The Effect of Fe Concentration on the Quality and Quantity of Biogas Produced From Fermentation of Palm Oil Mill Effluent

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***Abstract*—The purpose of this research is to study the effect of Fe concentration as a trace metal on the quality and quantity of biogas produced from the fermentation of palm oil mill effluent (POME). Raw POME as feed was obtained from one of the palm oil mills belong to PTPN IV, other materials used were hydrochloric acid, sodium bicarbonate, and trace metals. Observed variables were volume of biogas, concentration of Fe in raw POME and biodigester, degradation rate of total solid (TS) and volatile solid (VS), M-Alkalinity, pH, H_2S and CO_2 concentration in biogas at hydraulic retention time (HRT) 6 days. Before HRT of 6 days reached, initial trace metal compositions were 25.2 mg/L of Fe, 0.42 mg/L of Co, and 0.49 mg/L of Ni. After that, composition of trace metal were consisted only Co and Ni. The results showed that Fe as a trace metal did not affect the production or quantity of biogas. When Fe concentration reached over to 330 mg/L then concentration of CH_4, total solid (TS) and volatile solid (VS) decreased. Moreover, the higher the Fe contents the smaller of H_2S production. Fe content in POME from the same mill had different concentration, as the consequence biogas with different H_2S concentrations were produced as well. Thus, Fe in the trace metals is no longer required if high concentration of Fe already existed in POME because it can reduce the formation of H_2S. In addition, too high concentration of Fe in POME can be toxic for microorganism in the fermentation of biogas.**

***Keywords*—methane (CH_4), palm oil mill effluent (POME), Fe concentration, trace metal**

I. INTRODUCTION

Currently, Indonesia becomes the biggest country in producing crude palm oil (CPO) in the world. However, new problem appears as the consequence, namely more waste are generated. Generally, one ton of fresh fruit bunch can yield 0.2 tons of CPO, on the other side approximately 0.66 ton is converted into palm oil mill effluent (POME) (Chisti, 2007). POME can be utilized as biogas where its major component is methane (CH_4). The utilization of CH_4 as energy source has high economic value and appropriate for clean development mechanism (CDM) project. One cubic meter of CH_4 equals to 0.65 kg of LPG, thus by using CH_4 can save the utilization of fuel from unrenewable energy sources (Wintolo et.al., 2011).

Some of the particular metals have an important role in the growth and metabolism of microorganisms, but these metals can also be toxic if it is at a high concentration. Those metals are often called trace metal as the required concentration is relatively small. It has been found that the Fe content of 5 - 650 mg/L had no effect in inhibiting the shift to anaerobic digestion (Speece, 1996).

Zitomer et. al. reported that the addition of metal nickel (Ni), cobalt (Co), and iron (Fe) in thermophilic anaerobic fermentation process increased CH_4 production, especially if the fermentation conducted in a short retention time (Zitomer, 2008). Takashima and Shimada determined the minimum concentration of metallic Fe, Ni, Co and Zn in the fermentation of glucose to produce CH_4 and they reported that the minimum concentration for the fermentation were 3.5, 0.40, 0.45, and 2.0 mg/L respectively (Takashima and Shimada, 2004). Zandvoort et al. also reported that the precipitate formed by the addition of the metal in an anaerobic bioreactor did not limit the activity of methanogenesis (Zandvoort et.al., 2003).

Biogas is a mixture of methane, carbon dioxide, and depending on the feedstock used, traces gases such as nitrogen, ammonia, sulfur dioxide, hydrogen sulfide, and hydrogen. H_2S are toxic elements and substances that can cause corrosion of the equipment, if the biogas containing these compounds, it will cause a hazardous and corrosive gases (Horikawa, et.al., 2004). H_2S concentrations above 100 ppm have been highly toxic (Agrinz, 2008).

As we know, the price of each metal trace element is relatively expensive; so it should be really considered if implemented for large-scale commercial. Therefore the purpose of this research is to study the effect of Fe concentration for biogas production in fermentation process of palm oil mill effluent, in order to obtain amount of Fe required in the fermentation while maintaining the quantity and quality of produced biogas, especially maintaining the concentration of H_2S in biogas at low concentration.

