

Preliminary Study of using Palm Oil Mill Effluent to produce Bio Hydrogen as Biofuel

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Abstract

Indonesia has the largest oil palm plantations in the world and it produces about 32 million tonnes of palm oil annually. During palm oil processing, Palm Oil Mill Effluent (POME) is generated and this organic waste has very high chemical oxygen demand (COD) of between 30,000 ppm and 100,000 ppm. POME can be converted directly to hydrogen biogas and this is very desirable because it can be used as both fuel and chemical reagent. Efforts to produce more hydrogen biogas rather than methane biogas can be done via consortium fermentation by suppressing methanogenesis microorganism in activated sludge using physical treatment. In order to maintain the fermentation for hydrogen biogas production, the pH was controlled in a rather acidic condition (pH 5-7). The characteristic of this process was studied by doing batch fermentation. To maintain the desirable fermentation condition, 10% phosphate buffer and 5% NaCl were added. It was discovered that hydrogen biogas fermentation using the smallest batch process was influenced by hydrostatic pressure, fermentation time and the amount of active sludge. Therefore, to maximize hydrogen biogas production, the process was done with a bioreactor in order to minimize hydrostatic pressure.

In the bioreactor system, hydrogen biogas flows directly to the sampling gas and as a result, the hydrogen biogas produced has a hydrogen concentration reaching 50% and its yield reached 0.7 mL/mL POME in the batch system. The amount of hydrogen biogas increased in the bioreactor by 0.9 mL/mL POME because the hydrostatic pressure was minimized. As for the semi-continuous process, the cultivation was treated to one day of anaerobic fermentation without additional POME. During this fermentation phase in the bioreactor, the hydrogen biogas generated was 1,200 mL in 2.5 L of working volume reactor. In the continuous stage, the hydrogen biogas yield was stable at 0.9 mL/mL POME for inlet POME 4.10 mL/min.

Keywords: Hydrogen biogas, POME, consortium microbes, physical suppressing methanogenesis, semi continuous fermentation.

Introduction

Due to the depletion of fossil fuel sources, efforts to explore renewable energy resources need to be boosted to meet energy needs such as building renewable energy-based power plants. The government aims to increase renewable energy utilization by 0.5% in 2014 and to 9.5% by 2030¹. Hydrogen produced from organic waste is an alternative fuel from renewable sources, simply labelled as "Waste to Energy". Hydrogen can be utilized directly as fuel for Fuel Cell to produce electricity. This fuel cell system is a viable alternative power source for the rural areas in which the State Owned Company for Power (PLN) does not have this infrastructure up yet.

Adding hydrogen to methane in turbulent combustion processes is similar to that of integrated gas turbine power plants. It has an impact on all physical and chemical parameters of the reactive system². Indonesia is the largest palm oil producer in the world with total production of crude palm oil (CPO) standing at about 32 million tonnes annually. This enormous palm oil production has led to the accumulation of a huge amount of palm oil mill effluent (POME), which is disposed of as liquid wastes. It is estimated that for each tonne of COP yield, 2.5 tonnes of POME is produced. This effluent contains extremely high quantities of organic content - the chemical oxygen demand (COD) and biological oxygen demand (BOD) are about 30,800 and 7,800 ppm, respectively^{5,6}.

The characteristics of raw POME are summarized in table 1. Due to the extremely high content of organic pollutants, POME should not be dumped directly into the stream. In fact, the organic content in POME can be used as a carbon source for microbes. Hence, POME can be used as a raw material for hydrogen production, which is an energy carrier⁷. An enzymatic treatment of POME⁸, for example using lipase, can decompose oil or grease, but its application is constrained by the price of lipase.

This study assesses the production of hydrogen from POME by utilizing active sludge from the palm oil industry and mixing it with cow manure. The resultant active sludge tended to produce hydrogen with much lower H₂S⁹. In addition, for the ratio of hydrogen and methane, this consortium pathways tended to produce more hydrogen than methane too.

Material and Methods

Materials: POME for this study was provided by Kertajaya Ltd, a state-owned palm oil company (PTPN VIII), located

in Malimping, Banten province. The head office of PTPN VIII is in Bandung, West Java.

Table 1
Characteristics of fresh POME.

Characteristics	Concentration (ppm)
COD	30,800
BOD	7,800
Total suspended solid (TSS)	9,800
Oil and grease	1,800
pH	4.0–4.5

Active sludge containing microbial consortium that was developed from POME was obtained from Adolina Ltd., Medan, North Sumatera. The active sludge was mixed with cow manure to enrich hydrogen concentration in biogas. Initial gas production testing conducted for POME by PTPN III and PTPN VIII yielded similar results.

