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Kinetics of Anaerobic Digestion of Palm Oil Mill Effluent (POME) in Double-Stage Batch Bioreactor with Recirculation and Fluidization of Microbial Immobilization Media

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Abstract. Palm Oil Mill Effluent (POME) becomes big problem for palm oil industries, especially for Crude Palm Oil (CPO) industry since it produces 3 tons of POME for every ton of CPO production.The high amount of organic loading in POME makes it potential as a substrate in anaerobic digestion to generate biogas as renewable energy source. The most common but conventional method by using open lagoon is still preferred for most CPO industry in Indonesia to treat POME because of its simplicity and easiness. However, this method creates new major problem for the water bodies since it has no significant chemical oxygen demand (COD) removal and needs wide area. Besides, greenhouse gas (CH_4) is also released during the process. An innovation was made in this study by designing vertical column process equipment to run an anaerobic digestion of POME. The vertical column was functioned as anaerobic fluidized bed reactor (AFBR). To enhance the digestion rate in AFBR, natural zeolite was used as the immobilization media and the inoculum was taken from digested biodiesel waste. This research aimed to determine the kinetic constants of double-stage anaerobic POME digestion for COD removal and biogas production. To get close to the real condition, the POME used in this experiment had 8,000 mg/L of sCOD (the real sCOD was ±16,000 mg/L). The experiment was conducted under room temperature with up-flow velocity between 1.75 and 2.3 cm/s for optimum fluidization of immobilization media.

1. Introduction

POME is a highly polluting wastewater causing serious problem to the environment due to its highly pollutant content. For every ton fresh fruit bunches processed in Palm Oil Mill, there will be 120-200 kg crude palm oil (CPO), 230-250 kg empty fruit bunches, 130-150 kg fiber, 60-65 kg nuts and 0.7 m^3 wastewater effluent [1]. Almost every palm oil mill in Indonesia uses opened lagoon method to treat the wastewater namely POME. However, the effectiveness of this method is not reliable due to the high retention time and wide area required. Besides, greenhouse gas, for instance, CO_2 and CH_4 are released directly to the atmosphere. On the other hand, the existence of CH_4 in the gas released during POME treatment represents the potential to be used as the source for biofuel production. What made POME different from any other wastewater is its high volatile fatty acid (VFA) content. The presence of abundant VFA in POME makes it an attractive substrate for anaerobic digestion due to the higher methane yield obtained than proteins or carbohydrates. In this case, high VFA content waste can be regarded as a large potential for renewable energy source [2].

The solution of the aforementioned problem related to the ineffectiveness of open lagoon method is anaerobic digestion. By this process, the biogas produced during treatment can be controlled and space can be saved by using compact vertical process equipment. In general, anaerobic digestion process consisted of acidogenesis and methanogenesis process [3]. The former focuses on removing the pollutant represented by Chemical Oxygen Demand (COD) parameter while the latter focuses on converting organic material represented by VFA parameter into biogas. Both processes can run simultaneously and sequentially. Because of different optimum pH level for both processes, the optimum operating can be achieved if anaerobic digestion process is conducted separately and sequentially. Two-phase anaerobic digestion system had been recommended for the treatment of wastewater containing high VFA content such as dairy waste [4], ice cream factory effluents [5], fish meal processing waste [6], slaughterhouse waste [7], and olive mill solid waste [8].

In this work, POME was treated sequentially by separating acidogenesis and methanogenesis processes into two anaerobic fluidized bed reactors (AFBR). Acidogenesis process ran on the first reactor and methanogenesis process ran on the second reactor. The vertical column AFBR was used due to its effectiveness to process high organic loading rate (OLR) wastewater with lower hydraulic retention time (HRT). To prevent wash-out phenomenon, natural zeolite was used in this study as the microbial immobilization media. The immobilization media was then fluidized to maximize the contact area between substrate and microorganism [9] so that the microorganism growth could be enhanced. The aim of this research was to study the kinetics of anaerobic digestion of POME in double-stage anaerobic fluidized bed reactor by synthesizing mathematical modelling for batch process.

