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To cite this article: A Gumilar *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **314** 012008

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# Biohydrogen as a renewable energy and its potential production from the conversion of palm oil mill effluent by anaerobic processes

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**Abstract.** Biohydrogen is one of the promising alternatives to be used as a source of energy in the future. Several studies related to the production of biohydrogen through the process of conversion of organic wastewater by anaerobic process have been done with different reactor conditions. However, biohydrogen is not the main products produced in the process, even biohydrogen is produced in relatively few amounts compared to other acidogenesis products such as volatile acids. The aims of the study are to determine the optimum conditions of biohydrogen production through the control of pH are 5.5; 6.5; 7.5 and 8.5. This factor affects to the metabolism pathway. The study was conducted using the wastewater from the palm oil mill effluent as a substrate, pure culture and mixed culture bacteria as a biomass and performed in the laboratory using an anaerobic batch reactor which will be operated for 72 hours. Sampling was done every 6 hours and then analysed the product of acidogenesis produced. The results show that the optimum conditions for biohydrogen production occurs in the reactor with the pH 5.5-6.5 are  $15.27\% \pm 0.404\%$  to  $15.40\% \pm 0.265\%$ .

## 1. Introduction

The utilization of renewable fuels is the main topic of discussion to overcome the problem of fossil fuels. This is due to the limited number of fossil fuels from fossils while the world's energy needs continue to increase. At present, the average energy use per capita in the world is 2.5 kW. The population in the world in 2050 is predicted to be 9.6 billion people, then the energy needed to meet all human needs is 24 TW. The use of energy per capita in the world tends to increase along with the standard of living in 2050 to 6.5 kW, so the energy needs in the world in 2050 are also predicted to increase to 50 TW [1].

Bioenergy such as biogas, bioethanol, methanol, biodiesel, and biohydrogen are high-quality renewable fuels that can be used to replace fossil fuels [2]. Biohydrogen is one of the feasible alternatives to be developed and used as an alternative to fossil fuels [3]. The choice of biohydrogen compared to other biogas such as methane is based on several considerations, including hydrogen having a greater heating value of  $142 \text{ MJ kg}^{-1}$  compared to methane ( $55 \text{ MJ kg}^{-1}$ ) and combustion from hydrogen in the form of  $\text{O}_2$  and  $\text{H}_2\text{O}$  which is very environmentally friendly [4].

The availability of cheap raw materials which are not classified into food is one of the obstacles in the bioenergy industry in Indonesia [5]. So far, the raw materials used for the production of biohydrogen is cane sugar, corn and cassava [6]. However, these materials are economic commodities



that are economical and classified as food commodities, so it is necessary to strive to use non-food raw materials to support the realization of the domestic biofuel industry [7]. To overcome this problem, it can be done using wastewater containing high concentration organic compounds from agro industrial activities such as palm oil, rubber, cocoa, sugar and coffee wastewater which has a chemical oxygen demand (COD) content of more than 4000 mg L<sup>-1</sup> through the process anaerobes [8]. The utilization of palm oil industry wastewater as a substrate for bioenergy formation has also been carried out, which produces ethanol of 2267.29 mgCOD L<sup>-1</sup> [9].

The production of biohydrogen by anaerobic microorganisms is distinguished by pathway conversion of pyruvic acid to acetaldehyde which is then reduced to hydrogen and ethanol by alcohol dehydrogenase [10,11,12]. The first pathway is the conversion of pyruvic acid to acetyl-CoA and CO<sub>2</sub> and then reduced to acetaldehyde. This pathway is used by mixed anaerobic culture bacteria which can utilize high concentration organic wastewater as a substrate [13]. The second pathway is the direct conversion of pyruvate acid to acetaldehyde with the help of pyruvate decarboxylase enzyme used by *Zymomonas mobilis*, *Sarcina ventriculi*, *Erwinia amylovora*, acetic acid bacteria and *Saccharomyces cerevisiae* [14].

The metabolism pathway and growth rate of microorganisms are defined by the pH of a reactor during the anaerobic processes. Any change in hydrogen ion concentration results in a change in pH and eventually leads to a change in redox potential [15].

