Effect of Ni and Co as Trace Metals on Digestion Performance and Biogas Produced from The Fermentation of Palm Oil Mill Effluent

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Abstract—Macro and micro nutrients are important ingredients for successful anaerobic digestion. The presence or lack of nutrients can enhance or limit the functioning of the fermentation process. Micro-nutrients most often reported as stimulatory are trace metals such as nickel, cobalt, iron, and zinc. The purpose of this research is to study the effect of nickel and cobalt as trace metals on digestion performance and biogas produced from the fermentation of palm oil mill effluent (POME). Anaerobic digestion was performed in a two litres stirred tank reactor and operated at a thermophilic temperature (55 ^{o}C). As raw material, a real liquid waste (POME) from palm oil mill was used. Fresh POME was obtained from a fat pit of palm oil mill's waste water treatment facility belongs to one of the palm oil company in North Sumatera which has VS concentration of 26,300 mg/L and COD value of 42,000 mg/L. To gain precise results, complete recording and reliable equipment of digester were employed. Supporting materials were also needed such as sodium bicarbonate, ammonium bicarbonate, and hydrochloric acid solution. Variables observed were included M-alkalinity, total solid (TS), volatile solid (VS), and biogas production. Hydraulic retention time (HRT) was maintained at 6 days. Experimental results concluded that the reduction of trace metals concentration did not affect the TS and VS concentration and M-alkalinity.

Keywords—anaerobic digestion; biogas; palm oil mill effluent trace metal; thermophilic

Submitted: September 4, 2012 Accepted: December 15, 2012

I. Introduction

Palm oil mill effluent (POME) is one of byproducts which come out from various units in palm oil mills such as, sterilization process, clarification process, hydro cyclone (clay bath), and washing unit. POME cannot be directly discharged into the environment because concentration of chemical oxygen demand (COD) is more than 50,000 mg/L (Ngan, 2000). It is necessary to treat this POME before being discharged into the environment. Moreover, the amount of organic matter content in POME is potentially to be processed into biogas through anaerobic digestion process.

Anaerobic digestion is the biological conversion of organic matter into methane (CH_4) and carbon dioxide (CO_2). In general, composition of biogas is 55-75 % volume of CH_4 and 25-45 % volume of CO_2. The biogas can be upgraded to vehicle gas (96-97% volume of methane) or used for production of heat. A part of the generated biogas can be used at the biogas plant itself in order to provide for the internal energy requirement and digested slurry which is formed can be used as fertilizer (Appels et. al., 2008).

Macro- and micro-nutrients are important ingredients in anaerobic digestion. The presence of nutrients can enhance the functioning of the fermentation process. Macronutrients needed in the system are commonly considered to be nitrogen and phosphorus while micro-nutrients most often reported as stimulatory include the trace metals nickel, cobalt, iron, and zinc (Speece, 1996). However, the trace metals; nickel, cobalt, and iron are not necessarily present in adequate amounts. Furthermore, these trace metals are not necessarily bioavailable.

The addition of trace metals (nickel, cobalt, and iron) in fermentation of municipal waste can enhance biogas production from 14 to 50%, because it exhibited increased acetate and/or propionate utilization rates upon supplementation with either nickel, cobalt, iron, or all three metals (Zitomer et. al., 2008). Furthermore, the addition of trace metal 15 mg/L Ni and 10 mg/L Co in the fermentation of molasses can increase COD reduction efficiency from 44% to 58% and also enhance biogas production up to 14.8% L/day (Espinosa et. al., 1996).

The effect of cobalt and nickel on the corrinoid and F430 content and on the growth of *Methanosarcina barkeri* on methanol was studied by Jiang (2006). Cobalt and nickel limitation was achieved and competition between cobalt and nickel uptake was observed. Uptake efficiency of cobalt was high at low cobalt concentration and decreased when the cobalt concentration in the medium was increased. Corrinoid and F430 content correlated positively with the cell content of the corresponding metal, but incorporation in the corrinoid (Jiang, 2006).

