Anaerobic Digestion of Palm Oil Mill Effluent with Lampung Natural Zeolite as Microbe Immobilization Medium and Digested Cow Manure as Starter

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Abstract. Indonesia is well-known as the world's biggest palm oil producer with 32.5 million tons of annual production. Palm oil processing contributes to 60% wastewater, leading to environmental problem caused by excessive production of wastewater. This wastewater, i.e. Palm Oil Mill Effluent (POME), has high organic content (40,000-60,000 mg COD/L) which is potential for biogas production. However, its low pH value and long chain fatty acid content likely inhibit the anaerobic digestion. Porous media might reduce the inhibitory effect during POME digestion since the media act as both immobilization media for bacteria and as inhibitor adsorbent. Excessive amount of porous media might interfere with the nutrient consumption by microbes. There will be an optimum amount of porous media added, which depends on the wastewater characteristics. This research studied Lampung natural zeolite as immobilization media in digesting POME. The batch experiment was conducted for 40 days with different amount of natural zeolite, i.e. 0; 45; 100; and 200 g/g COD. Digested cow manure was used as the starter inoculum, considering the abundance of anaerobic bacteria therein. Zeolite addition was proven to accelerate COD reduction and stabilized the volatile fatty acid as the intermediate product of anaerobic digestion. The addition of natural zeolite up to 45 g/g COD is considered enough to increase the COD removal (85.695 %), maintain the methane content up to 50%, and enhance the bacteria activity. However, larger amount of natural zeolite lowered the methane production and COD reduction, which indicated nutrient adsorption on to the media and hence caused decreasing nutrient access by the microbes.

Keywords: Anaerobic digestion; Digested cow manure; Natural zeolite; Palm Oil Mill Effluent (POME)

INTRODUCTION

Palm oil is one of the most consumed oils since its price and wide applications in food, hygiene products, and fuel. Around 85-90% of total global palm oil is supplied by Indonesia and Malaysia. Indonesia as the largest palm oil producer has produced 32.5 million tons of palm oil this year. This number will increase to 40 million tons by 2020, as aimed by the government in response to global demand.

The goal, however, will give another challenge as the production of palm oil generates polluted wastewater known as palm oil mill effluent (POME). Around 5-7.5 tons of water is required in producing 1 tons of crude palm oil, while 50-60 % of the water ends up as POME. Its typical characteristics, i.e. 25,000 mg/L biochemical oxygen demand (BOD), 40,000-60,000 mg/L chemical oxygen demand (COD), pH 4-5, and 19,000 mg/L suspended solid (SS), restrict the direct discharge of POME into the environment [3].

Biological treatment, consists of anaerobic and aerobic ponding systems, has been accepted as common practice of POME treatment in Indonesia. Ponding system is considered as easy operating system, but on the other hand it needs long retention time (90-120 days), large land (5-7 ha), and high maintenance cost. The methane emission, approximately 5.5 kg of CH_4 per ton of treated POME, cannot be collected in ponding system, leading to environmental problem because of the green-house gases (GHG) release [2]. The need for efficient treatment system is emerged in order to preserve the environment and give economic benefit to the oil palm industries.

Recent researches have shifted from conventional system, e.g. ponding system, to high-rate anaerobic digesters, considering their advantages in collecting biogas and reducing the space requirements for treating POME [2, 3] The addition of support media in anaerobic digester, such as porous media, could also reduce the inhibitory effect during POME digestion caused by low pH value and long chain fatty acid contained in POME. Its roles as immobilization media for bacteria and inhibitor adsorbent will improve the digestion system by increasing organic removal and decreasing hydraulic retention time [4].

Zeolite is a natural mineral usually used in anaerobic digestion due to its high immobilization capacity. Its abundance makes zeolite appropriate as immobilization media, especially when it is applied in industrial scale. The amount of zeolite added for POME digestion need to be optimized since small amount of zeolite means less space for bacteria immobilization, meanwhile the excessive amount of zeolite might interfere the nutrient consumption by microbes [7].