## 2. Materials and Method

### 2.1. Raw material and biomass

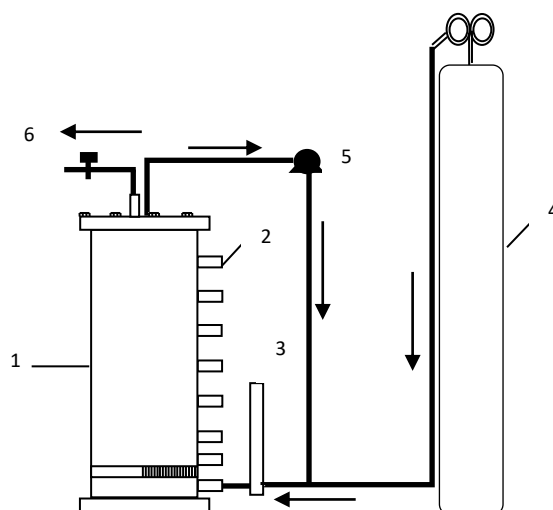
The fresh raw palm oil mill effluent (POME) was collected from the influent basin of PT. Condong, Garut, Indonesia. Biomass as mixed culture bacteria was taken from the sludge of palm oil mill effluent mixed by cow rumen with the ratio of 50:50 and has been acclimated to the POME. The acclimated biomass concentration used for the anaerobic batch reactor in terms of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS), were about 4.81 g SS/L and 3.72 g VSS/L respectively.

### 2.2. Circulating bed reactor

Circulating bed reactor (CBR) with the working volume of 5L were operated with the flushing N<sub>2</sub> 1L/min for 24 h and continued operates for 72h by internal biogas (Figure 1). The reactor filled with a mixture of consisted of 20% (v/v) mixed culture bacteria and 80% (v/v) of POME as a substrate. The pH of the reactor was set at 5.5; 6.5; 7.5 and 8.5 in the room temperature. Sample was collected every 6h and analyze for biogas (biohydrogen), volatile fatty acid and volatile suspended solid.

### 2.3. Analytical method

Biological oxygen demand (BOD), chemical oxygen demand (COD), TSS, oil and grease, total nitrogen and pH were analyzed according to standard methods. Gas composition was analyzed using Gas Chromatography (Shimadzu GC 8A) equipped with column Porapak P 8A serial D-4167 and TCD detector types, operating condition at 100°C, injector and detector temperature are 130°C, He pressure at 60 kPa with sample injection of 1 µL. Volume of biogas produced during the anaerobic process measured by displacement water method and the pressure measurement using manometer Lutron PM9100.



**Figure 1.** Circulating bed reactor (CBR), (1) CBR; (2) sampling port; (3) flowmeter; (4) nitrogen; (5) circulation pump; (6) gas outlet