II. EXPERIMENT, MATERIALS AND METHODS

A. Experiment and materials

Experiment was performed at Ecology and Environmental Laboratory, Department of Chemical Engineering, University of Sumatera Utara. In this study, palm oil mill effluent as raw material was obtained from one of the palm oil mills belong to PTPN IV. The experiment was conducted using a continuous stirred tank reactor (CSTR) with a volume of 2 liters, stirring rate 150-200 rpm and hydraulic retention time (HRT) at 6 days. The fermentation process was maintained with 34% recycle sludge of fresh POME. Variables checked and analyzed here consisted of volume of produced biogas, pH, M-alkalinity, total solid, volatile solid and concentration of CO_2 and H_2S. Other examinations such as CODcr, T-N, elemental composition analysis (C, H, N, S) and Fe content were completed at external laboratory.

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).

Raw POME without pretreatment was fed into the feeding tank which equipped with baffles and then added by $NaHCO_3$ and trace metals ($FeCl_2\ 4H_2O$, $NiCl_2\ 6H_2O$, $CoCl_2\ 6H_2O$). Composition of the initial concentration of each trace metal elements Fe, Ni, Co were 25.2, 0.49, 0.42 mg/L respectively. After HRT 6 days was achieved, there were only Co and Ni in the trace metals. Then the feed was pumped into the fermentor where the fermentation process of POME converted to biogas take place. Volume of biogas was measured by using wet gas meter (SHINAGAWA) and next kept inside the gas collector. Sludge from the bottom of the fermentor was pumped into the a storage and let to settle to the bottom of the tank for 6 hours, then recycled back to the feed tank 34% of raw POME.

III. Results and Discussions

A. *Biogas production in anaerobic fermentation*

The biogas generation in units of volume per mass of VS and time (L/mg VS day) is shown in figure 1. As described on Figure 1, biogas generation in anaerobic fermentation without the addition of Fe in raw POME have similar trend with the biogas generation with the addition of Fe as a trace metal.

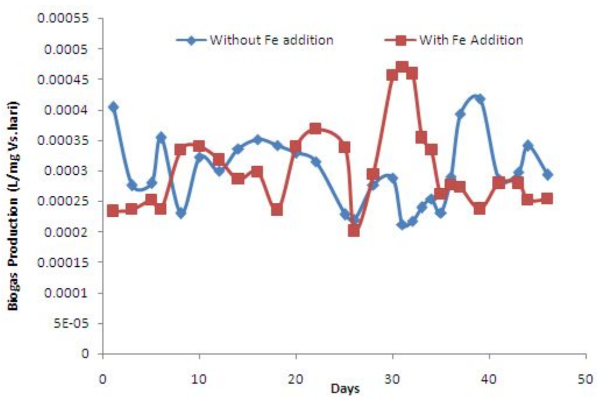

Figure 1. Biogas generation in POME fermentation

Trace metal can increase the rate of biogas generation. The most influential micronutrients include nickel, cobalt and iron (Zandvoort et. al., 2004). However, based on the results obtained, almost similar quality of biogas generation were produced with or without the additional of Fe as a trace metal. This research proved that the addition of Fe as trace metal in raw POME in the fermentation process did not affect biogas generation.

B. *Effect of Fe on the degradation rate of total solid and volatile solid*

The effect of Fe on the degradation rate of total solid and volatile solid is illustrated on figure 2. As shown on figure 2, there are two graphs of total solid and volatile solid which have similar trend. The graphs also show, with the increasing concentration of Fe, degradation rate of total solid and volatile solid increase in the beginning and decrease finally. This is in accordance with Rao and Seenayya in their research in improving methanogenesis of cow manure and poultry waste by adding the iron in 20 mM $FeSO_4$ each day, increased methanogenesis by 42%, and also increased the turnover rate of total solid, volatile solid and volatile fatty acids (Rao and Seenayya, 1994).

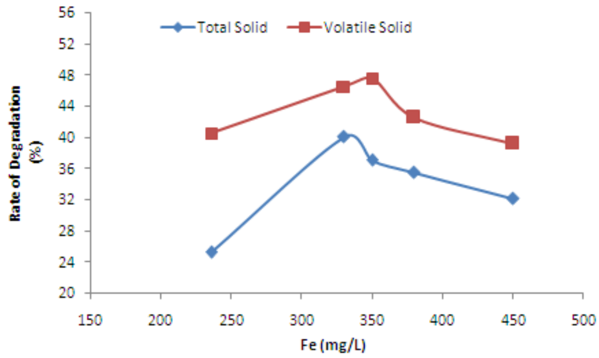

Figure 2. The effect of Fe on the degradation rate of total solid and volatile solid

When concentration Fe extremely increased from 236 to 330 mg/L, the degradation rate of total solid and volatile solid also increased, however, as the increase of Fe, the degradation rate of total solid and volatile solid decreased finally. It can be explained that microorganisms require certain essential metals, particularly the methanogenic archaebacteria which are known require Fe, Co, and Ni. However, at high concentrations, some of these metals can be toxic (Speece, 1996). The decrement is probably due to high content of Fe excessively in the fermentor, thus it become toxic for microbial metabolic processes and causing slow degradation of organic contained in POME.