2. Methodology/experimental

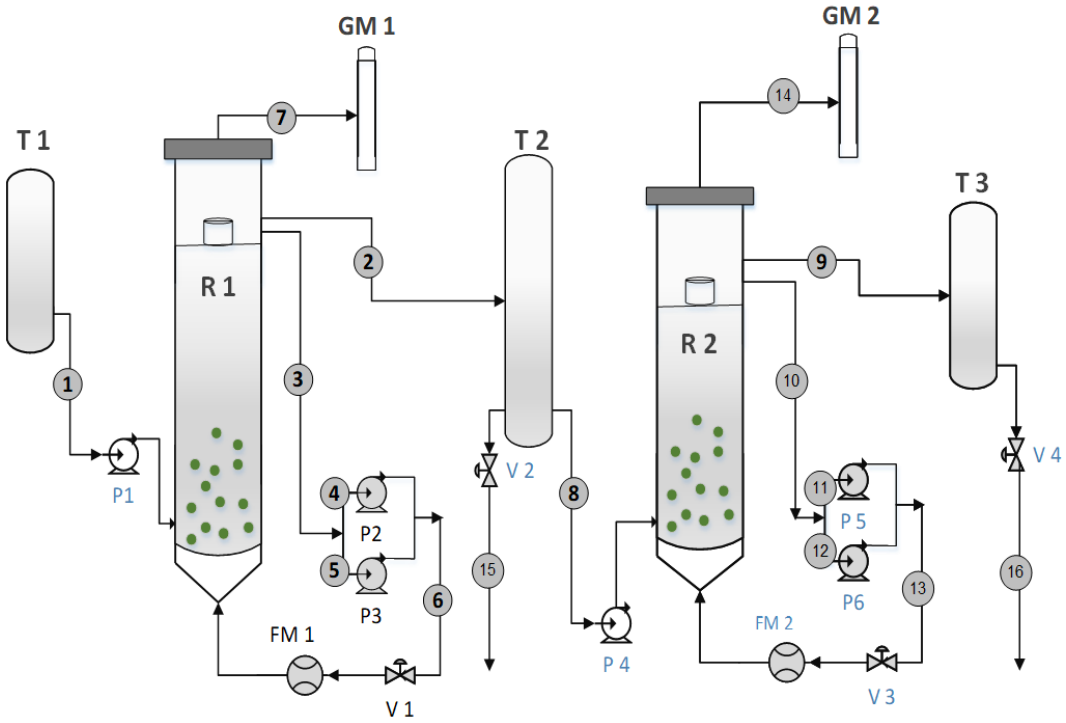
2.1 Materials

The materials needed in this research were Palm Oil Mill Effluent (POME), natural zeolite as the immobilization media and digested biodiesel waste as microorganism isolate source. The POME was obtained from PT. Perkebunan Nusantara VII, Lampung, Indonesia with Chemical Oxygen Demand (COD) as much as 13,580 mg/L and pH 4.48. Digested biodiesel waste was taken from the biodiesel industry operating in East Java with the COD of 1,980 mg/L and pH of 7.53. The natural zeolite with diameter range of 2-2.38 mm came from Tasikmalaya, West Java.

2.2 Anaerobic digestion of POME

Anaerobic digestion was conducted in two bioreactor columns made of acrylic equipped with close loop recirculation system for fluidization (figure 1). The first AFBR was a 15 L acidogenic bioreactor and the second one was a 10 L methanogenic bioreactor with 150 gram of immobilization media from natural zeolite in each bioreactor. This system was supported by one dosing pump and two centrifugal pumps working 24 hours a day with on-off system for each bioreactor.

To ensure that in the first AFBR there was only acidogenesis process and in the second AFBR there was only methanogenesis process, the pH level was set at acidic condition (pH 5-5.5) and neutral condition (pH 7) respectively. The pH inside the second AFBR was adjusted by adding NaOH to the methanogenic bioreactor. These batch bioreactors ran for 14 days for acidogenic bioreactor and 21 days for methanogenic bioreactor.



