METHANE PRODUCTION POTENTIAL OF POME: A REVIEW ON WASTE-TO-ENERGY [WTE] MODEL

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ABSTRACT: This review article presents the research outcomes published in various scientific journals on methane production from palm oil mill effluent (POME) in line with WtE aiming to contribute to achieving energy and environmental sustainability. The total number of articles reviewed for this study is 76 in order to addressee answers to questions arising related to methane production from POME through the aid of anaerobic reactors. This study rebuilds that methane yield depends on the density of organic elements, volatile suspended solids, pH, sludge age, Hydraulic retention time, temperature and C/N ratio of POME. It has been reported that the methane potential of POME is about $15m^3CH_4(1.0m^3POME)^{-1}$; which emits to air as the Greenhouse Gas and have been appearing as 25 times higher global warming potential than carbon dioxide. The review concludes that this article would be a potential reference in selecting the model to estimate methane potential and developing the anaerobic reactor for capturing methane from POME.

Keywords: Methane Potential; Anaerobic Reactor; Energy Sustainability; Environmental Sustainability; Waste to Energy

1.0 INTRODUCTION AND BACKGROUND

Methane emission from POME has been identified as one of the vital source of Global Warming Potential [1, 2]. It has been also stated in various journals that the Global methane potential of POME is about 600 million m³ per year; and this gas emits to air as the GHG which is 25 times higher Global Warming Potential (GWP) than carbon dioxide [3, 4] It has been also stated that methane is a heat and energy sources [5-8] which currently appearing as a GWP and contributing to increasing climate change. With this background, the review has structured to gather information on methane capturing process by aiming to contribute to achieve sustainable energy supply and to reduce carbon emission to the atmosphere.

This review article aims to identify the various options used for producing methane from POME. Special emphasis has given to collect several models used to estimate CH_4 potential in POME. The priority was given to gather information on methane production process and effectiveness of anaerobic reactors in optimizing methane (CH_4) capturing from POME. The optimal operating condition of the anaerobic reactor for maximum biogas production has also highlighted in this article.

This review article answers to question arising from the aspect of designing, anaerobic reactor building and operation related to optimize methane production from POME. However, this paper primarily focused on two areas that include methane potential in POME and the application of different types of anaerobic reactor used to methane capture. This review also gathered information on models associated with organic elements and volatile suspended solids (VSS) of POME that used to estimate methane potentials.

The total number of papers reviewed in this work is 76 and published within the years 2000-2018. More than 22 percent of the papers outlined in discussing the energy potentials of POME. The models to estimate the methane potentials due to COD and VSS loads in POME has discussed in 15 percent reviewed papers. About 44 percent of the reviewed papers discussed on various type of anaerobic reactors used to produce methane from POME. Rest of the papers reviewed demonstrated the effect of methane capturing from POME on environmental sustainability.

It has been reported that during POME treatment in open tank, COD and VSS of POME convert to methane gas and emits to the air as Greenhouse gas (GHG) [9, 10]. It has been demonstrated that methane must be captured from POME for using in energy purpose and to protect the environment as well [6, 11]. On this view, this review has organized to collect information on the ways of capturing CH_4 from POME efficiently.

Indeed, this review could be a potential information source for researchers involved in innovation activities of renewable energy harvesting from waste; and it would be also providing a guideline in selecting the model to capture methane to mitigate GHG emission. However, the novelty of this review is to unlock the methane production potential of hazardous POME in line with the waste to energy [WtE] management.

1.1 The Energy Potential of Hazardous POME

This section of review demonstrates the research findings on methane potentials of POME. Historically, POME has always been regarded as a highly polluting wastewater generated from palm oil mills [9, 10, 12] during CPO production [13]. POME is a brownish liquid composed of biomass, BOD and COD. POME is also recognized as a source of CO_2 and CH_4 emission responsible for GWP [14, 15]. However, various research findings demonstrated that methane potential of POME could be a dependable renewable energy source instead of carbon emission [16]. It has been reported that about 28 m³ of biogas could be produced from 1.0 m³ of POME [17], which has the methane potentials of about 15m³ [18]. However, the composition of biogas produced from POME is listed in Table 1.

The data listed in Table 1.0 demonstrated that the methane gas is the major component in biogas produced from POME [19]. The review of this section concludes that CH_4 gas potential in POME is significantly high, which shall capture to achieve sustainability in energy supply.

