Batch process for bio-hydrogen production on small scale bioreactor from palm oil mill effluent (POME)

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Abstract

In this study, treatment of palm oil mill effluent (POME) was carried out under anaerobic fermentation process with the intention to produce bio-hydrogen by micro flora. Experiment was investigated in 500mL bioreactor under mesophilic operation at 35°C and different pH value. Raw POME was collected from cooling pond which is final discharge of effluent from the mill and POME sludge was collected from the anaerobic pond of a POME treatment plant at same Labu palm oil mill respectively. Source of inoculum was used is POME sludge as hydrogen producing bacteria. A batch reactor was found producing higher hydrogen at optimum parameter of pH 5.5 and 10% POME sludge (w/v) with maximum hydrogen production yield of 5988.96 mL H_2/ L-med and maximum hydrogen percentage in the biogas of 36% were obtained at pH 5.5. Throughout the study, there is no methane gas was observed in the evolved gas mixture.

Keywords: Bio-hydrogen, POME sludge, Raw POME,

INTRODUCTION

Currently, in Malaysia there are 432 palm oil mills included in Sabah and Sarawak. As mentioned by Rupani et al, (2010), it has been estimated that 5 - 7.5 tonnes of water is required for the production of 1 tonne crude palm oil (CPO) and more than 50% of the water ends up as palm oil mill effluent (POME). Pre-discharge POME treatment is inadequately performed by palm oil industries and this is mostly due to the conventional treatment technologies which are predominantly time consuming, environmentally not sustainable, and require high cost of operation. In addition, based on the characteristics of treated POME remain biochemically incompatible for discharge and still give pollution into environment which is the continuous discharge of untreated or low-level-treated POME into the environment has culminated into high rates of diminishing freshwater reserves and contaminated marine and land systems. Due to the contents of high total solids in POME, attempt have been made to reuse and recycle the palm oil mill effluent (POME) by convert this waste into valuable products such as feed stock and organic fertilizer that will be used by farmers into their crops.

In addition, palm oil mill effluent (POME) generated by the milling process has a high soluble organic content, and biochemical oxygen demand/ chemical oxygen demand (BOD/COD) > 0.45. This is indicative that it is a good source material for biological performance, especially in a tropical climate such as in Malaysia, thus making anaerobic digestion the most economical and most applicable technology to treat POME. By treatment of POME, the emission of greenhouse gases can be reduced through biogas harnessing. Thus, energy is generated for multiple uses, and therefore climate change can be potentially mitigated and the palm oil industry will be more sustainable.

A few technologies will be conducted for biogas harnessing, by our local country and also foreign including conducted in a closed-tank anaerobic digester system, an open digester tank, or in a covered lagoon. Currently, the established techniques used for treating wastewater in anaerobic digestion systems are the continuous stirred-tank reactor (CSTR), the up- flow anaerobic sludge blanket/bed (UASB), or the more advanced expanded granular sludge bed, (EGSB) and the up-flow solids reactor (USR). These are among the most commonly used technologies in Malaysia. Besides, lab scale will be used CSTR and small reactor (Scott bottle) as biogas production including methane and bio-hydrogen as small scale fermentation.

Nowadays, there is much on uses of POME including biological production of bio-hydrogen. The major advantage of energy from hydrogen is the zero carbon emissions Since more countries dependence on fossil fuels tends emission to the air, so this bio-hydrogen generation from renewable biomass would reduce dependence on fossil fuel, decrease the carbon dioxide emissions and produce usable bioenergy (A. A. Y. Atif et al., 2005). There is various methods to produce bio-hydrogen, and biological method is known to be less energy intensive, instead it can be carried out at ambient temperature and pressure. Moreover, in between produce hydrogen from organic wastes by fermentative hydrogen production, it plays the dual role of waste reduction by

COD removal and bioenergy production. Recently, more attention has been received on fermentative hydrogen production to find alternative energy sources that are environmentally friendly and renewable (Wang & Wan, 2008).