Annotations:

R1	:	Acidogenic AFBR	GM 1,2	:	Gas meter
R2	:	Methanogenic AFBR	FM 1,2	:	Flow meter
Tank 1	:	Influent tank	Stream 1,8	:	Influent stream to R1 and R2
Tank 2	:	Intermediate tank	Stream 2	:	Effluent stream from R1
Tank 3	:	Effluent tank	Stream 3,9	:	Suction stream for recirculation
P1,P4	:	Dossing pump	Stream 4,14	:	Influent stream into cirulating pump 1
P2,P5	:	Circulating pump 1	Stream 5,12	:	Influent stream into cirulating pump 2
P3,P6	:	Circulating pump 2	Stream 9	:	Effluent stream from R2
V1,V3	:	Controlling valve for circulating stream	Stream 6, 13	:	Influent stream to AFBR for fluidization
V2, V4	:	Controlling valve for effluent stream	Stream 7, 14		Effluent stream of biogas
			Stream 15, 16	:	Effluent stream

Figure 1. Experimental set up

2.3 Analysis of sCOD, VFA and CH_4

In this work, parameter used to represent organic loading of the POME was soluble Chemical Oxygen Demand (sCOD) while to represent available substrate for biogas production, it was used Volatile Fatty Acid (VFA). The analysis of sCOD and Volatile Fatty Acid (VFA) during the experiment followed the standard procedure by APHA [10]. The sCOD analysis was conducted with closed reflux colorimetric method. The VFA analysis used the titrimetric method. The gas volume was measured by using the

gasometer method outlined by Walker et al [11] while the methane content was analyzed by using Gas Chromatography (GC) Shimadzu GC 8A.

2.4 Mathematical modelling for Batch AFBR

The growth rate for both acidogenic and methanogenic cells were defined from cell mass balance combined with specific growth rate represented by Contois equation [12,13,14] due to its slow rate process. The Contois equation for the growth rate of acidogenic and methanogenic microbes were described by equation (1) and equation (2).

$$\frac{dX_1}{dt} = \left(\frac{\mu_{m1}.C_{sCOD}}{K_{SX1}.X_1 + C_{sCOD}} - k_{d1} \right).X_1 \quad (1)$$

$$\frac{dX_2}{dt} = \left(\frac{\mu_{m2}.C_{VFA}}{K_{SX2}.X_2 + C_{VFA}} - k_{d2} \right).X_2 \quad (2)$$

Batch mathematical modelling for AFBR was developed based on the mass balance of sCOD, VFA and CH_4. The developed model still assumed that both acidogenesis and methanogenesis existed together. From the models, it was expected that the different pH application could lead to the conclusion in which constants were affected by pH adjustment after the kinetic constants were all determined. The determination was conducted by fitting the experimental data using MATLAB R2016b by means of *ODE15S* and *FMINCON* solver. The simultaneous ordinary differential equations were shown by equation (3) – equation (7).

$$\frac{d(C_{sCOD})}{dt} = -\frac{1}{Y'_{X1/CsCOD}} \left(\frac{\mu_{m1}.C_{sCOD}}{K_{SX1}.X_1 + C_{sCOD}} - k_{d1} \right).X_1 \quad (3)$$

$$\frac{1}{Y'_{X1/CsCOD}} = \frac{1}{Y_{CVFA/CsCOD}}.Y_{CVFA/X1} + \frac{1}{Y_{X1/CsCOD}} \quad (4)$$

$$\frac{dC_{VFA}}{dt} = \left[\frac{1}{Y_{CVFA/CsCOD}}.Y_{CVFA/X1} \right] \left(\frac{\mu_{m1}.C_{sCOD}}{K_{SX1}.X_1 + C_{sCOD}} - k_{d1} \right).X_1 - \frac{1}{Y'_{X2/CVFA}} \left(\frac{\mu_{m2}.C_{VFA}}{K_{SX2}.X_2 + C_{VFA}} - k_{d2} \right).X_2 \quad (5)$$

$$\frac{1}{Y'_{X2/CVFA}} = \frac{1}{Y_{X2/CVFA}} + Y_{CCH4/X2} \quad (6)$$

$$\frac{d(C_{CH4})}{dt} = Y_{CCH4/X2} \left(\frac{\mu_{m2}.C_{VFA}}{K_{SX2}.X_2 + C_{VFA}} - k_{d2} \right).X_2 \quad (7)$$