Based on the previous researches mentioned above, therefore the purpose of this research is to study the effect of Ni and Co as trace metals upon digestion performance and biogas produced from the fermentation of palm oil mill effluent (POME).

II. Experiment, Materials and Methods

A. Experiment and materials

Material used in this research was POME taken from a fat pit of palm oil mill's waste water treatment facility belongs to one of the palm oil company in North Sumatera. As supporting materials were $NaHCO_3$, hydrochloric acid solution, metallic solution of trace metal; $FeCl_2$, $NiCl.6H_2O$, and $CoCl_2.6H_2O$. The addition of $NaHCO_3$ is to maintain pH at 6.8 to 7.2 and content of M-Alkalinity $\geq$ 3000 mg/L. While the addition of $FeCl_2$ is to minimize H_2S production, and the addition of $NiCl.6H_2O$ and $CoCl_2.6H_2O$ are required for anaerobic microbial metabolism.

B. Methods

The fermentation process took place in a 2-litre-capacity transparent jar digester (EYELA, Model MBF 300ME) which was provided with double walled water jacket to control the temperature, valves for sampling, conduit for discharge and feeding, turbine propeller, and alarm indicator bulb anticipating temperature disorder. A data logger (KEYENCE, Model NR-250) was connected to computer to enable automatic recording of temperature and pH, provided by censoring equipments attached to digester (Irvan et. al., 2012). The pH was maintained in the range of 6.5 - 7.8 and M-alkalinity was maintained ≥ 3,000 mg/L with the addition 2.5 g of $NaHCO_3$/L POME and addition of nickel 0.49 mg/L and cobalt 0.42 mg/L at the loading up process.

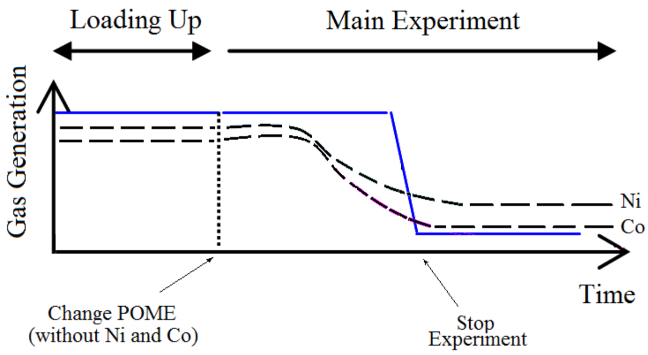

Figure 1. Experiment plan

Loading up was carried out based on several indications such as: the increased production of biogas which measured by using a gas meter, the decreased concentrations of total solids (TS) measured by weighing the samples which had been dried in an oven at 110 °C for 4 hours, and the decreased concentrations of volatile solids (VS) as measured by weighing the dried sample which had been heated in a furnace at a temperature of 700 °C for 2.5 hours. If the biogas production increased by 20%, then the loading up was increased by 20% until it reached HRT 6 days. When HRT 6 days was reached, the addition of trace metal nickel and cobalt was stopped. The experiment was stopped when fermentor did not produce biogas anymore. It might be occurred when the fermentation process was lack of trace metal nickel and cobalt. Figure 1 shows experiment plan of this research. Concentration of H_2S and CO_2 in the biogas were measured by using a suction gas injector (GASTEC, GV-100S type) and inspection tube (GASTEC, 25~1600 PPM).

III. Results and Discussions

A. Biogas production during the fermentation process

The measurement of biogas produced during the fermentation process was performed by using a dry test gas meter (SINAGAWA, model DS). Figure 2 shows biogas generation during the fermentation process. During the loading up, the addition of nickel and cobalt at the beginning of the fermentation process were 0.49 and 0.42 mg/L respectively. After HRT 6 days was reached (on the 55th day) and loading up was achieved (shown by the rise of biogas production which indicating microorganism in the fermentor has adapted well) the addition of nickel and cobalt were stopped. Stephenson and Lester has evaluated loading up process in the fermentation of livestock waste and obtained that loading up time was approximately 50 days by observing the increasing of biogas volume and the reduction COD value (Stephenson and Lester, 1986).