The phosphate buffer that was used only at the start of the anaerobic fermentation process was provided by Merck EMD Millipore Corporation, a German firm. KH_2PO_4 and K_2HPO_4 were mixed in varying ratios to get pH 5.0, 5.5, 6.0, 6.5 and 7.0.

Methods

Suppressing methanogenesis: Active sludge, through indirect heating, was heated to 95°C for 1.5 hours in order to suppress methanogenesis microbes.

Batch experiment: Biogas production for hydrogen was done in a closed 100 mL bottle and the working volume was between 50 and 80 mL. The bottle was closed tightly and the biogas produced was measured every two days.

Semi continuous experiment: Biogas production was scaled up in a semi-continuous system with total incubation time of five days. The fermentor used has a volume of 2.5 L and a working volume of about 2 L. This system is equipped with a separator to separate POME liquid waste from the resulting gas. The feeding of POME included using a peristaltic pump with minimum speed. The fermentor system also features a pH monitoring tool. Increased hydrogen production was also done with the semi continuous process by using Continuous Stirred Tank Reactor (CSTR) with 2 L working volume.

Analysis

The COD was analyzed using the Lovibond MD 100 COD kit with 0-15,000 ppm COD / CSB vials containing potassium dichromate, HgSO_4 and 61% sulfuric acid. Generally, fresh POME has a range of between 15,000 and 100,000 ppm¹⁰, so the sample should be diluted using aquadest of 2-8 times according to COD prediction. Gas chromatograph thermal conductivity detector (GC-TCD Shimadzu 8A) was used to analyze the hydrogen, carbon

dioxide (CO_2) and methane (CH_4). Injection temperature, cooling temperature and final temperature were 100, 50 and 50°C respectively. Gas in the sampling bag was inserted by pushing the sampling bag smoothly for 30 seconds.

Water displacement was used to measure the total biogas produced. The gas that had passed through this water displacement was collected in a sample bag to analyze its composition with GC-TCD Shimadzu 8A.

Results and Discussion

The preliminary biogas production test using POME and cow manure showed that methane was less than 5%. Thus, this consortium not only produced minimum H_2S ⁹ but also tended to produce more hydrogen than methane. Moreover, after physical treatment, methanogenesis was suppressed so that the amount of methane was much less and can be ignored as shown in figure 1. The biogas produced is referred to as "hydrogen biogas".

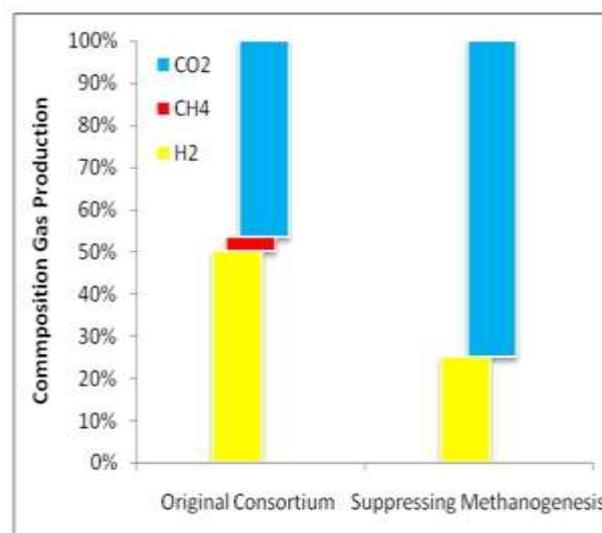


Figure 1: POME and Activated Sludge for Hydrogen Biogas Production.

The effectiveness of converting POME to hydrogen biogas was determined by measuring the reduction of COD and BOD. The COD and BOD were measured before and after the production of hydrogen biogas as shown in figure 2. The COD dropped by only 26.1% whereas almost all the BOD degraded or was consumed by microorganisms. The data gathered proved that hydrogen biogas production was not effective in reducing COD. However, COD reduction can be done by methane biogas production whereby the decomposition of COD can reach 80-95%¹¹. Anyway, hydrogen biogas production was shown to be effective in reducing BOD where less than 2% was left.

Another characteristic of hydrogen biogas production using the batch system was the effect of incubation time. As shown in figure 3, in the beginning of cultivation in an anaerobic process, the ratio of hydrogen/carbon dioxide was very high hitting 50%.