 Table 1.0: Composition of Biogas Produced from POME [19]

| Element | Formula | Composition (Vol. percent) |
|-------------------|------------------|----------------------------|
| Methane | CH_4 | 50 - 75 |
| Carbon dioxide | CO_2 | 25 - 45 |
| Water | H ₂ O | 2 – 7 |
| Oxygen | O_2 | < 2 |
| Nitrogen | N_2 | < 2 |
| Hydrogen Sulphide | H_2S | < 2 |
| Ammonia | NH ₃ | < 1 |
| Hydrogen | H ₂ | < 1 |

2.0 MODELS TO ESTIMATE METHANE POTENTIAL

This section presents the different models used to estimate methane potential of POME. The models listed in this section have been published in various journals and used for designing an anaerobic reactor to capture methane from POME. The most common models are:

2.1 Gompertz Model Equation

Gompertz Model has been using to estimate methane of municipal solid waste (MSW) and POME [20]. The model is: $M_p = P_m - \exp [\exp\{R_m/P_m(X_0 - X)e + 1\}]$ (Eq. 1) Where M_p = Methane yield (mL). P_m = Methane potentials (mL). R_m = Methane production rate (mL/day). X = Lagphase time (days). e=Exponential value as constant (2.718). This particular model is useful to estimate methane emission from Leachate of MSW and POME.

2.2 Modified Gompertz Model Equation

The scope of using this model is to evaluate the kinetics of biogas production. Modified Gompertz equation was used to estimate cumulative biogas production. The modified Gompertz equation is [21, 22] :

 $Y(t) = A \exp[-\exp(\mu e/A(\lambda-t) + 1)]$ (Eq. 2) Where: $Y(t) = Cumulative biogas production (ml). A = Biogas production potential (ml). <math>\mu$ =Maximum biogas production rate (d-1. λ = Lag phase period. t = Cumulative time for biogas production (days). e = Mathematical constant (2.718).

2.3 Vedrenne Model

Vendrenne develops this model to estimate methane production from bio-fuild [23]:

 $Q(CH_4) = B_o x M_o x MCF x S_g$ (Eq. 3) Where: B_o = methane potential per kg of biodegradable matter. M_o = biodegradable matter. S_g = Part of faeces directed towards the anaerobic system. MCF= Methane conversion factor(range 0.4 to 0.77).

2.4 CDM Model

CDM is a popular model in the palm oil mill domain in estimating methane potential [24]. The model is:

2.5 COD Equivalent Model

This model has been used to estimate methane potentials from POME [25]. The model is:

 $Q_{MP} = Q \times COD \times Efficiency \times MCF \times B_0 \times UF \times GWPCH_4$ (Eq. 6)

Where: Q=Volume of POME. COD=Chemical oxygen demand of POME. MCF=Methane correction factor for POME. Efficiency=COD removal efficiency. B_o =Methane production capacity of POME (methane yield). UF=Model correction factor to account for model uncertainties. GWP(CH₄)=Global warming potential of methane.

2.6 COD Proportional Model

The coefficient of biogas yields calculated from the following equation [26]:

 $\begin{array}{ll} CH_4 \ (m^3/d) = (COD_{methane})(0.00035) & (Eq. \ 7) \\ COD_{methane} \ (g/d) = COD_{in} - COD_{vss} - COD_{eff} & (Eq. \ 8) \\ COD_{in} \ (g/d) = [COD_{in} \ (g/m^3)](Q) & (Eq. \ 9) \\ COD_{eff} \ (g/d) = (1 - RE/100)Q & (Eq. \ 10) \\ OD_{vss} \ (g/d) = (1.42 \ gCOD/gVSS) \ x \ (0.04 \ gVSS/gCOD)(1 - RE/100)(COD_{in}) & (Eq. \ 11) \\ \end{array}$

Where, $COD_{in} (g/d) = COD$ concentration in influent. $COD_{eff} (g/d) = COD$ concentration in effluent. $COD_{vss} (g/d) =$ volatile suspended solids in POME. $COD_{methane} (g/d) = COD$ associated with methane yield. $CH_4 (m^3/d) =$ Methane yield per day. Q $(m^3/d) =$ Inlet flow rate of POME.RE = COD removal efficiency.

2.7 The Modfied COD Equivalent Model

The scope of using this model is to estimate methane potential of POME.

 $\begin{array}{lll} CH_4 \; [m^3(gCOD_{MP})^{-1}] = (COD_{MP})(0.00035) & (Eq.\;12) \\ COD_{MP}(g) = COD_{in} - COD_{vss} - COD_{eff} & (Eq.\;13) \\ COD_{vss} \; & (g) \; = \; (1.42gCOD/gVSS)(0.04gVSS/gCOD)(1-RE/100)(COD_{in}) & (Eq.\;14) \\ COD_{eff} \; (g) = (1-RE/100)Q & (Eq.\;15) \\ COD_{in} \; (g) \; = \; [COD_{in} \; (g\; m^{-3})](Q) & (Eq.\;16) \end{array}$

Where: COD_{MP} = Methane potential of POME. COD_{vss} (g) =VSS equivalent. COD_{eff} (g)= Organic materials density in POME at outlet. COD_{in} (g) = Organic materials density in POME at inlet of reactor.