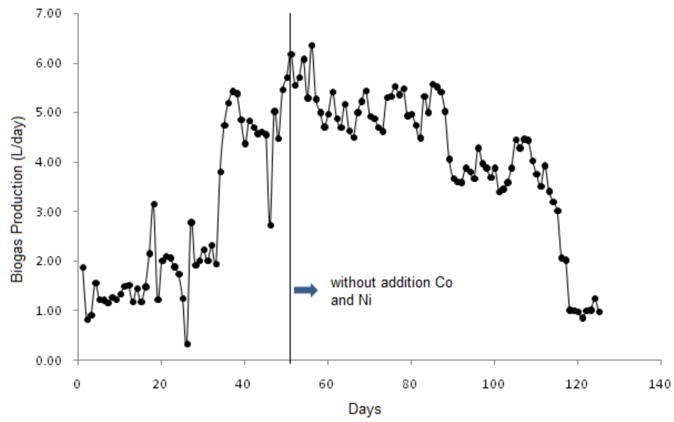

Figure 2. Biogas generation during the fermentation process

As shown in figure 2, gas generation at the beginning of fermentation was low. At this stage the microorganisms adapted to its environment. From the initial day to the 33rd day, biogas was obtained at the range 0.82 – 2.78 L/day which indicating microorganism started to adapt. Biogas generation started to increase on the 34th day and reached its higher volume 6.36 L/d on the 56th day. Indicating that microorganisms inside the fermentor, especially methanogens, have adapted very well, therefore it could produce biogas in large volume and high methane composition. (> 60%). This is in accordance with start up process for fermentation of glucose performed by Alkarimiah et.al. They reported that methane composition during 40 days of initial experiment only reached 15%, then increasing up to 36% after reaching the 45th days which giving indication that microorganisms condition have been stable (Alkarimiah et.al., 2011).

After the addition of nickel and cobalt were stopped on the 52nd day, the gas generation decreased gradually although until the 89th day the gas volume relatively high, above 4.7 L/day. This high volume of biogas could be obtained because biogas producer microorganisms were still stable since environmental condition and nutrient (such as trace metals) were still sufficient for the needs in the activity of methanogenic bacteria. The presence of nickel, cobalt, and iron can enhance biogas production significantly (Raju et. al., 1991). On the 113th day, biogas production kept on decreasing although no troubles were occurred to the equipment or controller of the fermentor.

Low concentration of nickel and cobalt in the fermentor became the main reason of low biogas production because the rest of trace metals in the fermentor were insufficient for methanogenic bacteria to work optimally. Obstruction of biogas formation caused accumulation of volatile fatty acid nd then disturbing fermentation process (Zitomer et. al., 2008). Until the 126th day of the experiment, biogas production only achieved 1 L/day, no progress at all, then finally stopped on the 128th day. This was due to trace metals presented in the fermentor has reached in very small concentration which was insufficient for the needs in the activity of methanogenic bacteria.

Based on volume of biogas obtained during the fermentation process it was observed that removal of nickel and cobalt as trace metals affecting on biogas production. When trace metals concentration inside the fermentor decreased then biogas production also decreased, this was due to the presence of trace metals can enhance acetate utilization rate to be converted to methane by methanogenic bacteria (Speece, 1996). Table 1 shows the trace metals composition in liquid fermentor after loading up and no addition of trace metals anymore.

Tabel 1. Trace metals concentration inside the fermentor and biogas production

Days	Biogas (L/day)	Nickel (mg/L)	Cobalt (mg/L)
52	5.85	0.53	0.45
54	6.07	0.5	0.39
100	3.88	0.18	0.08
126	0.25	0.14	0.04

On the 52nd day, nickel and cobalt concentration were still 0.53 and 0.45 mg/L respectively. These concentration values were accumulation of trace metals in POME and added trace metals into the fermentor. On the 55nd day, nickel and cobalt concentration started to decrease and day after day became lower. This indicated methanogenic bacteria grew well using nickel and cobalt which presented inside the fermentor for their metabolism. If methanogens growth reached to 4.8 and 30 g/L, then nickel and cobalt consumption will be high (Zhang et. al., 2003). Based on the values, on the 100th day when trace metals concentration have reduced to 70 – 80%, biogas still can be produced although the volume have decreased.