Biological hydrogen production as a byproduct of the metabolism of the microorganisms includes newly developed technologies utilizing various renewable resources including food waste, wood industries, palm oil industries, and so on. Furthermore, the aim of this work is to determine the simplest promising methods for attaining hydrogen in the future (Bičáková & Straka, 2012). Additionally, uses of hydrogen are predominantly for the production of methanol and ammonia and in the refining industry. However, several countries tend to make R&D about the methods to acquiring hydrogen through various technologies for its broad application and ecological aspects. Atif et al., 2005, concluded at present, the usually method to treat POME is methane production, but an innovative alternatively is production of hydrogen. In this study is focusing on palm oil mill industries as main objective of the development the processes of bio-hydrogen production to achieve of a higher yield of the produced hydrogen through an economically acceptable method. Bio-hydrogen from POME was studied by using micro flora in source of inoculum POME sludge from anaerobic ponds.

MATERIALS AND METHODS

Palm oil mill effluent (POME)

Raw POME was collected from palm oil mill (Labu's Oil Mill, Sime Darby Plantation Sdn. Bhd, Negeri Sembilan, Malaysia). The POME was used as substrate for the culture medium. The samples were immediately transferred to the laboratory and stored in a cold room at 4°C before use. The characteristics of raw POME are summarized in Table I Characteristics of palm oil mill effluent (POME)

Seed sludge

Palm oil mill effluent (POME) sludge containing anaerobic microorganism and micro flora was collected from anaerobic pond of POME treatment plant at palm oil mill (Labu's Oil Mill, Sime Darby Plantation Sdn. Bhd, Negeri Sembilan,Malaysia). The bacterial population used as inoculum in the production of hydrogen from POME in this experiment. The sludge was initially passed through a mesh screen to remove any fragments. The total volatile solids concentration of the sludge was measured 31600 mg/L and total suspended solids was measured 38000mg/L.

Table I Characteristics of palm oil mill effluent (POME)

Parameter[a]	**Average concentration**
Physical characteristics	
Total suspended solid, TSS	47690
Volatile suspended solid, VSS	30870
Temperature, T	80 ± 1
pH	3.4 ± 0.1
Chemical property	
COD	69500
BOD_5	37750
Total Nitrogen	692

[a] Except for pH and temperature all other parameters are in mg/L, temperature in °C

Experimental set-up

In this study, 500mL serum bottle were used as a batch reactor. The **Figure I** Schematic diagram of a batch reactor used in the study showed a schematic diagram of a batch reactor. The culture medium contained 400mL POME with different parameters. Firstly, six 500 mL serum bottles were used for each run at 10% w/v sludge at value pH 4.5, 5.0, 5.5, and 6.0. Raw POME and POME sludge were acclimatized at room temperature for two day before used in experiments. After POME sludge was measured insert into serum bottles, raw POME was added into each bottle to obtain a final working volume of 400 mL. The pH of mixture in each bottle was also adjusted to set point pH 4.5, 5.0, 5.5, and 6.0 respectively before initiating the batch test. In order to obtain an anaerobic condition for the bacteria, the entire serum bottle volume (headspace plus liquid) was established by replacing the gaseous phase with nitrogen for 15 min at a flow rate of 10 mL/s. To inhibit the activity of photosynthetic bacteria, the culture was carried out without illumination. The run was conducted at 35°C without agitation rate into incubator. The batch runs lasted for 14 days and all experiments were performed in three replicates.

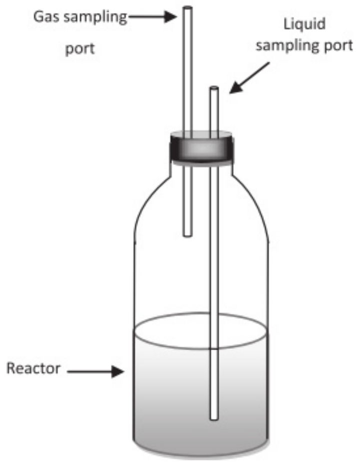

Figure I Schematic diagram of a batch reactor used in the study

Analytical methods

The amount of evolved gas was monitored via gas sampling at regular intervals at room temperatures. A syringe was used to extract measured volume of gas sample from each test bottles. Gas sample was taken once per day, and the gas composition was determined by gas chromatography (Shimadzu Co., Kyoto, GC-14B) under the following conditions: column: molecular sieve 5A and Porapack-Q, carrier gas: helium, flow rate: 33 ml/min, column temperature: 40 ◦C, injection temperature: 50 ◦C, detector temperature: 50 ◦C, detector: thermal conductivity detector (TCD), The gas sample (1 mL) was injected in replicates. Other parameters, including chemical oxygen demand (COD), biochemical oxygen demand, (BOD), pH, total suspended solids (TSS) and volatile suspended solids (VSS) were determined in accordance with the procedures described in the standard methods (APHA, 1999).