3. Result and discussion

3.1 sCOD removal and VFA formation in acidogenic AFBR

Main function of anaerobic fluidized bed reactor on the first stage as the acidogenic reactor was to convert sCOD into Volatile Fatty Acid (VFA). Acidogenic AFBR ran on acidic condition (pH 5-5.5) with starting values of sCOD and VFA consentration as much as 1,925 mg/L and 4,518 mg/L. In this work, sCOD measurement was all the soluble organic matter besides VFA. Acidic condition was preferred on this stage to maximize the growth of acidogenic microbes and to prevent the growth of methanogenic microbes which is too sensitive toward pH decreasing. The figure 2 (a) showed that sCOD concentration decreased significantly until day 12. After 12 days of experiment, the sCOD was relatively stable. This phenomenon indicated that first, the acidogenic microorganism could possibly grow well

(must be confirmed with the VFA profile) and the second, the system was ready to be switched into the continuous operation if removal of sCOD was the main concern.

VFA formation is the most important aspect that indicates acidogenesis process ran well. The VFA concentration profile within 13 days of process is shown on figure 2 (b). The decrease of VFA at the beginning (until day 3) indicated that the microorganism was still in the adaptation period by consuming substrate. However, it started to increase from day 4 to day 10. This indicated that acidogenic microorganism started dominating after 3 days of anaerobic digestion under acidic condition. However, the increase of VFA content inside the reactor has its maximum value. After day 10, the VFA content decreased again and was followed by significant biogas production as shown by figure 2 (c). By this situation, it could be seen that the acidogenic microorganism had maximum tolerance to the VFA concentration of the substrate.

