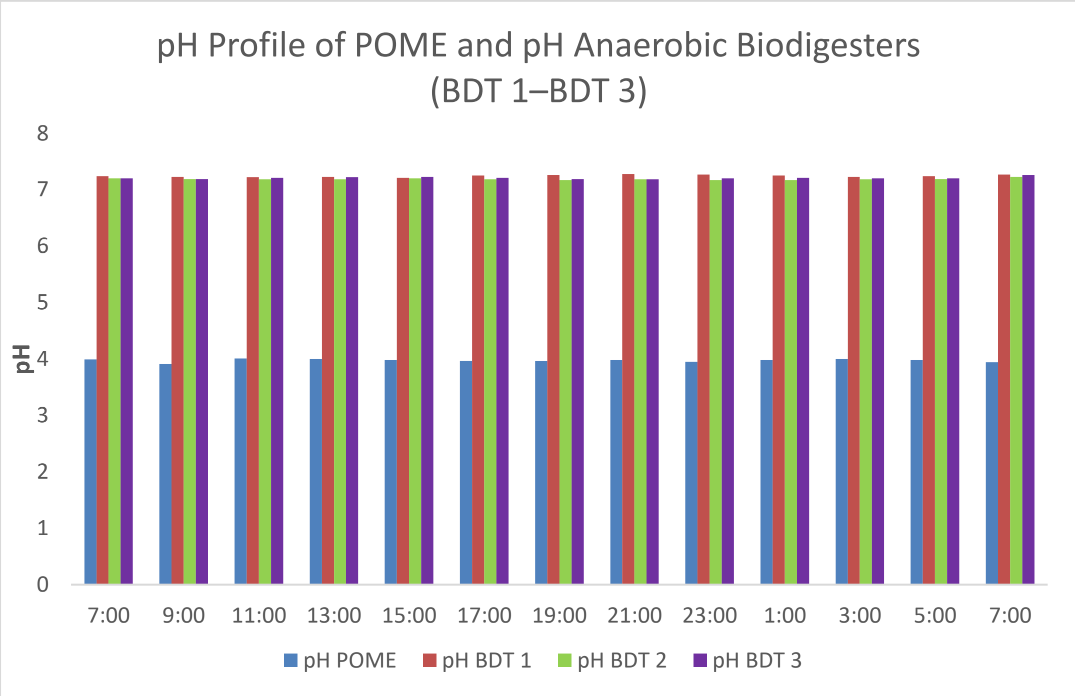

Figure 5. pH Profile of POME and Anaerobic Biodigesters (BDT 1–BDT 3)

The stability of pH in the biodigesters is closely associated with the balance between the stages of anaerobic digestion, particularly acidogenesis and methanogenesis [22]. During acidogenesis, complex organic compounds are converted into volatile fatty acids (VFA), which tend to lower the pH. However, in the subsequent acetogenesis and methanogenesis stages, these VFAs are converted into methane (CH_4) and carbon dioxide (CO_2) [23]. The consumption of acetic acid and hydrogen by methanogenic microorganisms reduces acid accumulation, resulting in an increase and stabilization of reactor pH within the neutral range.

Biogas formation predominantly proceeds through two main pathways, namely the conversion of acetate into methane and the reduction of carbon dioxide by hydrogen.

$$CH_3COO^- \rightarrow CH_4 + CO_2 \quad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

Both reactions are highly sensitive to pH, with optimum conditions occurring within the range of pH 6.8–7.5. The relatively constant pH values observed in BDT 1 to BDT 3 indicate that the environmental conditions inside the digesters were favorable for efficient and sustained methanogenesis.

Overall, the stable pH profile in the biodigesters signifies that the system possessed sufficient buffering capacity to withstand fluctuations in acid formation during the digestion process. This condition plays a crucial role in maintaining the continuity of biogas formation reactions and preventing inhibition of methanogenic microorganisms. Therefore, effective pH control is a key factor in ensuring the stability of the anaerobic digestion process of POME and in optimizing methane production [24].

The POME fed into the biodigesters had a Chemical Oxygen Demand (COD) value of 41,700 ppm, indicating a high organic content. After undergoing anaerobic digestion, the average COD value in the biodigester effluent decreased to approximately 7,200 ppm, corresponding to a COD removal efficiency of 83%. This significant reduction in COD demonstrates that most of the organic matter was degraded through anaerobic microbial activity and converted into biogas, primarily methane (CH_4) and carbon dioxide (CO_2) [25]. These results confirm that the biodigester system operated effectively in reducing pollutant load while simultaneously producing renewable energy.

CONCLUSION

The results of this study indicate that the anaerobic digestion process of Palm Oil Mill Effluent (POME) operated in a stable manner, as evidenced by the balance between volatile fatty acid formation and the system's alkalinity buffering capacity. Relatively low and stable VFA concentrations, supported by high Total Alkalinity values, resulted in a VFA/TA ratio of approximately ±0.09, indicating that the digester operated within a safe zone without any risk of acidification. The significant reduction in COD from the influent to the biodigester effluent demonstrates that organic compounds in POME were effectively degraded and converted into biogas. The stability of the Suspended Solids parameter further confirms that solids degradation and the sustainability of microbial biomass were well maintained, thereby supporting the successful progression of the methanogenesis stage. The stability of these biological parameters directly influenced the methane content of the biogas produced, which remained within an optimal range for energy utilization. All biogas generated was fully utilized without flaring, either for gas engine operation or for high-pressure (HP) boilers. These findings indicate that the stability of the anaerobic digestion process of POME contributes significantly to energy efficiency and the sustainability of industrial-scale biogas systems.

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