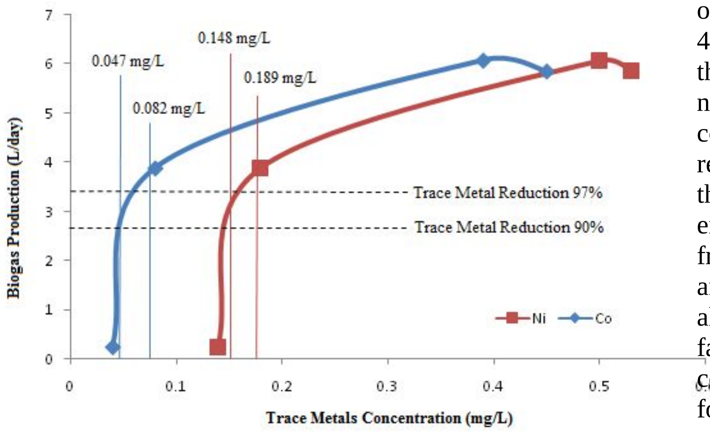

Figure 3. Trace metals concentration vs biogas production

Figure 3 shows trace metals concentration versus biogas production. As shown in figure 3, the decline of biogas amount was along with the decline of trace metals concentration inside the fermentor. Then, experiments were performed by reducing trace metals up to 97% from the initial concentration. Although the concentration was reduced until 97% but biogas in adequate amount was still obtained. Therefore, concentration of trace metals up to 90% or 97% are still possible to be reduced because biogas produced was still obtained in adequate amount.

B. Effect of no addition of nickel and cobalt to total solid and volatile solid in fermentor

Total solid (TS) is the amount of organic and inorganic matter contained in the waste water. While, volatile solid (VS) is the amount of organic matter converted into biogas in waste water (Schnurer and Jarvis, 2010). Biogas production is affected by amount of TS and VS in fermentor during the fermentation process. Figure 4 shows the amount of TS and VS of digested slurry in fermentor.

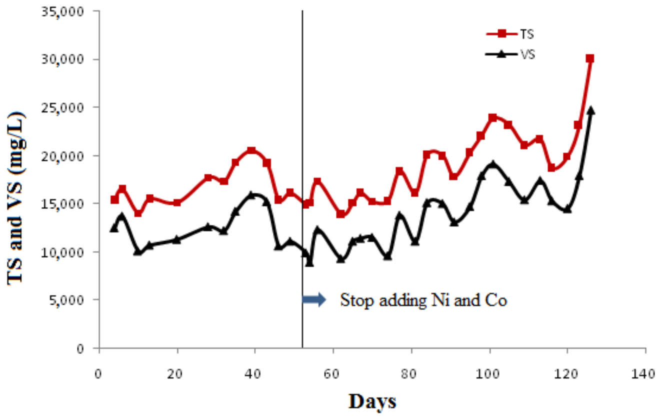

Figure 4. TS and VS inside the fermentor

As shown in figure 4 the tendency of TS reduction curve is similar to VS reduction curve. TS and VS concentrations inside the fermentor were high enough around 30,000 and 25,000 mg/L. In the beginning of the experiment, it was shown that TS (range 15,000 to 20,000 mg/L) and VS (range 12,000 to 16,000 mg/L) concentration were relatively high, this was due to microorganism were still in adaptation phase. Therefore they were not able to degrade organic matters optimally. TS and VS concentration tend to decrease after the 46th day, indicating that microorganism have adapted well, therefore enough VS to be degraded. After the addition of nickel and cobalt was stopped, the 52nd day, VS and TS concentration were still below 15,000 and 20,000 mg/L respectively until the 97th day. It might be occurred because the amount of nickel and cobalt in fermentor were still high enough since the accumulation of trace metal which came from fresh POME, previously. The presence of trace metals in anaerobic process can enhance methanogenesis up to 42% and also increase degradation rate of volatile solid and volatile fatty acid (Rao and Seenayya, 1994). On the 101st day, VS concentration increased up to 19,100 mg/L and 23,900 mg/L for TS, although the decline of TS and VS concentration still occurred on the next day, however the values were still relatively high. Until the day of 126th, VS and TS concentration achieved to 24,700 and 30,100 mg/L respectively.