C. *Effect of Fe on CH_4 and CO_2 content in generated biogas*

Methane content in biogas generated from POME fermentation is shown in figure 3. As shown on figure 3, CH_4 content in biogas initially increased and then decreased with increasing of Fe concentration. Same reasons are given for this condition, where excess Fe was overload in the fermentor, thus it became toxic, therefore, CH_4 which is one of the largest component of the biogas decreased. The similar trends are shown in figure 3 and figure 2. This is reasonable because, basically volatile solid is a percentage that indicates the potential of biogas generation.

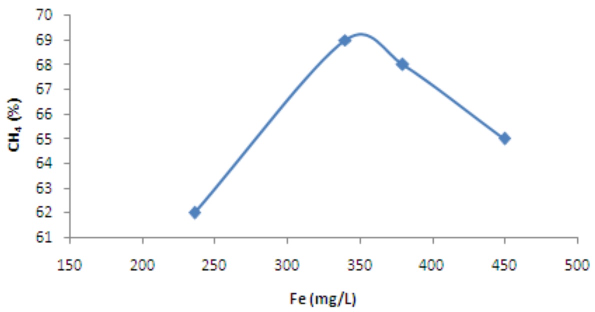

Figure 3. The effect of Fe on CH_4 content in generated biogas

Figure 4 shows the effect of Fe on CO_2 content in generated biogas. Produced CO_2 during the fermentation process of POME tends to decrease with the increasing of Fe concentration. Based on the previous discussion about the effect of Fe on CH_4, it was obtained that CH_4 production tends to increase with the increasing amount of Fe in fermentor, so it can be associated that the decreasing of CH_4 will cause the increasing of produced CO_2 during the fermentation process. Therefore, the correlation of produced CO_2 in the fermentation process is inversely proportional to produced CH_4.

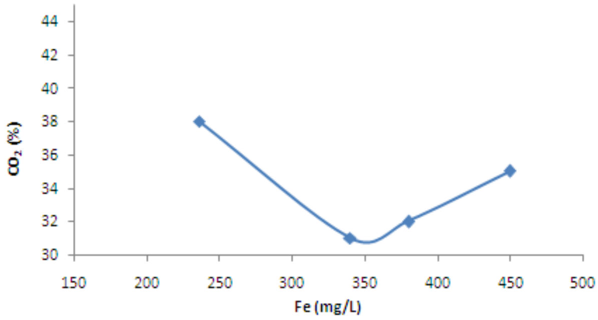

Figure 4. The effect of Fe on CO_2 content in generated biogas

D. Effect of Fe on H_2S content in generated biogas

Figure 5 shows the profile of Fe in fermentor and biogas production during fermentation. While figure 6 shows the produced H_2S during the fermentation process.