There seven models have listed in this section which have been commonly used in various projects in producing methane from bio-fluid. The models described in subsections 2.6 and 2.7 have appeared relevant to estimate methane potential of POME.

3.0 POTENTIAL FACTORS INVOLVED IN METHANE PRODUCTION FROM POME

This section reports the review finding on manipulating operating variables of anaerobic reactor involved in methane production from POME.

3.1 Chemicals Process in Anaerobic Reactor of WtE process

It has been reported that the biochemical reactions involved in POEM in converting COD and VSS to methane has four stages; and these reactions have taken place in the anaerobic reactor [27-32]. These stages are reported in Figure 1.



Fig. 1: Schematic Representation of Anaerobic Biodegradation [27]

3.2 Hydraulic Retention Time in Anaerobic Reactor of WtE Process

It has been reported that Hydraulic Retention Time [HRT] of POME process is an important variable in methane production [33, 34]. The HRT can be estimated from the following equation:

$$HRT(t) = \frac{1}{Q}$$
(Eq. 17)

Where V=Volume of aeration tank (m³). Q= Influent flow rate (m³/h). The value of HRT could affect the yield of methane and hydrogen [35, 36]. It has also reported that HRT is associated with the organic loading rate (OLR) and substrate concentration. It has been reported that for efficient digester operation for methane production optimization, selection of HRT value is important; the range of HRT could vary from 5-10 days [36, 37].

3.3 Solid Retention Time in Anaerobic Reactor of WtE Process

Halalshah et al. reported that Solid Retention Time (SRT) is a key parameter which can affect methane production factor significantly [38], and it is a key factor in the success of hydrolysis and methanogens process [28–32]. SRT could be estimated from the following model:

$$SRT(t) = \frac{x_i v_i}{O_r X_r}$$
(Eq. 28)

Where, X_i = Mixed liquor suspended solids (MLSS) in each reactor (mg/L). V_i = Individual reactor volume. Q_x = Excess bio-solids removal rate (m³/d). X_x = MLSS in the excess bio-solids flow (mg/L).

Mahmoud et al. stated that methanogenesis starts between 5 and 15 days of SRT at a temperature of 25° C [39]. He also stated that at lower process temperature, for methanogenesis needs higher time. For example, Methanogenesis starts between 30 and 50 days of SRT at a temperature of 15° C. It has been also stated that the most substantial portion of the digestion of proteins, carbohydrates, and lipids occurs within the first 15 and 10 days at process temperatures of 25° C and 35° C, respectively [39].

3.4 Organic Loading Rate in Anaerobic Reactor of WtE Process

It has been stated that Organic Loading Rate (OLR) to the anaerobic reactor is an important manipulating variable in achieving operational efficiency in producing methane from POME [40–42]. The OLR can be expressed in the following form: $0 \times COP$

$$OLR = \frac{Q \times COD}{V}$$
(Eq. 29)

Where, OLR = Organic loading rate (kg COD/m³.d). Q= Flow rate (m³/d). COD= Chemical oxygen demand (kg COD/m³). V= Anaerobic Reactor volume (m³).

3.5 Up-flow Velocity in Anaerobic Reactor of WtE Process

It has been reported that Up-flow velocity of POME inside the anaerobic reactor plays a vital role in forming methane [43], [44]. The required up-flow velocity could be calculated from the following equation:

$$U_{up} = \frac{n}{HRT}$$
(Eq. 30)

Where, $U_{up} = Up$ -flow velocity in m.(hr)⁻¹. h= Height of the reactor. HRT= Hydraulic retention time. The up-flow velocity in an anaerobic reactor was setup between 0.1 and 1.4 m. (hr)⁻¹ [43, 44]. It has been reported that by effluent recirculation between reactor and feedstock required up-flow velocity could be maintained [45].

3.6 pH of POME in Anaerobic Reactor of WtE Process

Nayono stated that pH is an essential parameter which controls the performance of anaerobic reactor in biogas production [46] as methanogens bacteria are sensitive to pH. It has been reported that the maximum biogas yield from POME found was between pH 6.5-7.8 [46]. At pH levels below 6.5, the methanogenic activities decrease due to the slowed growth rate of methanogens [47]. Therefore, at pH lower than 6.5 and higher than 7.6 may result in the reduction of the biogas production rate. A study conducted by Wong et al. reported that methane production increases as pH increases up to 7.5 in POME processing [48]. It has been also reported that at acidogenesis process, the optimal pH value is ranging between 5.5 and 6.5 [49]. Due to different optimal pH value in both processes, a two-stage anaerobic digestion is a preferable ways to separate the hydrolysis and acidification and acetogenesis and methanogenesis processes [49-52].