The increasing of TS and VS values were possibly caused by the low performance of degradation process of microorganism due to the lack of trace metals in the fermentor. Therefore, it can be concluded that trace metals can affect conversion of VS to biogas. The drop in TS and VS concentration at significant values indicated that methanogenesis process was working successfully, as a result optimum biogas production can be obtained.

If VS percentage in waste water is high enough then volume of biogas produced is also high. VS is amount of organic solid, higher VS concentration in waste water, higher biogas production if treated using anaerobic process (Igoni et.al., 2008). The drop in VS concentration of waste indicating that biodegradation process of organic matter occurred which increasing biogas production (Chiemchaisri et. al., 2007).

C. Effect of no addition of nickel and cobalt to volatile solid decomposition

The effect of no addition of nickel and cobalt to VS decomposition in the formation of biogas is shown in figure 5. High percentage of VS decomposition indicated that biodegradation of organic matters occurred in the fermentor, and trace metals have an effect on the VS decomposition. Organic matter which degraded in anaerobic process will produce methane as final product, high decomposition of VS can be assumed as organic matter converted into biogas.

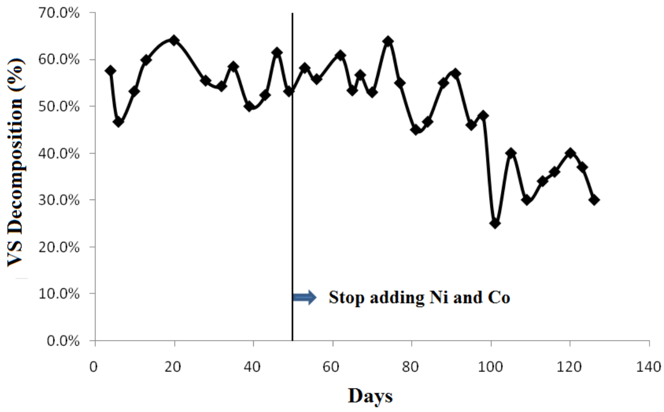

Figure 5. Volatile solid decomposition in the fermentor

As shown in figure 4, percentage of VS decomposition is still high, where an average VS decomposition percentage is above 50% at the initial experiment and even after the addition of nickel and cobalt is stopped. It might be because microorganisms consisted in the fermentor which degraded organic matters were in very good condition for growing since they have enough nutrition. However, on the 97th day, VS decomposition percentage decreased up to 40%, because the rest amount of trace metal in fermentor were insufficient for the needs in the activity of microorganisms. The presence of trace metals can influence the digestion or degradation of VS in anaerobic systems (Rao and Seenayya, 1994).

IV. CONCLUSIONS

Results indicated that biogas generation reached its higher volume of 6.36 L/d on the 56th day, indicating that microorganisms inside the fermentor could produce biogas in large volume and high methane composition. Biogas production stopped on the 128th day, due to trace metal concentrations were no longer sufficient for bacterial activity. Trace metals can affect conversion of VS to biogas, the drop in TS and VS concentration indicated that methanogenesis process was working well. VS decomposition percentage was above 50% initially, stable after no metals addition, and then dropped after that. Trace metals influenced the degradation of VS in fermentation of POME.

ACKNOWLEDGEMENT

This research was supported by Hibah Kompetitif Penelitian Unggulan Strategis Nasional No. 169/SP2H/PL/Dit.Litabmas /III/2012, date March 7th, 2012 and Metawater Co., Ltd-Japan.

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