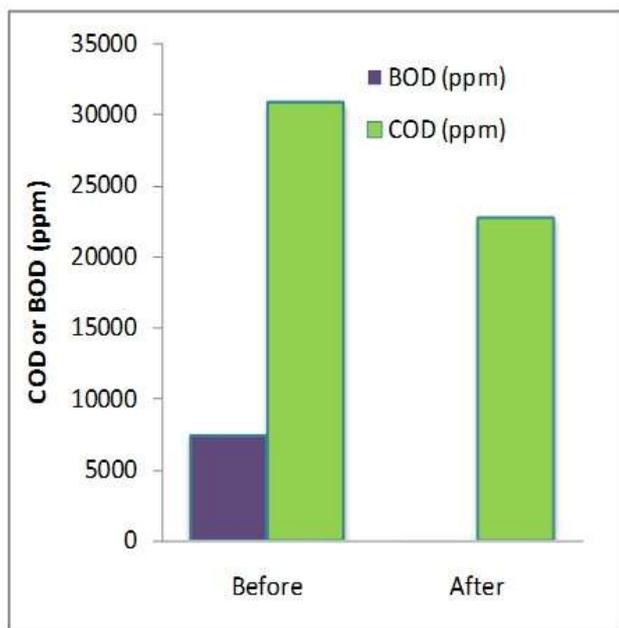


Figure 2: COD and BOD removal during the Hydrogen biogas production of POME.

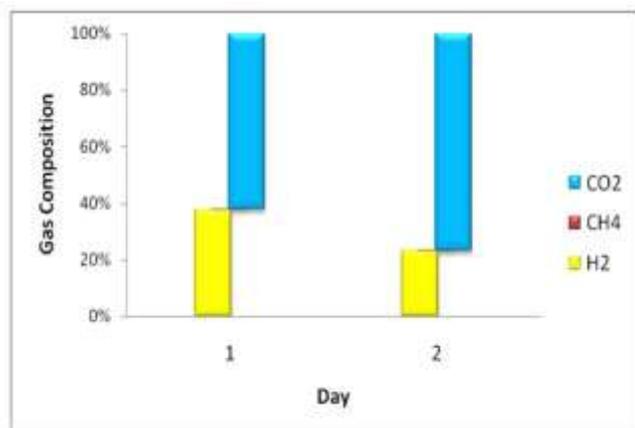


Figure 3: Gas composition in hydrogen biogas Production in a batch system.

This is due to the fact that in the beginning of the process, the amount of consortium microbes was relatively low when compared to the amount of substrate. In addition, the consortium's secondary metabolism was still working well then. Thus, hydrogen, as the effect of secondary metabolism, was maximally produced. But on the 3rd to 4th day, the number of microbe consortium grew much more and with fewer substrate residues. Therefore, primary metabolism activity was more dominant than the secondary one. This was reflected by the increasing percentage of carbon dioxide as the effect of primary metabolism. Conversely, the percentage of hydrogen decreased as the secondary metabolic effect declined in number.

The characteristic of the last process observed was the effectiveness of the working volume at 100 mL bottle capacity for the batch process. In several experimental bottles, the production of hydrogen biogas was monitored

under varying working volumes. The productivity of hydrogen biogas was found to be at the optimum when 60 mL POME was used. In addition, with this working volume, the ratio of hydrogen biogas to POME used was also at an optimum - 0.70 mL hydrogen biogas/mL POME. This result confirms that with anaerobic digestion, hydrostatic pressure has an adversely negative influence on methanogenesis and hydrogen production as well¹².

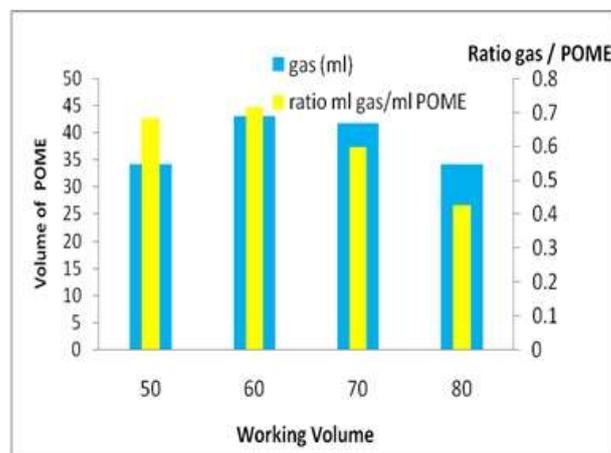


Figure 4: Effects of the working volume against the total volume on the effectiveness of hydrogen biogas production and the hydrogen biogas / POME ratio.

Semi continuous of hydrogen biogas production: In a semi continuous system, anaerobic digestion was conducted in order to determine the weaknesses of the batch system such as hydrostatic pressure and substrate ratio to microbe consortium. The effect of hydrostatic pressure was anticipated with the presence of a gas separator, where the gas formed would flow out with the digested medium. The outflowing gas was measured in total volume and an analysis of the gas composition was done. At certain times, the gas flowed directly into the Fuel Cell. This was to study how much power can be achieved in the continuous hydrogen biogas production.