This study is a part of the studies on improving anaerobic treatment of POME to obtain higher organic removal and methane production. In this study, various zeolite/liquid ratios were tested in batch digesters using digested cow manure as inoculum. Digested cow manure was used as the starter inoculum, considering the abundance of anaerobic bacteria therein which can reduce the start-up period. The purpose of this study was to obtain the optimum zeolite/liquid ratio to improve POME digestion which could be used as a base in the next studies.

METHODOLOGY

Characterization of POME and Inoculum

Raw POME was obtained from ponds in a palm oil mill located in Lampung, Indonesia, meanwhile the digested cow manure was collected from active biogas installation treating cow manure in Sleman, Special Region of Yogyakarta, Indonesia. The characteristics of Lampung POME and inoculum starter are presented on Table 1 and 2.

TABLE 1. Characteristics of Lampung Palm Oil Mill Effluent (POME)

Parameter	Value	Unit
pH	3.97	-
Chemical Oxygen Demand	11,995	mg/L
Protein	0.15	%
Nitrogen	0.0295	%
Total sugar	0.314	%
Fe	0.258	mg/L
Sulfide	5.8	mg/L
Phosphate	37.175	mg/L
Phenol	≤ 0.0001	mg/L
Nickel	0.143	mg/L
Oil and grease	115	mg/L
Potassium	1,459.86	mg/L
Sulphate	1,032.93	mg/L
Ammonia	125	mg/L

TABLE 2. Characteristics of digested cow manure as inoculum starter

Parameter	Value	Unit
pH	7.37	-
Chemical Oxygen Demand	2,830.0	mg/L
Volatile Solid	66,647.409	mg/L
Volatile Fatty Acid	1,382.347	mg acetic acid/L
Total anaerobic bacteria	10^6	cell/mL

Characterization of Natural Zeolite

Granular natural zeolite (clinoptilolite) was supplied from Lampung, Indonesia. Prior to the experiment, the zeolite was washed using aquadest and dried in an oven at 110°C for 3 h. The chemical and physical characteristics of the zeolite are tabulated in Table 3.

TABLE 3. Physical and chemical properties of Lampung natural zeolite

Chemical properties		
Si	60.7	% mass
K	11.5	% mass
Ca	10.0	% mass
Fe	8.48	% mass
Al	8.21	% mass
Mg	0.422	% mass
Mn	0.386	% mass
Sr	0.201	% mass
Rb	0.0896	% mass

Physical properties	
Specific surface area (m^2/g)	42.16
Total pore volume (cc/g)	0.1475
Average pore radius (Å)	194.63

Experimental Procedure

The batch digester, with 2.8 L of total volume and working volume 2.1 L, was connected to bubbler as gas visual indicator and through gasometer for gas measurement (Fig. 1). The gasometer was filled with acidified salt water to reduce biogas solubility [13]. The experiment was carried out in duplicate for 40 days in room temperature. Diluted POME (SCOD 5,000 mg/L) and digested cow manure were mixed with ratio 3:1 (v/v) and filled into the digester without pH adjustment. Different masses of zeolite were added, i.e. 45, 100, and 200 g zeolite/ g SCOD digester liquid, and one digester was set as control without zeolite addition. The nitrogen flushing was done for five minutes before the observation.