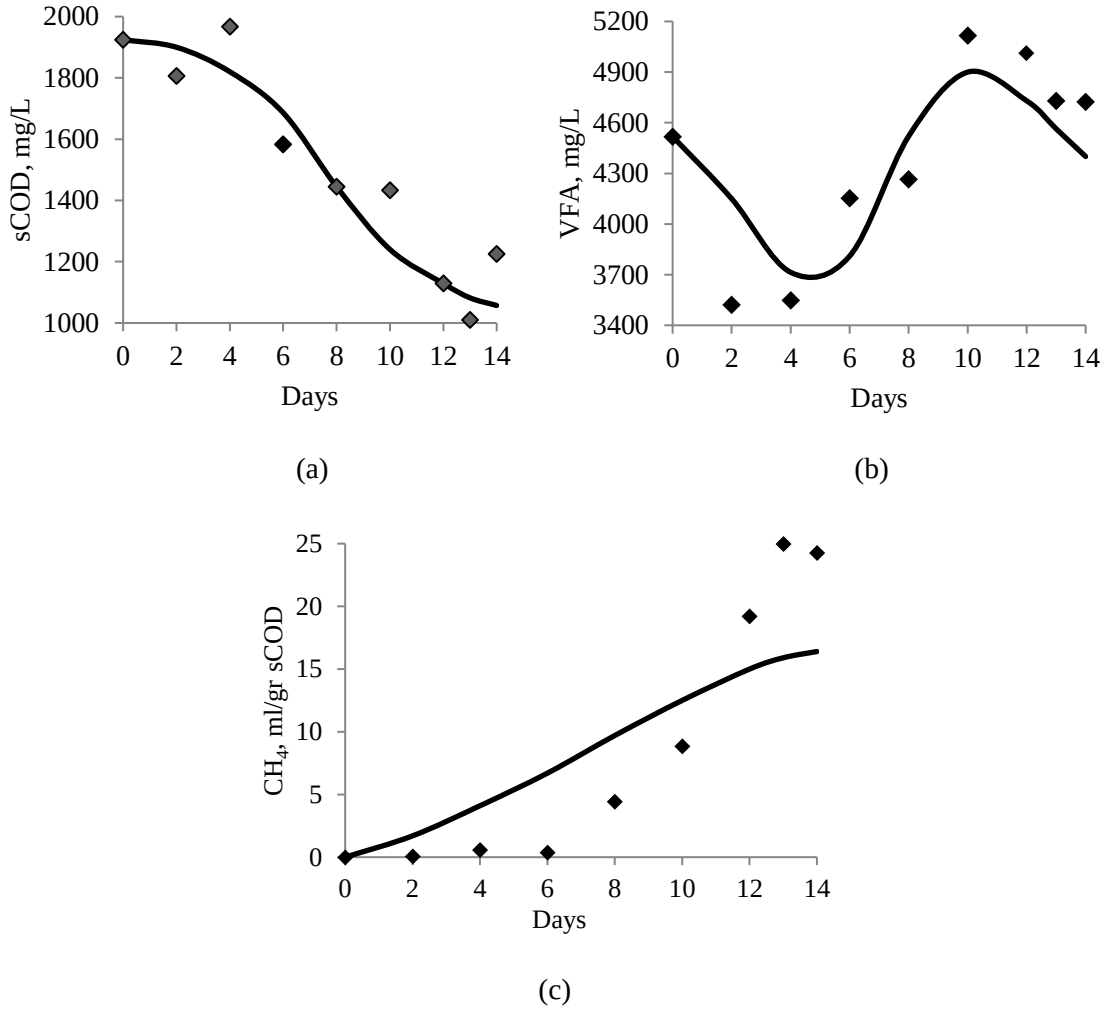
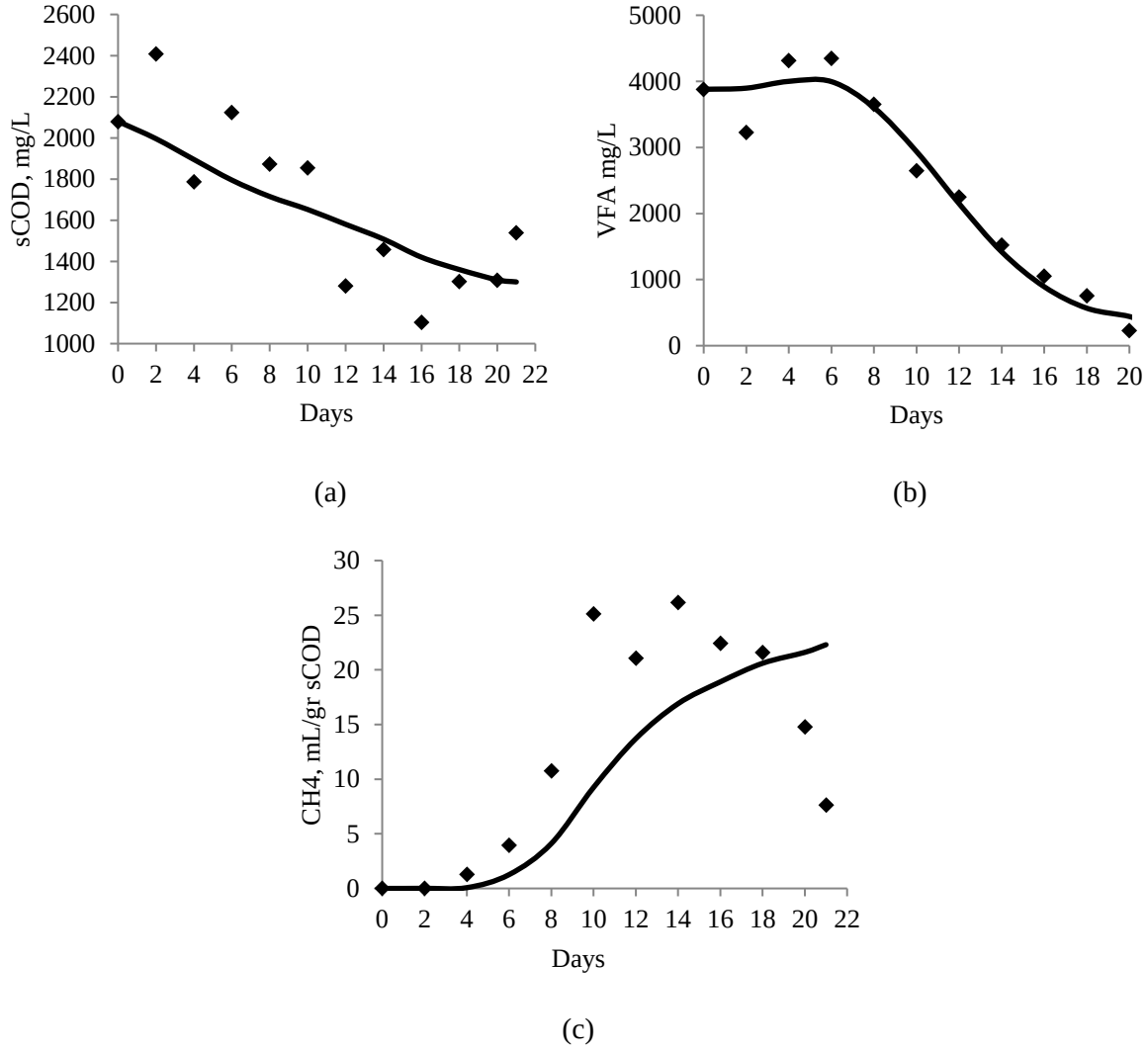