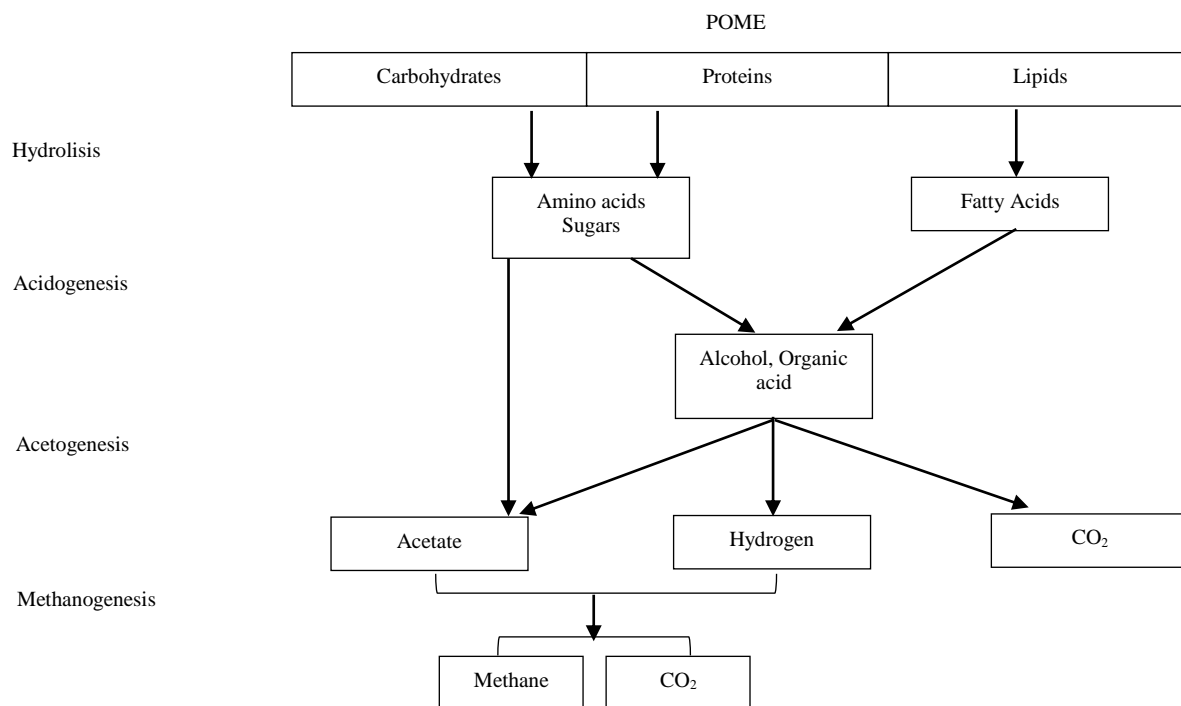
### 3. Results and Discussion

#### 3.1. Characteristic of palm oil mill effluent

The characteristics of palm oil mill effluent (POME) are given in Table 1. POME contains complex carbohydrate polymers such as hemicelluloses and lignocelluloses which resulted to high COD concentration about 15,000-100,000 mg/L [16], and it can be used as a substrate for biohydrogen production by anaerobic processes [16-21]. Anaerobic wastewater treatment is one of the main processes that can produce energy. In general, the processes that occur in anaerobic wastewater treatment process divided up into four stages, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis [22] as represented in Figure 2.

**Table 1.** Characteristic of palm oil mill effluent (POME)

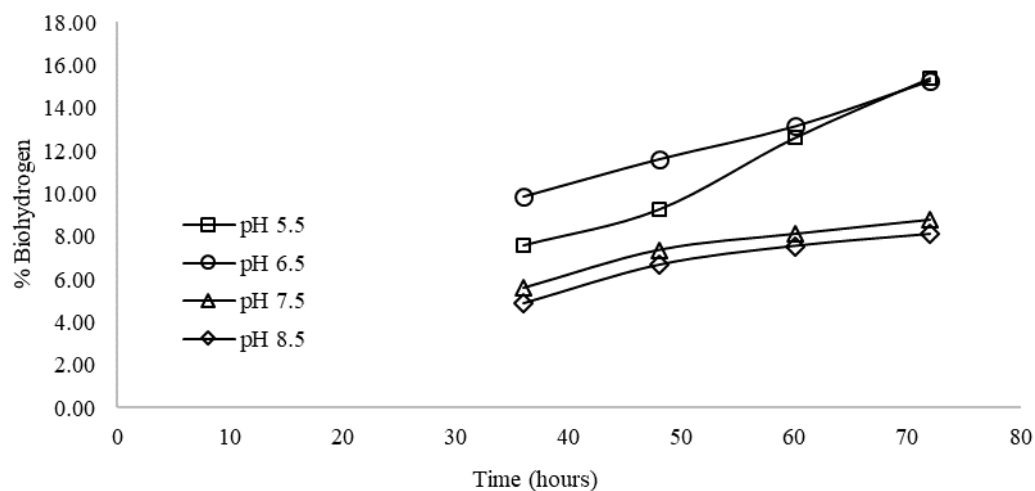
Parameter	Unit	Results
BOD	mg/L	16,810
Soluble COD	mg/L	19,475
Total COD	mg/L	23,270
TSS	mg/L	9,400
Oil and Grease	mg/L	245
Nitrogen Total	mg/L N	186
Ethanol	mg/L	23.8
Volatile fatty acids	mg/L	1024.8
pH	-	5.63