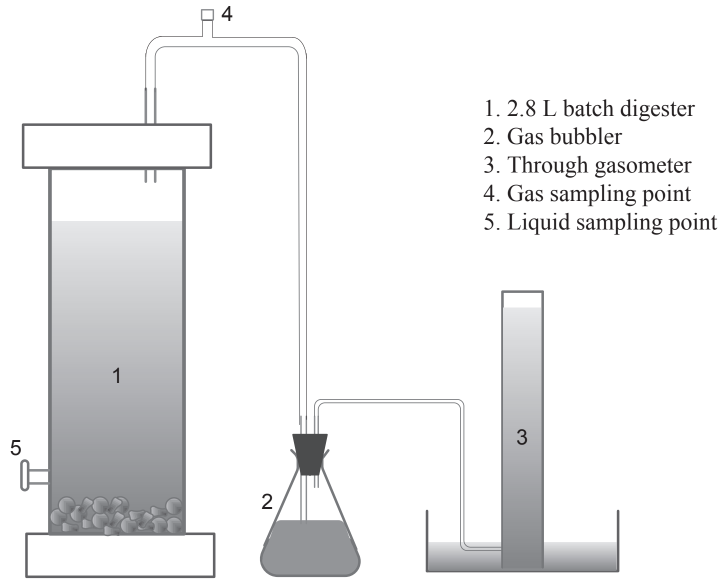

FIGURE 1. Experimental batch digester with granular Lampung zeolite equipped with bubbler and through gasometer for gas measurement

Analytical Methods

Biogas production was calculated using the through gasometer equation [13]. The determination of soluble chemical oxygen demand was carried out by closed reflux colorimetric method (APHA, 2005) by means of COD heater HI 839800 and Hach DR 900 colorimeter. The analysis of volatile fatty acid was conducted by distillation method, resulting VFA concentration as acetic acid [1]. The pH was measured by Lutron pH meter PH-208, calibrated with 7.0 buffer solution. Methane concentration was measured by Gas Chromatography Shimadzu GC 8A, Japan. The number of total anaerobic bacteria was analyzed by total plate count procedure.

RESULTS

The effect of Lampung zeolite addition in POME digestion could be investigated by monitoring the concentration substrate and product in anaerobic digestion stages, that is soluble chemical oxygen demand (SCOD), volatile fatty acid (VFA) as the intermediate product (product of acidogenic stage as well as substrate for methanogenic stage), and methane. Fig. 2 shows the average SCOD concentration during 40-days batch digestion with different zeolite/liquid ratios.

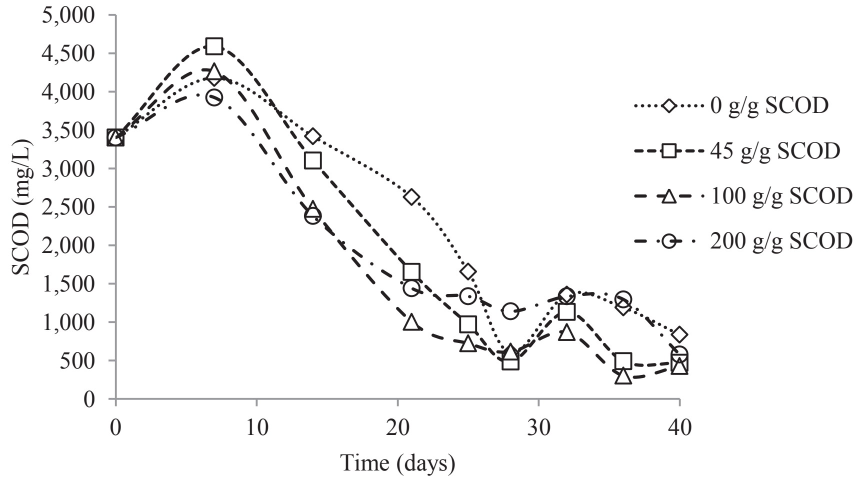

FIGURE 2. Average SCOD concentration in liquid phase of digesters with different zeolite/liquid ratios during batch digestion of diluted POME using digested cow manure

SCOD concentration increased at the beginning and in the end of experiment, as the indication of organic matter release due to hydrolysis stage, where insoluble organic compounds were converted to small soluble molecules, or acidogenic stage where the acidogenic bacteria formed acid that is known as VFA. VFA as intermediate product can be used as the parameter of process stability. Figure 3 illustrates the average VFA concentration for different zeolite/liquid ratios. VFA will be converted to biogas by methanogenic bacteria as shown in Figure 4.