Figure 2. Profile of a). sCOD change against time b). VFA formation against time c). CH_4 production against time in acidogenic AFBR

3.2 Profile concentration of COD and VFA at methanogenic AFBR

Batch phase of methanogenic AFBR was observed for 21 days. The sCOD profile insignificantly decreased in this reactor. This condition proved that neutral condition had an important role to minimize acidogenesis process even this process was still existed (see figure 3). The VFA increase in the first 5

day of digestion, as shown by figure 3 (b), showed the adaptation phase of the microorganism. On the next day, decreasing VFA profile indicated that methanogenic microorganism started dominating in the anaerobic digestion under neutral condition. It was confirmed by CH_4 formation shown by figure 2 (c). Methane as methanogenesis process result started to be formed on day 4 and significantly increased on day 15. The decrease of CH_4 formation from day 15 indicated that for biogas production, there was minimum concentration of VFA between 1,000 – 1,500 mg/L.



(a) (b)

(c)

Figure 3. Profile of a). sCOD change against time b). VFA formation against time c). CH_4 production against time in methanogenic AFBR

The highest methane volume was 1,948.76 mL on day 14 and the highest purity achieved on day 18 was 63.16 % v/v methane. Methane purity aimed in this research was higher than batch anaerobic digestion of POME by using natural zeolite as immobilization media in the packed bed bioreactor done by Ayu et al. [1] and Purnomo et al. [15] which was about 54%. Fluidization system used in this work had been proven as an effective way to optimize anaerobic process based on the previous study by Ayu et al. [1].

3.3 Kinetics constants

The table 1 showed the kinetics constant of the kinetics equations. On the first stage AFBR of POME digestion, acidogenesis was observed as the dominant process. For acidogenic and methanogenic cells,

the growth rate (μ_m) and the death rate (k_d) in acidogenic AFBR showed relatively the same values. Nevertheless, sCOD reduction for both VFA conversion and acidogenic cell maintenance represented by $Y'_{X1/sCOD}$ as large as 235.4989 mg acidogenic cell/mg sCOD showed that the process dominating in this AFBR was acidogenic. It was confirmed by low yield of cell formation per mg VFA reduction ($Y'_{X2/VFA}$) as a parameter of methanogenic process.