3.7 Carbon to Nitrogen ration in Anaerobic Reactor of WtE Process

Carbon-to-nitrogen (C/N) ratio is an important manipulating variable in optimizing biogas production from organic waste fluid including POME [53]. It was reported that higher carbon content contributes to increasing carbon dioxide formation and lower pH, while the high value of nitrogen will enhance the production of ammonia gas that could increase pH [54]. However, several authors agree on an optimal C/N ratio of between 30 and 50 for anaerobic digestion for POME in biogas production [55–57]. The methanogenic bacteria require optimum C/N ratio of more than 30 reflecting a

moderate N concentration for sufficient metabolism. Nurul et al. reported that the C/N ratio of the POME is in the range of 10.08–11.44 [58] which is significantly lower than required C/N value. The C/N ratio can be determined by dividing the total organic carbon content by the total nitrogen content [59]:

$$\frac{C}{N} = \frac{W1 \times C1 + W2 \times C2}{W1 \times N1 + W2 \times N2}$$

Where W1 and W2 are the weight of volatile solid (VS) in a single substrate in the mixture. The C1 and C2 are the organic carbon content (g kg⁻¹VS) in each substrate. N1 and N2 are the nitrogen content (g kg⁻¹VS) in each substrate.

The review of this section concludes that methane production optimization from POME depends on a few operating factors which are HRT, SRT, ORL, the Up-flow velocity of POME, pH and C/N ratio. The conclusion of this section is, two stage anaerobic reactor is preferable ways to optimize methane production from POME with C/N ratio between 30 to 50. It was also reported that the anaerobic would be operated 5-12 days of HRT with maximum SRT of 15 days for highest yield of methane from POME.

4.0 ANAEROBIC REACTORS IN WTE FOR PRODUCING METHANE FROM POME

This section presents the review findings on the successful use of anaerobic reactors in methane production from POME. Total sixteen successful case studies have listed here on anaerobic reactor operations with various manipulating variables.

4.1 Methane Production from Combined Anaerobic Hybrid Reactor (AHR), and Anaerobic Baffled Filter (ABF)

Jeong et al.,(2014) conducted a study on methane production from POME with Anaerobic Hybrid Reactor (AHR) and Anaerobic Baffled Filter (ABF) [60]. The study was conducted under both mesophilic (37°C) and thermophilic (55°C) temperatures. The range of OLR to the reactor was from 2 to 15 kg COD m⁻³ d⁻¹ with HRT of 5 days for AHR and 6 days for ABF. The schematic diagram of methane production process is shown in Figure 2.



Fig. 2: Schematic diagram of AHR-ABF [60]

The methane production data demonstrated that the COD removal efficiency at thermophilic environment was about 93 percent at AHR and about 95 percent at ABF. The research

concluded that the combination of AHR and ABF in methane production operations from POME at thermophilic environment was higher than the mesophilic condition.

4.2 Methane Production from COD Enrich Biomass Suspended Closed Type Anaerobic Reactor

COD enrich biomass suspended closed type Anaerobic Reactor (SCAR) has been used by [48] for methanogenic degradation process to producing methane from POME. The schematic diagram of methane production process is shown in Figure 3.



Fig. 3: Schematic diagram of SCAR [48]

The SCAR had operated at HRT of 4, 6, 8, 10, and 12 days with the pH range of 6.89 to 7.34, and operating temperature of 35°C. In the beginning, the POME was feed to the continuous stirred for 16 hours, followed by another 6 hours to allow active sludge to settle at the bottom of the reactor.

The findings demonstrated that the COD removal efficiency increased with pH from 6.89 to 7.34. The highest COD removal efficiency was recorded as 66.09 percent at HRT of 12 days and was lowest 47.30 percent at HRT of 4 days. It was also reported that methane contents in biogas were 48.50 percent at HRT of 12 days and it reduced to 19.27 percent at HRT of 4 days. The best performance of SCAR was obtained at HRT of 12 days with contributing to COD removal efficiency of 66.09 percent and 48.05 percent methane composition in biogas. The study concluded that at pH 7.28 and at HRT of 12 days were the optimum operating conditions for SCAR to achieve the best performance to produce methane from POME.