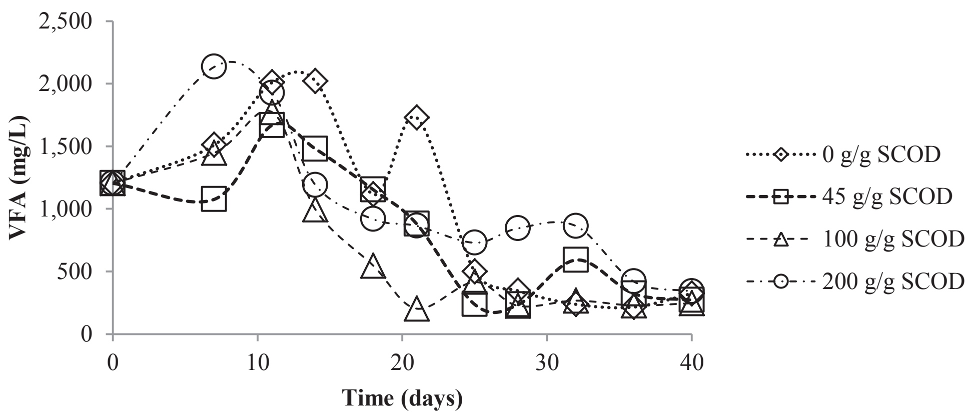

FIGURE 3. Average VFA accumulation in liquid phase of digesters with different zeolite/liquid ratios during batch digestion of diluted POME using digested cow manure

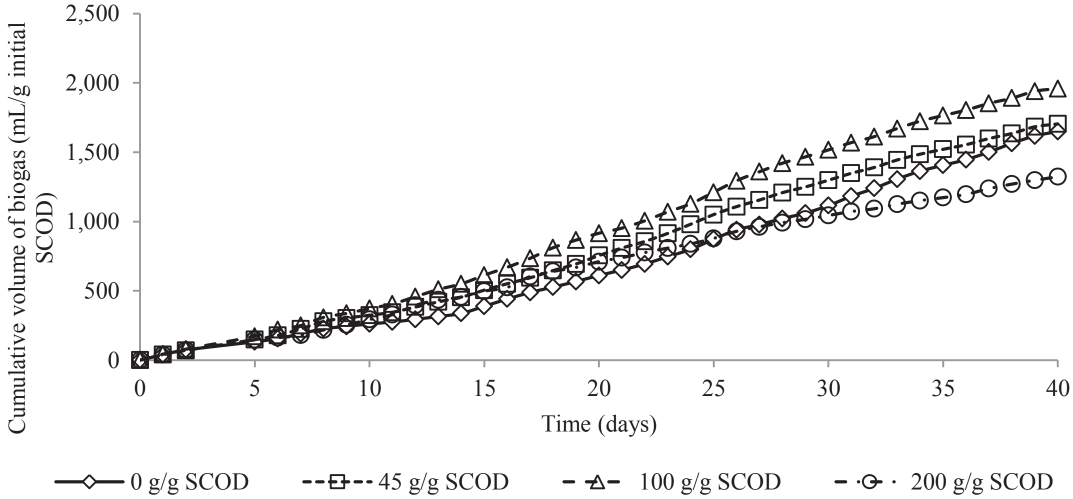

FIGURE 4. Average cumulative biogas volume (measured at 1 atm and 300K) of digesters with different zeolite/liquid ratios during batch digestion of diluted POME using digested cow manure

POME is fat-rich substrate for anaerobic digestion, giving theoretical ratio of CH_4: CO_2 70:30 % [12]. This value is higher than the methane concentration in this study, which is shown in Figure 5. However, up to 50% of methane produced from diluted POME digestion using digested cow manure, indicating good methanogenic bacteria activity.

Total number of anaerobic bacteria was measured in three time points in order to understand the effect of different zeolite/liquid ratios on bacteria growth. The result was tabulated in Table 4.