Table 1. Kinetics constants of batch AFBR

Constants	Value		Unit
	Acidogenic AFBR	Methanogenic AFBR	
μ_{m1}	2.1321	0.000	day^{-1}
μ_{m2}	2.1321	0.6735	day^{-1}
K_{SX1}	0.0066	175.3444	mg COD/mg acidogenic cell
K_{SX2}	173.3997	0.7618	mg VFA/mg methanogenic cell
$Y_{sCOD/VFA}.Y_{VFA/X1}$	235.4989	0.000	mg VFA/mg acidogenic cell
$Y_{X2/VFA}$	0.0283	3.3251	mg methanogenic cell/mg VFA
$Y_{CH4/X2}$	0.2285	0.0016	[mg CH_4/L]/[mg methanogenic cell/L]
$Y_{X1/sCOD}$	0.000	0.5792	mg acidogenic cell/mg sCOD
$Y'_{X1/sCOD}$	235.4989	0.0000	mg acidogenic cell/mg sCOD
$Y'_{X2/VFA}$	0.0281	3.3251	mg methanogenic cell/mg VFA
k_{d1}	1.000	0.0000	day^{-1}
k_{d2}	0.9441	0.0000	day^{-1}

In the second stage AFBR (the methanogenic one), methanogenesis was observed as the main process existed proven by the dominant growth of methanogenic microbes. The growth rate of methanogenic microbes (μ_{m2}) was 0.6735/days while μ_{m1} was equal to zero. It indicated that there were only methanogenic microbes could grow well in the methanogenic AFBR. The very low opportunity for acidogenic microbes to survive was shown by the values of sCOD reduction both for VFA conversion ($Y_{sCOD/VFA}.Y_{VFA/X1}$) and for cell maintenance ($Y_{X1/sCOD}$) which were very low. Although methanogenesis succesfully dominated the process, methane conversion was not satisfying yet. The yield of CH_4 formation ($Y_{CH4/X2}$) was only 0.0016 [mg CH_4/L]/[mg methanogenic cell/L] compared to the yield of methanogenic cell growth from VFA consumption ($Y_{X2/VFA}$) which was 3.3215 mg methanogenic cell/mg VFA. Optimization could be made by shifting the process configuration to continuous process and applying diferent retention time to the methanogenic AFBR.

4.Conclusion

In the acidic condition of acidogenic AFBR, acidogenic dominated the process although methanogenic microbes could still survive. The pH level had an important impact to separate acidogenesis and methanogenesis process on double-stage system. Under neutral condition, it could be claimed that methanogenic microbes were successfully dominating the second stage of AFBR. Further study could focus on identifying and measuring the real concentration of both acidogenic and methanogenic microbes together with trying new process configuration for biogas production optimization.

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Nomenclature

C_{sCOD}	soluble chemical oxygen demand (mg/L)
C_{VFA}	volatile fatty acid concentration (mg/L)
C_{CH4}	methane concentration (mg/L)
X_1	acidogenic cell concentration (mg/L)

X_2	methanogenic cell concentration (mg/L)
μ_{m1}	maximum specific growth rate of acidogenic cell (day^{-1})
μ_{m2}	maximum specific growth rate of methanogenic cell (day^{-1})
K_{SX1}	half-saturation constant associated with sCOD (mg sCOD/mg acidogenic cell)
K_{SX2}	half-saturation constant associated with VFA (mg VFA/mg methanogenic cell)
$Y_{X1/CsCOD}$	yield of cell formation per mg sCOD reduction (mg acidogenic cell/mg sCOD)
$Y_{X2/C\ VFA}$	yield of cell formation per mg VFA reduction (mg methanogenic cell/mg VFA)
$Y'_{X1/CsCOD}$	total yield of cell formation per mg sCOD reduction (mg acidogenic cell/mg sCOD)
$Y'_{X2/CVFA}$	total yield of cell formation per mg VFA reduction (mg methanogenic cell/mg VFA)
$Y_{sCOD/VFA.}Y_{VFA/X1}$	yield of VFA formation per mg acidogenic cell (mg VFA/mg acidogenic cell)
$Y_{CCH4/X2}$	yield of CH_4 formation per mg methanogenic cell/L increase (mg CH_4/L]/[mg methanogenic cell/L)
k_{d1}	death rate constant of acidogenic cell
k_{d2}	death rate constant of methanogenic cell
Abbreviations	
POME	Palm Oil Mill Effluent
AFBR	Anaerobic Fluidized Bed Reactor
sCOD	Soluble Chemical Oxygen Demand
VFA	Volatile Fatty Acid