4.3 Methane Production by Expanded Granular Sludge Bed Reactor from POME

Wang et al. tested methane production performance of an Expanded Granular Sludge Bed Reactor (EGSB) from POME with respect to COD removal efficiency [61]. The OLR to the reactor was 6.45 kg COD m⁻³ d⁻¹ at an operating temperature of 35°C. A dissolved air flotation (DAF) equipment and Cationic polymer (PAM) was used to increase suspended solids (SS) generation rate. The suspended solids and effluent were circulated in the system to increase the performance of

EGSB. The schematic diagram of methane production process is shown in Figure 4.0

Upward-flow Anaerobic Sludge Blanket



Fig. 4: EGSB Reactors [61]

The findings of EGSB operations demonstrated that the COD removal efficiency was 94.89 percent; and the biogas production was about 27.65 $CH_4m^3.m^{-3}POME$, which contains over 65 percent methane. The study concluded that the application of DAF and PAM in EGSB to contribute to reduce suspended solids and recycling of effluent are positively associated with higher production performance of biogas and methane from POME[61].

4.4 Methane Production from POME by using Continuous Stirred Reactors

Continuous Stirred Reactors (CSTR) was used by [62] in investigating the performance of two different types of CSTR. A typical CSTR and a modified CSTR with a deflector installed at its upper section for retaining the suspended solids inside were used for conducting this study. The Schematic diagram of the experiment is shown in Figure 5.



Fig. 5: Diagram of a conventional CSTR [62]

The OLR to CSTR were from 2.0g to 19.0g COD $L^{-1} d^{-1}$ where pH was from 7.0-8.0. The methane production report demonstrated that the average OLR at 19.0g COD $L^{-1} d^{-1}$ with HRT of 3.3 days gave a COD removal efficiency of 82 percent with a 68 percent methane content in biogas. The study concluded that the biogas production increased with increasing of OLR, and the yield of biogas started to decline as the OLR reached to 17.6g COD $L^{-1} d^{-1}$. It has also reported that methane content in the biogas increased with COD removal efficiency.

4.5 Methane Production from POME by Up-flow Anaerobic Sludge Blanket-Hollow Centre Packed Bed Reactor

Poh and Chong to (2014) was using POME test the methane production performance pf an Up-flow Anaerobic Sludge Blanket-Hollow Centre Packed Bed Reactor (UASB-HCPB) [63]. The methane production process was operated at thermophilic conditions (55°C) with various ranges of HRT, OLR, and volatile suspended solids (VSS). The experiment is shown in Figure 6.





The production report on the process stated that methane yield increased with OLR from 4.28 to 9.19 g L⁻¹ d⁻¹. The methane yield was almost constant between the ORL of 9.19 g L-1 d-1 to 13.75 g L⁻¹ d⁻¹. The methane production started to reduce from OLR of 13.75 g L⁻¹ d⁻¹. The best performance was achieved with VSS concentration of 14.98 g L⁻¹, HRT 5 days and OLR was 6.66 g L⁻¹ d⁻¹. The research concluded that OLR, VSS concentration, and HRT were the controlling factors to produce methane from POME[63].

4.6 Methane Production from POME by Anaerobic Sludge Blanket-Continuous Stirrer Tank Reactor

Krishnan *et al.*, evaluated the effects of various OLRs on H_2 and CH_4 production of Anaerobic Sludge Blanket-Continuous Stirrer Tank Reactor (UASB-CSTR) [2]. At the first stage, the UASB reactor was used to produce H_2 while the CSTR reactor was used in the next stage to produce CH_4 . The production was conducted at the thermophilic conditions (55°C). The experiment is shown in Figure 7.

The OLR was the manipulated variable in this experiment which varied at 25, 50, 75, 100 and 125 kg COD m^{-3} . d⁻¹ for UASB reactor. The ORL for CSTR were 4, 8, 12, 16, 20 kg COD m^{-3} d⁻¹. The HRT was 6 hours as constant for both reactors. The POME was mixture in CSTR at a constant 120 rpm.



Fig. 7: Schematic design of UASB-CSTR [2]

At UASB unit, the gas production rate was $4.5Ld^{-1}$ with COD removal rate of 40 percent at OLR of 75 kg COD m⁻³ d⁻¹. The performance of UASB started to reduce at OLR beyond 75 kg COD m⁻³ d⁻¹.

In the CSTR unit, the highest COD removal was 85 percent at OLR of 12 kg COD m⁻³. The highest values for CH₄ content in biogas was achieved at 35 percent and 68 percent. This research concluded that the microbial activities in two stages such as acidogenesis and methanogenesis were contributed to increase methane production [2].