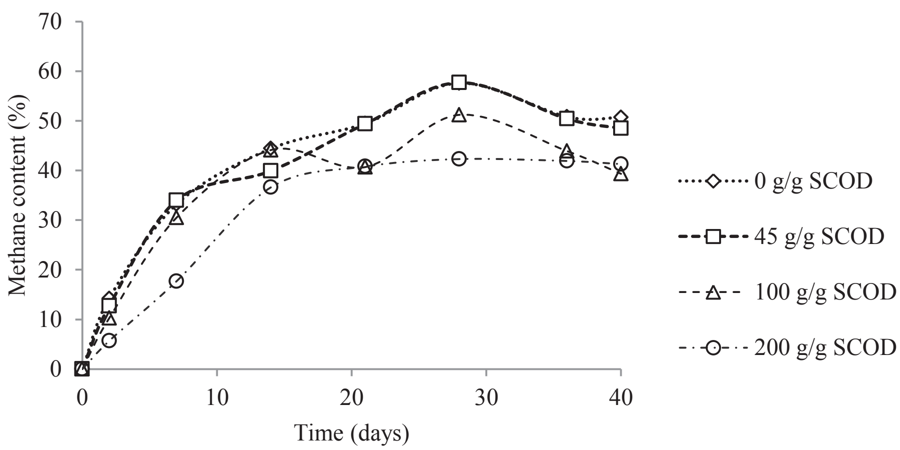

FIGURE 5. Average methane concentration of digesters with different zeolite/liquid ratios during batch digestion of diluted POME using digested cow manure as starter

TABLE 4. Result of total plate count analysis of liquid phase of digesters with different zeolite/liquid ratios during batch digestion of diluted POME using digested cow manure

Digester	Anaerobic bacteria (cell/mL)		
	Day 0	Day 28	Day 40
0 g zeolite/g SCOD	1×10^6	6×10^6	1.2×10^6
45 g zeolite/g SCOD	1×10^6	6×10^6	$(0.9 \pm 0.14) \times 10^6$
100 g zeolite/g SCOD	1×10^6	12×10^6	$(0.2 \pm 0.14) \times 10^6$
200 g zeolite/g SCOD	1×10^6	$(2 \pm 1.4) \times 10^6$	$(1.85 \pm 1.63) \times 10^6$

DISCUSSION

Inhibitors in Lampung POME and Their Effect in POME Treatment

Initial pH of diluted POME and digested cow manure mixture was 5.66, meanwhile the optimum pH for hydrolysis and acidogenic stage is 5.2-6.3. The pH value gradually increased to 7.0-7.5, reaching the optimum pH for methanogenic stage [6]. It showed that pH value did not reflect the existence of inhibitory substances in digestion of diluted POME.

The value of micronutrients in POME (Table 2), for example nickel and ammonia, do not exceed the inhibition concentration limit, therefore they can be utilized to enhance the bacteria growth. Some of the elements in POME do not meet the minimum concentration as trace elements, i.e. phenol and Fe. However, the concentration of potassium in POME is higher than 400 mg/L, potentially leading to process inhibition [5].

The main inhibitor in POME is long chain fatty acid (LCFA) since POME contained oil and grease (Table 1). LCFA absorption by bacteria disturbs the cell transport and protection, and finally causes sludge flotation and washout in continuous operation [5]. Sludge flotation was occurred in every digester, but the thickest sludge flotation was shown by digester with 200 g zeolite/g SCOD (picture not provided). It was suspected that the inhibition affected the microbial maintenance to be more dominant than the biogas production, explained by stationary number of total anaerobic bacteria during the digestion of diluted POME in digester 200 g zeolite/g SCOD (Table 4) although the organic removal was not different from other digesters (Fig. 2) and the VFA accumulation was the highest (Fig. 3).