The digested medium and sludge that came out brought about a number of microbe consortiums. At a flow rate of 2.7 mL / min during a duration of between 24 and 44 hours, the hydrogen biogas productivity was 4.10 mL / min. The production decreased during the 44 and 52 hours duration whereby only 1.5 mL / min of hydrogen biogas was produced. The reason is probably because the larger number of microbes could not be matched with the number of substrates included. In addition, the low flow rate was not able to push the sludge to flow out with other media.

By raising the flow rate of POME to 4.2 mL / min, the resulting hydrogen biogas remained the same in the first 24 hours. After that, the hydrogen biogas production increased to 2.8 mL / min. This condition remained stable until the 120th hour, where the hydrogen biogas yield was 0.9 mL / mL POME.

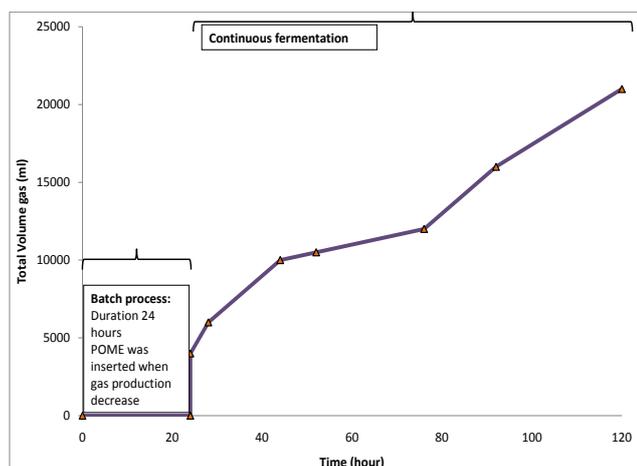


Figure 5: Semi continuous hydrogen biogas production of POME

Conclusion

In a batch system, this study found out that the production of hydrogen biogas is influenced by hydrostatic pressure, anaerobic digestion time and the amount of active sludge. It also represents the number of microbial consortia. At optimal condition, hydrogen concentration reached 50% and the yield of hydrogen biogas reached 0.7 mL / mL POME.

Further development in semi continuous system at 2.5 L of bioreactor working volume resulted in a maximum yield of hydrogen biogas of 0.9 mL / mL POME with a flow rate of POME 4.20 mL / min.

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References

1. PTPSE, Outlook energi Indonesia, PTPSE – BPPT, Jakarta (2011)
2. Bouras F., Attia M.E.H., Khaldi F. and Ameer M.S., Control of methane flame properties by hydrogen fuel addition: Application

to power plant combustion chamber, *International Journal of Hydrogen Energy*, **42**, 8932-39 (2017)

3. Directorate General of Estate Crops, The Crop Estate Statistics of Indonesia: 2015-2017 Palm Oil, Secretariat of Directorate General of Estate Crops, Jakarta (2016)

4. Ho C.C., Tan Y.K. and Wang C.W., The distribution of chemical constituent between the soluble and the particulate fraction of palm oil mill effluent and its significance on its utilization/treatment, *Agric. Wastes*, **11**, 61-74 (1984)

5. Taha M.R. and Ibrahim A.H., COD removal from anaerobically treated palm oil mill effluent (at-POME via aerated heterogeneous fenton process: Optimization study, *Journal of Water Process Engineering*, **1**, 8-16 (2014)

6. Wong Y.S., Kadir M.O.A.B. and Teng T.T., Biological kinetics evaluation of anaerobic stabilization pond treatment of palm oil mill effluent, *Bioresour. Technol.*, **100**, 4969-75 (2009)

7. Norfadilah N., Raheem A., Harun R. and Ahmadun F.R., Bio-hydrogen production from palm oil mill effluent (POME): A preliminary study, *International Journal of Hydrogen Energy*, **41**, 11960-4 (2016)

8. Wong K.M., Rahman N.A., Aziz S. and Sabaratnam V., Enzymatic hydrolysis of palm oil mill effluent solid using mixed cellulases from locally isolated fungi, *Research J Microbiology*, **3**(6), 474-81 (2008)

9. McKinsey-Zicari S., Removal of hydrogen sulphide using cow manure compost, Master Thesis, Department of Biological and Environmental Engineering, Cornell University (2003)

10. Madaki Y.S. and Seng L., Palm Oil Mill Effluent (POME) From Malaysia Palm Oil Mill, Waste or Resource, *International Journal of Science, Environment and Technology*, **2**(6), 1138 – 55 (2013)

11. Rahayu A.S., Karsiwulan D., Yuwono H., Trisnawati I., Mulyasari S., Rahardjo S., Hokermin S. and Paramita V., Handbook POME-to-Biogas: Project Development in Indonesia, Second Edition, USAID and Winrock International (2015)

12. Mateescu C., Influence of the hydrostatic pressure on biogas production in anaerobic digesters, *Romanian Biotechnological Letters*, **21**(5), 11941-48 (2016).