**Figure 2.** Metabolism pathway in anaerobic processes [23].

### 3.2. Effect of pH on biohydrogen production

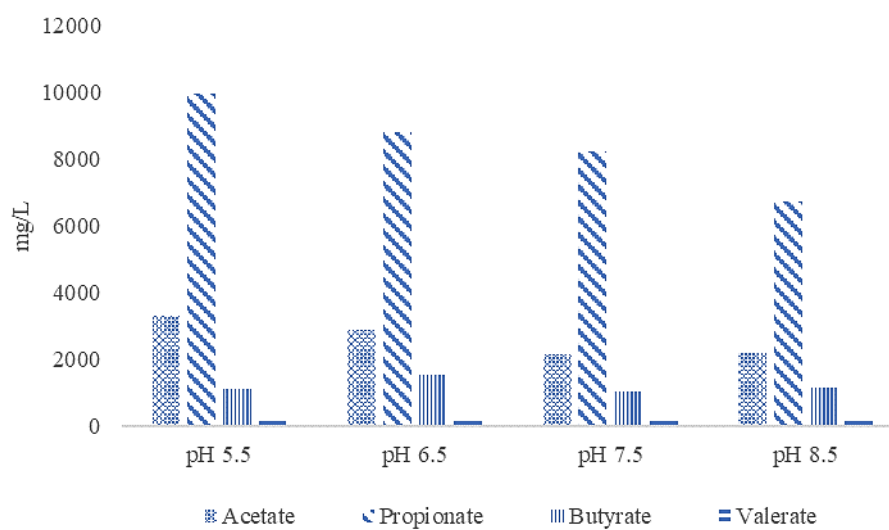
In Figure 3 shown the effect of pH on biohydrogen production. The maximum biohydrogen production obtained in the different condition pH of reactors for 5.5; 6.5; 7.5 and 8.5 are  $15.40\% \pm 0.265\%$ ;  $15.27\% \pm 0.404\%$ ;  $8.77\% \pm 0.129\%$  and  $8.10\% \pm 0.176\%$ . The results show a trend of  $\text{pH } 5.5 > 6.5 > 7.5 > 8.5$ . These results indicate that the optimum condition for biohydrogen production by anaerobic processes occurs at the pH value about 5.5-6.5. The similar results have been reported by Liu et al. (2011), the pH 5.5-6.8 are the optimum range for biohydrogen production and pH 4.5 seems to inhibit hydrogen production [15,24]. If the rate of hydrolysis phase faster than acidogenesis and acetogenesis phase, it will cause volatile fatty acid to accumulate and reduce the pH which can inhibit hydrogen production [25]. Another result showed that pH 6.0 is an optimum pH and the maximum hydrogen yield of  $28.3 \text{ mL g}^{-1} \text{ COD}$  was obtained [26]. Metabolism pathway and the growth of microorganism defined by the condition of pH. Any changes of the hydrogen concentration also influence to the pH and eventually leads to the changes of redox potential [24].



**Figure 3.** Biohydrogen production in the different pH condition

### 3.3. Effect of the control pH on anaerobic product production

Volatile fatty acids (VFA's) such as acetate, propionate, butyrate, valerate and biogas ( $\text{CO}_2$  and  $\text{CH}_4$ ) was produced during the experiments. Acetate and propionate are the main acidogenic product in the anaerobic processes. In Figure 4 shown the volatile fatty acid in every reactor. Maximum acetate and propionate concentration in the reactor by control are 3318.4; 2864.7; 2163.5 and 2691.5 mg/L for acetate and 9953.2; 8792.2; 8229.1 and 6726.4 mg/L for propionate respectively. Acidogenic product formation shown in Table

**Table2.****Figure 4.** Volatile fatty acid production in the different pH condition

**Table 2.** Acidogenic product formation in anaerobic processes

Parameter	Unit	pH			
		5.5	6.5	7.5	8.5
Biohydrogen	%	15.4	15.27	8.8	8.10
Acetate	mg/L	3318.4	2864.7	2163.5	2188.4
Propionate	mg/L	9953.2	8792.2	8229.1	6726.4
Butyrate	mg/L	1107.2	1527.4	1044.2	1126.2
Valeric acid	mg/L	172.3	208.4	248.8	267.5

#### 4. Conclusion

Controlling the reactor pH can be influence to the biohydrogen production and another product such as volatile fatty acid (acetate, propionate, butyrate, valeric acid) in anaerobic processes. The optimum biohydrogen production occurs in the reactor with the pH 5.5 was about 15.40%  $\pm$  0.265%.

#### Acknowledgments

This research was funded by *Program Penelitian, Pengabdian kepada Masyarakat dan Inovasi (P3MI) tahun 2018*.

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