The Effect of Different Zeolite/Liquid Ratios to Organic Removal and Methane Production

The Si/Al ratio of Lampung natural zeolite is 7.103 which classified as intermediate Si/Al zeolite. The Si/Al ratio is important characteristic of zeolites which contributes to the surface selectivity, thermal stability, and ion exchange capacity. The intermediate Si/Al zeolites have Si/Al ratio range 2 to 5, they are still hydrophilic in this Si/Al range [11]. It means that Lampung natural zeolite has selectivity of nonpolar sorbent, such as ammonia, than organic or polar sorbent, which give minor difference in organic removal.

The organic content in digester was represented by SCOD. Fig. 2 shows that the SCOD removal of each ratio was not different, i.e. 82.428; 85.695; 81.938; and 66.495 % for 0; 45; 100; and 200 g zeolite/g SCOD respectively. However, the addition of zeolite shortened the removal time, shown by lower SCOD concentration in zeolite digesters than SCOD concentration in control digester during week 2 to week 4.

Although the SCOD removal in each digester was not different significantly, the VFA accumulation in each digester fluctuated. The control digester shown more frequent VFA fluctuation (week 2 and 3) than other digesters. Meanwhile, the VFA accumulation of digester with 45 and 100 g zeolite/g SCOD were not different. It can be concluded that zeolite addition maintain the stability of VFA accumulation in digesting POME. Previous research also showed that zeolite addition decreased VFA accumulation in digesting inhibitory substrate such as ammonium and LCFA [9].

The VFA concentration in digester filled with 200 g zeolite/g SCOD was the highest during the anaerobic digestion, indicating the instability of VFA production by acidogen bacteria and VFA consumption by methanogen bacteria. This phenomenon has been found in some researches [7,10], that indicated the excessive adsorption of nutrient by the zeolite. The average pore diameter of natural zeolite was 389.26 Å, which is smaller than the anaerobic bacteria diameter [8]. High amount of zeolite would increase the nutrient adsorption on to internal surface area of zeolite, therefore affected the nutrient access for the bacteria.

Zeolite addition up to 100 g/g SCOD increase the biogas production up to 18.77% however, did not give significant effect on methane production (Fig. 4 and Fig. 5). Meanwhile, digester with 45 g zeolite/g SCOD only increased the biogas production 3.29% but maintained the methane concentration at the same level as the control digester. Addition up to 200 g zeolite/g SCOD on contrary decreased the biogas production and methane concentration.

The addition of 45 g zeolite/g SCOD did not increase significant amount of anaerobic bacteria compared to control digester (0 g/g SCOD), shown in Table 4. Nevertheless, the digester with 45 g zeolite/g SCOD had higher biogas production and lower VFA accumulation than control digester. It could be concluded that 45 g zeolite/g SCOD enhanced the activity of anaerobic bacteria although the total of anaerobic bacteria did not significantly different.

Although the Lampung natural zeolite addition gave positive effects in POME treatment, its characteristics was considered less appropriate to adsorb the main inhibitor in POME. Lampung natural zeolite has hydrophilic surface which tends to adsorb polar sorbents, while the main inhibitor in POME is organic LCFA. Modifying the Lampung natural zeolite by increasing its Si/Al ratio would increase its selectivity to organic sorbent. As the Si/Al ratio increases, the surface selectivity changes from hydrophilic to hydrophobic [11,14]. Increasing the hydrophobicity of the zeolite to bind more LCFA to the medium should be accompanied by immobilizing the appropriate microbes which could take LCFA as their main substrate. Instead of using cow manure as starter, the effluent of anaerobic reactor digesting palm oil biodiesel plant waste might be more suitable. Further research was necessary to explore the enhancement of POME anaerobic digestion using modified zeolites accompanied by finding the most beneficial sources of inoculum.

CONCLUSION

Zeolite addition in digestion of diluted POME could increase the organic removal rate, stabilize VFA fluctuation while maintaining biogas and methane production. The addition of natural zeolite up to 45 g/g COD was considered as sufficient range to enhance the activity of anaerobic bacteria. Larger amount of natural zeolite (up to 200 g/g SCOD) decreased the methane production and COD removal, which indicated nutrient adsorption on to the media and caused decreasing nutrient access by the microbes.

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