4.7 Methane production from POME by Two-Stage Thermophilic Fermentation and Mesophilic Methanogenic Process with UASB-ASBR reactors

Mamimin et al. studied the effects on process stability and microbial community on two-stage thermophilic fermentation and mesophilic methanogenic process for methane production from POME [64]. At the thermophilic temperature of 55°C, the ASBR reactor was tested for hydrogen production at pH 5.5 and HRT of 2 days. Subsequently, the UASB reactor was tested for methane production at mesophilic temperatures between 28-34°C, at pH 7.5 and HRT of 20, 15 and 10 days. The methane production process is shown in Figure 8.

While the ASBR was operated at OLR of 60 g COD L⁻¹ d⁻¹ and HRT of 2 days, the maximum hydrogen production rate was $1.84 \text{ L H}_2 \text{ L}^{-1} \text{ d}^{-1}$ with an average of $1.8 \text{ L H}_2 \text{ L}^{-1} \text{ d}^{-1}$. And at this operating condition, the COD removal rate was 38 percent. The maximum methane production rate was recorded of 2.6 l CH₄ $L^{-1} d^{-1}$ at HRT of 15 days and OLR of 6 g COD $L^{-1} d^{-1}$.

In the UASB unit, maximum hydrogen production rate was 1.84 L H₂ L⁻¹ d⁻¹ at the temperature of 55°C, HRT of 2 days and OLR of 60 gCOD L⁻¹ d⁻¹. The optimum HRT in the UASB was 15 days in which the maximum methane production rate was of 2.6 L CH₄ L⁻¹ d⁻¹.



Fig. 8: Schematic diagram of the two-stage hydrogen and methane process [64]

At this operating condition, the biogas composition was 51 percent CH_4 , 14 percent H_2 and 35 percent CO_2 . However, the research concluded that the two-stage fermentation and methanogenic process could recover more methane than single-stage process [64].

4.8 Methane Production from POME by Combined High-Rate Anaerobic Reactor

Choi et al. evaluated the methane production performance of the combination of high-rate anaerobic reactors (AHR), anaerobic baffled filter reactor (ABF) and anaerobic downflow filter reactor (ADF) [65]. The combination anaerobic system is shown in Figure 9.



Fig. 9: Schematic diagram of AHR, ABF, and ADF [65]

The production operation was conducted at the mesophilic temperature (35-37°C); pH 7, HRT was from 0.7 to 2.4 days, and OLR was from 0.91 to 23 kg COD m⁻³ POMEd⁻¹. A raw POME was pre-treated by a 3-phase screw decanter so as to remove excessed suspended solids SS and palm oil.

The maximum removal efficiency of COD was 95.6 percent at AHR reactor when the OLR was at 13 kgCOD m⁻³ d⁻¹. Subsequently, COD removal efficiency was 93.5 percent when this treated effluent fed from AHR into ABF and ADF reactors for further biogas production. The maximum level of biogas production was 110 L d⁻¹ at an OLR of 18.9 kg COD m⁻³ POME d⁻¹. The maximum methane yield obtained was 0.269L CH₄ gCOD_{removed}⁻¹.

The study concluded that the combination system of AHR, ABF, and ADF is the efficient way and effective to produce methane from POME[65].

4.9 Methane Production from POME by Up-flow Anaerobic Sludge Blanket Reactors with Calcium Oxide

Ahmad et al. studied methane production from POME by Anaerobic Sludge Blanket Reactors (UASB) [66]. The COA-CKD solution was added in POME to observe its effects on methane production. The production process is shown in Figure 10.



The production process was operated with the temperature of 35°C, the feed flow rate was set at 1.25 L d⁻¹ and HRT was fixed at 4 days. The OLR was 15 kg COD m⁻³ POME.d⁻¹. Six

fixed at 4 days. The OLR was 15 kg COD m⁻³ POME.d⁻¹. Six reactors were used to run the experiment with different concentration of CaO to compare among the different outputs.

Findings of the study stated that at OLR 12.5 kg COD m⁻³.d with 10 g L⁻¹ CaO addition, the average COD removal efficiency was 82.4 percent; and the average methane yield was $0.911 \text{ CH}_4 \text{ gCOD}_{\text{removed}}^{-1}$ [66].

The study concluded that the addition of CaO in POME enhanced the granulation process which contributes to increase precipitation as well as improved adhesion of cells by microbial activities. It was also stated that due to the growth of microbial cells and granules in reactors, the methane production performance increased.

4.10 Methane Production from POME by Up-flow Anaerobic Sludge Blanket-Expanded Granular Sludge Bed Reactors

Fang et al. conducted a research on POME with Up-flow Anaerobic Sludge Blanket-Expanded Granular Sludge Bed Reactors (UASB-EGSB) [67]. UASB-EGSB reactor was operated with thermophilic conditions at 55°C. The pH was adjusted to 7.0 by adding NaHCO₃ in the POME₁ The reactor was operated at HRT of 10 days with the OLR from 1.3 to 10.4 gVS L^{-1} .