RESULTS AND DISCUSSION

Many factors, such as the substrates, their concentration, volume of inoculum feed, pH and temperature will be influenced the fermentative hydrogen production. Based on previous study, Wang & Wan, (2008) was investigated temperature is a very important factor because it can affect the activity of hydrogen producing bacteria since influence the hydrolysis process in production of hydrogen. But, its concluded increasing temperature from 20°C to 40°C will be increased the bio-hydrogen production. Therefore, this study fix the temperature at mesophilic 37°C and study effect of pH and inoculum percentage on production of bio-hydrogen.

The pH range was selected based on a literature search which is 4.5, 5.0, 5.5, and 6.0 values. The initial pH of POME was found to be in the range of 3.4-3.6. Therefore, after mix culture with POME sludge, the pH becomes 4.8. Thus, pH adjustment was done using 5M NaOH and 5M H_2SO_4 before initiating the batch test accordingly to each pH values. The results showed that hydrogen production was strongly inhibited by pH values as low as pH 5.5. Based on previous published results where hydrogen production was maximized at a pH value as low as pH 4.5 with mixed micro flora. So, this finding is differed from previous work.

The results in Table 2 show the comparison between literature search and this study on bio-hydrogen production. Among the study before this, the production of hydrogen was affected and terminated by low pH; fermentation experiments were started at neutral pH, and terminated at pH 4 ± 0:1. Atif et al., (2005) was studied, the optimum pH for production of hydrogen was observed in the pH range of 5–6. The different medium was used shows the low evolved rate was obtained from the study.

Table II Comparison of hydrogen yield with the literature study

Microorganism	Substrate	H_2 yield mol/mol hexose	Reference
Mixed culture	Glucose	2.1	Fang and Liu (2002)
Mixed culture	Glucose	2.39-1.42	Ueno et al. (2001)
Mixed culture	Glucose	1.7	Lin and Chang (1999)
Mixed culture	Cellulose	2.4	Ueno et al.(2004)
Mixed culture	POME	5988[a]	This study

[a] **unit in ml H_2 yield /l-med**

Table III Comparison of the bio-hydrogen production using palm oil mill effluent (POME) as substrate on different fermentation mode

References	Substrate	Fermentation mode	pH	T (°C)	H_2 yield (ml/l-med)	Evolution rate (ml/(l-med h)	Gas composition (%)	
							H_2	CO_2
This study	POME	Batch	5.5	37	5988	499	36	64
F.A Sukaina, 2007	POME	Semi-continuous	5.0	60	ND[b]	830	64	36
Wang & Wan, 2008	Glucose	Batch	7.0	40	275.1[a]	ND	ND	ND
Atif et al., 2005	Glucose	Fed batch	5.5	60	4708	454	66	34
Morimoto, 2004	Glucose	Continuous	Uncontrolled	60	3195	1034	68	32