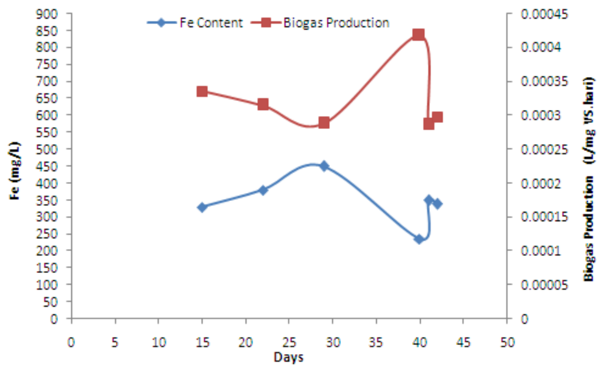

Figure 5. Profile of Fe and biogas production during the fermentation

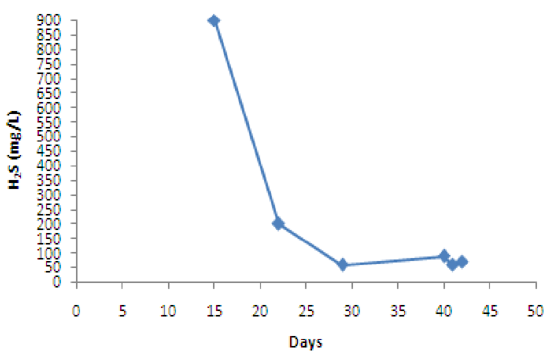

Figure 6. Profile of H_2S content in biogas

Many processes can be performed for the desulfurization of biogas, one of them is by adding Fe^{3+} or Fe^{2+} ions to the fermentor. It causes stable precipitation of iron sulfide and sulfur which still remain in the residue (Speece, 1996). Reations occured between Fe^{3+} or Fe^{2+} ions and H_2S are shown in equation 1 and 2.

$$Fe^{2+} + H_2S \longrightarrow FeS + 2H^{+} \quad (1)$$

$$2FeCl_3 + 3H_2S \longrightarrow 2\ FeS + S + 6HCI \quad (2)$$

From figure 6, it can be seen that H_2S production in the fermentation with recycle sludge tends to decrease even though no addition of trace metal Fe during the fermentation process. This is due to the fact that POME as raw feed has already contained high concentration of Fe and contained in different concentration of POME which taken from the same mill. Table 1 shows the Fe content in POME taken from same mill at different pick up dates.

Tabel 1. Fe content in raw POME at different pick up dates

Pick up dates	Fe concentration (mg/L)
May 7th, 2010	75
June 15th, 2010	66
July 3rd, 2010	220
August 1st, 2010	77

Concentration of produced H_2S during the fermentation process depend on Fe concentration in the raw POME. Based on figure 5 and 6, H_2S fluctuates with the fluctuation of Fe in raw POME. If Fe concentration is high then H_2S concentration tend to be low. Furthermore, figure 5 shows Fe concentration increased as biogas generation decreased and vice versa. It can be concluded that Fe contained in raw POME has stronger influence in reducing H_2S than as micronutrients to support methanogenesis.

E. Effect of Fe on M-Alkalinity

M-Alkalinity is an important factor for fermentor to work successfully. The required alkalinity value can be fulfilled by giving additional chemicals such as: sodium bicarbonate, sodium carbonate, ammonium hydroxide, sodium hydroxide, and kalium hydroxide (Khanal, 2008).

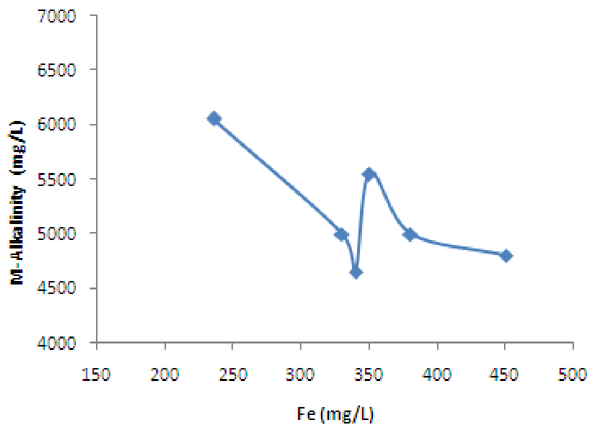

Figure 7. The effect of Fe on M-alkalinity

In anaerobic fermentation process, in order to neutralize volatile acids and to maintain pH changes, allowable values of alkalinity are in the range of 2,000 to 5,000 mg/L (Zitomer, 2008). The effect of Fe on M-alkalinity of liquid fermentor is shown on figure 6. As described on figure 6, alkalinity of liquid fermentor is still in the range of allowable values. Interesting results were shown when 236 and 350 mg/L of Fe obtained, alkalinity values were 6,050 and 5,550 respectively (over 5,000 mg/L). These were occurred on the 40^{th} and 41^{st} day of fermentation. It can be explained that high concentration of bicarbonat in recycled sludge caused excess bicarbonat in fermentor and then made alkalinity over the allowable value.