The production report demonstrated that the maximum methane yield achieved was about 503 mL-CH₄ gVS⁻¹. When de-oiled POME used in the same reactor, the maximum methane yield was 610 mL-CH₄ gVS⁻¹. The study concluded that the combination of UASB-EGSB with de-oiled POME has higher methane potential.

4.11 Methane Production from POME by Up-flow Anaerobic Sludge Blanket Reactors with Mesophilic And Thermophilic Conditions

Khemkhao et al. evaluated the effects of OLR and operating temperature on the methane production performance of Up-flow Anaerobic Sludge Blanket (UASB) Reactors [68]. The tests were conducted in two UASB for mesophilic (35° C) and thermophilic (55° C) temperatures. Sodium hydroxide (NaOH) was added into the POME to obtain a pH value of 7.0. The HRT of production operation was 2.4 days with an up-flow velocity of 0.3 m hr⁻¹ while OLR was varied subsequently at 2.23, 3.95, 5.76, 7,77 and 9.47 g COD L⁻¹.d.

The study report stated that performance of UASB operated at thermophilic (55°C) with OLR of 9.47 g COD L⁻¹.d, the COD removal efficiency was more 80 percent with methane yield 76 percent of its potential. On the other hand, the performance of UASB operated at mesophilic (35°C) at the same ORL, the COD removal efficiency was less than 80 percent with methane yield 75 percent of its potential.

The study concluded that thermophilic anaerobic digestion was the preferable operating condition to treat POME and methane production as compared to mesophilic anaerobic digestion.

4.12 Methane Production from POME by Up-flow Anaerobic Sludge Blanket Reactor with CaO Under different OLR and HRT

Ahmad & Ghufran evaluated the production performance of Up-flow Anaerobic Sludge Blanket (UASB) Reactor for methane production [69]. To conduct the experiment, different types of biomass-based granule substrate have been used in the UASB reactor. The substrate was fed into the reactor at a flow rate of 0.53 L d⁻¹ with HRT from 3.35 to 34.5 days. A stirrer of 5-rpm was installed in the reactor to prevent cake of CaO. The reactor was continuously fed with an initial OLR of 4.5 kg COD m⁻³d⁻¹ and varied from 1.5 to 46 kg COD m⁻³d⁻¹ while keeping pH 7.5.

The output data of the experiment demonstrated that the removal efficiencies of COD achieved 97 percent and 79 percent respectively as HRT was increased from 12.5 to 24.5 days. The methane production increased up to 2.5 L d⁻¹ at

HRT of 24.5 days. At COD concentration of 46 gL⁻¹, the methane production attained 0.85 L CH4 g $\text{COD}_{\text{removed}}^{-1}$.

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The experiment concluded that using CaO as the substitute for lime to increase the pH value had enabled methanogens to grow and produce the maximum amount of methane in a neutral environment.

4.13 Methane Production from POME by Thermophilic Continuous Stirred Tank Reactor

Irvan et al. evaluated the methane production performance of a continuous stirred tank reactor (CSTR) under thermophilic temperature (55°C) [14]. The pH value was adjusted by the addition of NaHCO₃ with POME. A premixed chemical solution comprised of FeCl₂, NiCl.6H₂O and CoCl₂.6H₂O were also added as food for methane-producing bacteria.

At HRT of 4, 6 and 8 days, the production information indicated that the biogas produced at HRT of 4 days was $16.14 \text{ L} \text{ d}^{-1}$ which was 53.5 percent of its potentials. At 8 days of HRT, the biogas production was 63.5 percent of its potentials.

The experiment concluded that at 8 HRT days with the temperature of 55°C and pH 7.0 were optimum conditions for this CSTR reactor to produce the highest amount of methane.

4.14 Methane Production from POME by Membrane Anaerobic System

Abdurahman et al. tested the methane production performance from POME by using a Membrane Anaerobic System (MAS) [70]. This system comprised a cross flow ultra-filtration membrane (CUF) and an anaerobic reactor. The membrane was used to separate biomass solids from the solid suspension in order to be recycled. The schematic diagram of the process is shown in Figure 11.



Fig. 11: Experimental set-up of MAS [70]

The reactor was operated with OLR ranging from 2 to 13 kg COD m⁻³ d⁻¹, SRT from 8.0 to 11.6 days and HRT from 4.6 to 5.7 days while maintaining pH value within the optimal range of 6.7 to 7.8.