[a] unit in mL/ g glucose

[b] ND not detected

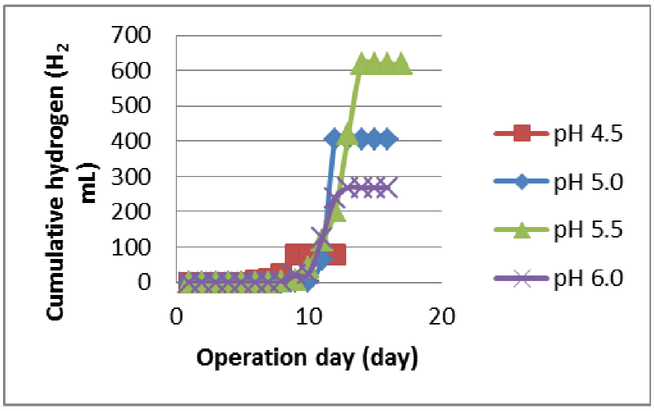

Figure II Cumulative hydrogen produced on varying pH value versus operating day

The effect of pH on the fermentative hydrogen for HRT of 17 d is shown on Fig. 2. The anaerobic fermentation was carried out for varying initial pH of 4.5, 5.0, 5.5, and 6.0 respectively for an influent COD concentration of 32000 mg/L to 86400 mg/L. The highest hydrogen produced at HRT 14 d at pH 5.5 of 618.83 mL H_2. As shown in the Fig. 2, hydrogen produced at different HRT on varying pH value. At HRT 7d for pH 4.5, the cumulative hydrogen gas was found to be 77.62mL while at HRT 11d accumulated hydrogen generation is 403.30mL and 268.23mL for pH 5.0 and 6.0, respectively. Thus for pH 5.5 was mentioned above as highest generation hydrogen. Therefore, the cumulative hydrogen generation depending on the digestion of pH for a given organic strength. Slightly changed in value of pH will be effected the hydrolysis processes in fermentative hydrogen.

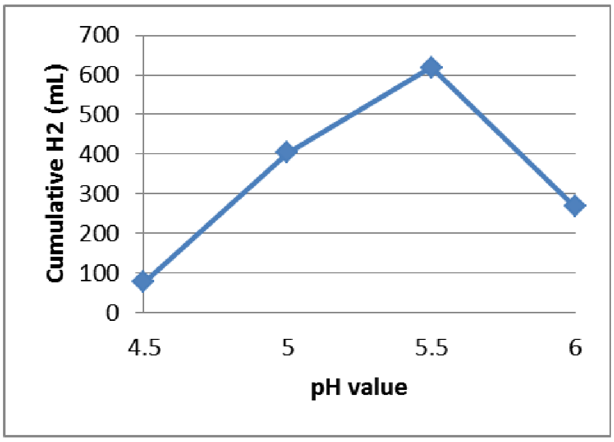

Figure III Cumulative hydrogen generation versus fermentation pH

As shown in Fig. 3, a pH value of 5.5 was found to be the optimum towards hydrogen generation from the POME. Based on the optimized pH value, the treatment of POME was carried out at varying influent inoculum percentage of 10%, 7.5%, 5.0% and 2.5%. The results in Fig. 4 and Fig.5 shows the effect of inoculum percentage feed by hydrogen produced versus operating day and the cumulative hydrogen generation versus inoculum percentage feed in culture medium respectively. Increasing of inoculum percentage into culture medium will increase the hydrogen produced into biogas since the seed sludge (inoculum) was consume the hydrogen producing bacteria to produce more hydrogen gas at HRT 10 d.

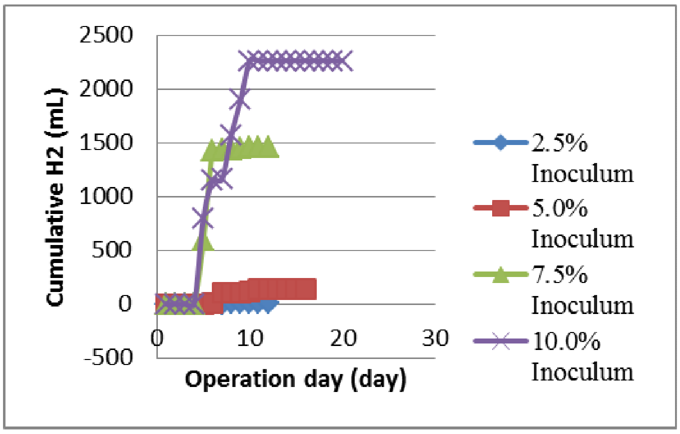

Figure IV Effect of inoculum percentage feed with accumulated hydrogen versus operating day