From figure 7 it can also be seen that the higher the Fe content in the raw POME, the lower the value of alkalinity. According to Gammons and Frandsen (2001), sulfate reducing bacteria (SRB) catalyzes the reduction of dissolved sulfate in waste into hydrogen sulfide, thereby increasing the alkalinity as indicated by the following reaction :

$$SO_4^{2-} + 2CH_2O \longrightarrow H_2S + 2HCO_3^- \quad (3)$$

The presence of Fe in the fermentation process inhibits the growth of SRB because sulfides which are supposed to be catalyzed by SRB have been precipitated by Fe previously. Therefore, the alkalinity value become low with the increasing of Fe concentration in the fermentor.

IV. Conclusions

Results indicated that biogas generation was not affected by the addition of Fe as a trace metal. However it affected others such as CH_4, CO_2, and H_2S content in biogas, degradation rate of total and volatile solid, and alkalinity of fermentor liquid. With the increasing of Fe concentration in the fermentor, produced CH_4 in biogas and degradation rate of total and volatile solid decreased, but CO_2 increased. This could be due to the concentration of Fe was too high so that it became toxic for microorganism and lowered their performance in degrading organic compounds.

During the fermentation process occured H_2S concentration tend to be fluctuative, this was due to Fe content in raw POME were different day by day, although the raw POME were obtained from the same mill.

Alkalinity decreased with the increasing Fe content in the fermentor, this was due to the presence of Fe in the fermentation process inhibits the growth of sulfate reducing bacteria (SRB) because sulfides which were supposed to be catalyzed by SRB had been precipitated by Fe previously.

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References

[1] Y. Chisti, "Biodiesel from microalgae", *Biotechnology Advances*, vol. 25, pp. 294-306, 2007.

[2] Wintolo, Marhento dan R. Isdiyanto, "Prospek Pemanfaatan Biogas dari Pengolahan Air Industri Tapioka", *Ketenagalistrikan dan Energi Terbarukan*, vol. 10, no. 2, pp. 103-112, 2011.

[3] R.E. Speece, "*Anaerobic Biotechnology for Industrial Wastewater*", Archae Press. USA, Nashville, 1996.

[4] D.H. Zitomer, C.C. Johnson and R.E. Speece, "Metal Stimulation and Municipal Digester Thermophilic/Mesophilic Activity", *Journal of Environmental Engineering*, vol. 134, no. 1, pp. 42-47, 2008.

[5] M. Takashima and K. Shimada, "Minimum requirements for trace metals Fe, Ni, Co, and Zn in thermophilic methane fermentation from glucose." *Proc., 10th World Congress Anaerobic Digestion*, Montreal, pp. 1590–1593, 2004.

[6] M.H. Zandvoort, R. Geerts, G. Lettinga, and P.N.L Lens, "Methanol degradation in granular sludge reactors at sub-optimal metal concentrations: role of iron, nickel and cobalt", *Enzyme and Microbial Technology*, vol. 33, pp. 190-208, 2003.

[7] M.S. Horikawa, F. Rossi, M.L. Gimenes, C.M.M. Costa and M.G.C. da Silva, "Chemical Absorption of H_2S for Biogas Purification", *Brazilian Journal of Chemical Engineering*, vol. 21, no. 03, pp. 415-422, 2004.

[8] G. Agrinz., "*Biogas purification and assessment of the natural gas grid in Southern and Eastern Europe*", Biogas for Eastern Europe, Leitbnitz, 2008.

[9] Irvan, B. Trisakti, V. Wongistani, Y. Tomiuchi, "Methane emission from digestion of palm oil mil effluent (pome) in a thermophilic anaerobic," *International Journal of Science and Engineering*, vol. 3 no. 1, pp. 32-35, 2012.

[10] M.H. Zandvoort, J. Gieteling, G. Lettinga dan P.N.L. Lens, "Stimulation of methanol degradation in UASB reactors: in situ versus pre-loading cobalt on anaerobic granular sludge", *Biotechnology and Bioengineering*, vol. 87 no. 7, pp 897-904, 2004.

[11] P.P. Rao dan G. Seenayya, "Improvement of methanogenesis from cow dung and poultry litter waste digesters by addition of iron", *World Journal Microbiology and Biotechnology*, Vol.10, pp. 211-214, 1994.

[12] S. Khanal, *Anaerobic Biotechnology for Bioenergy Production: Principles and Applications*, Wiley-Blackwell, 2008.

[13] C.H. Gammons and A.K. Frandsen, "Fate and transport of metals in H_2S-rich waters at a treatment wetland", *Geochemical Transaction*, Vol. 2, no. 1, 2001.