The methane production report described that at OLR of 13 kg COD m⁻³ d⁻¹, the MAS attained COD removal efficiency of 94.8 percent, which produced effluent with COD of 2279 mg L⁻¹. The COD removal efficiency was in the range of

94.8-96.5 percent as HRT was increased from 4.6 days to 5.7 days. In the aspect of biogas production, the rate increased from 0.27 L gCOD⁻¹ d⁻¹ to 0.83 L gCOD⁻¹ d⁻¹ as OLR was increased from 2 to 13 kg COD m⁻³ d⁻¹, where the methane content decreased subsequently, ranging from 68.7 percent to 74.2 percent. The study concluded that biomass separation by MAS and recycled back to the process has contributed to increasing methane production performance.

4.15 Methane Production from POME by Carrier Anaerobic Baffled Reactor with Polymeric Media

Malakahmad and Yee (2014) investigated the biogas production rate from POME by using a Carrier Anaerobic Baffled reactor (CABR) [71]. The CABR system contained a series of up-flow packed-bed attached growth reactors where the substrate was forced to flow under and over the vertical packed-bed baffles. The schematic disarm of the process is represented in Figure 12.

The CABR was operated at initial OLR of 0.46 g COD L^{-1} .d and a constant HRT of 4 days, with the temperature, maintained at around 35°C and a pH value of 7.2.



Fig. 12: The schematic diagram of CABR [71]

The output information demonstrated that the COD removal efficiency was steady throughout the experiment. The CABR system achieved COD removal efficiency of 82 percent with an OLR of 11.38 g COD $L^{-1} d^{-1}$. The methane yield improved from 0.05 L-CH₄ gCOD⁻¹ to 0.25 L-CH₄ gCOD⁻¹ as the OLR increased, giving methane content of 54-75 percent of the biogas produced.

The study concluded that CABR increased the contact time between the substrate and active biomass, which contributed to making effluent free from biological solids. It was also reported that this system is able to sustain high COD loading which required small reactor volumes.

5.16 Methane Production from POME by Ultrasonic Membrane Anaerobic System

Nour and Nour (2017) evaluated the methane production performance from POME and kinetics of an ultrasonic membrane anaerobic system (UMAS) [72] based on Monod [73], Contois [74], and Chen and Hashimoto [75] models. In this design comprised a cross-flow ultrafiltration membrane and an anaerobic reactor as shown in Figure 13.



Fig. 13: Experimental set-up of UMAS [72]

The UMAS was operated at different COD concentration of 70,400 to 90,200 mg L⁻¹ where HRT and OLR in the UMAS were varied from 500.8 to 14.7 days and 1.5 to 9.0 kg COD m⁻³ d⁻¹ respectively. The pH value of raw POME was adjusted to around 7.0 by addition of NaOH into the reactor. The research output data stated that the influent fed with COD concentration of 70,400 mg L⁻¹ at OLR of 1.0 kg COD m⁻³ d⁻¹ produced a COD removal efficiency of 98.3 percent. The effluent fed with COD concentration of 90,200 mg L⁻¹ at OLR of 15 kg COD m⁻³ d⁻¹ produced a COD removal efficiency of 92.8 percent.

It was also stated that COD removal efficiency decreased from 98.3 to 92.8 percent as HRT decreased from 5.8 to 8.6 days. It was also recorded that biogas production increased from 0.48 L $gCOD^{-1} d^{-1}$ to 0.81 L $gCOD^{-1} d^{-1}$ due to increasing of OLR from 1.0 to 15 kg COD m⁻³ d⁻¹.

At conclusion it was stated that to achieve COD removal efficiency of more than 90 percent, the UMAS reactor could be used, and as well as to capture methane from POME over 60 percent of its potential.

5.0 CONCLUSION

The major findings of the review article could be divided into three groups. Firstly, the four stages of chemicals process must be understanding before starting the designing of methane capturing plant machinery. Secondly, the manipulating variables need to configure. The third group is of selecting anaerobic reactor and set up the operating condition. The summary of the findings is two stage anaerobic reactor would be preferable ways to optimize methane production from POME. At the first stage, the anaerobic reactor shall be configured for hydrolysis and abiogenesis at operating pH below 6.5. In the second stage, the anaerobic reactor shall be configured for acetogenesis and methanogenesis at operating pH between 6.5 and 7.5. It was also found that the preferable C/N ration shall be between 30 and 50. It has been reported that the anaerobic reactor shall be operated with HRT between 5-12 days with SRT maximum 15 days.

Various, researches have confirmed that by using WtE concept, waste methane could be captured and used as renewable energy for producing heat and electricity [70], [71], [76] for contributing to achieving sustainability in energy supply and environment. However, this review could be potential information sources for researchers involved in the field of renewable energy production from hazardous POME and another waste biofluids. This article would be a guideline in selecting anaerobic reactor and operating variables to capture methane.

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