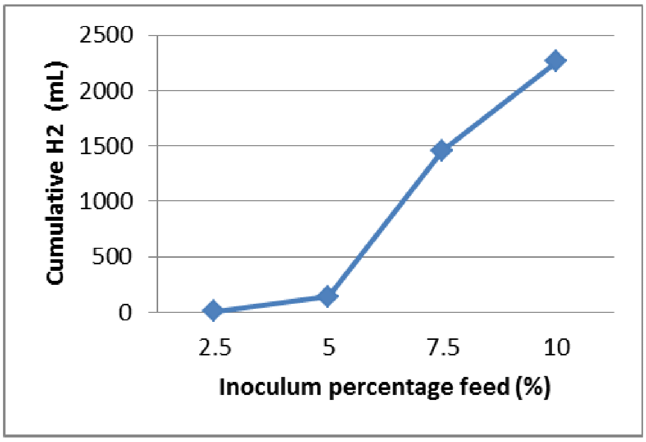

Figure V Cumulative hydrogen generation versus inoculum percentage feed

Fig. 6 shows the variation of hydrogen yield and COD concentration versus operating day. The observation based on value of hydrogen yield is gradual rise in biogas production. This evidently shows that the microbes are adapted to degrade the palm oil mill effluent hence increasing the COD removal efficiencies. At optimized condition of pH 5.5 and 10% inoculum feed, the influent COD concentrations of 76800mg/L as run at HRT 14 days. As increase the HRT, a higher metabolic reaction could reach the end point resulting in a higher gaseous end product. Besides, the initial start-up produce low biogas could be due to the accumulation of intermediate products. Therefore, at the end of processes, effluent COD concentrations of 44520mg/L. This clearly shows the COD removal increased as HRT increased with the COD removal of 42%. Thus, maximum COD removal occurred at pH 5.5, 10% inoculum feed.

Experiments were conducted successively in batch fermentation mode to determine the optimum HRT for maximum hydrogen productivity of mixed micro flora. Regarding the organic loading rate (OLR) parameter will be studied for step-continuous into 5L fermenter after this. Furthermore, Table 2 shows the condition and results of this study to producing bio-hydrogen in batch process by micro flora.

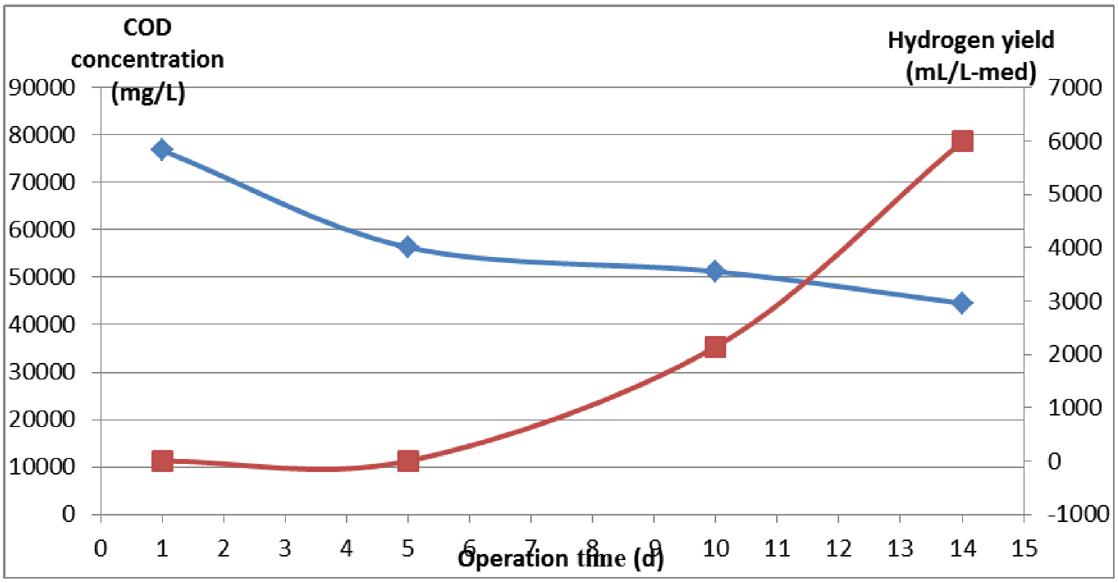

Figure VI Variation of hydrogen yield and COD concentration versus operating day at optimum pH 5.5, 10% inoculum feed

Table IV Parameters at mesophilic condition of Anaerobic POME treatment system for hydrogen production.

Parameter		**Value / range**
	Operating condition	
Temperature (℃)	35	35 ± 2
pH	5.5	5.5 ± 0.1
HRT (day)	14	14 ± 1
	Treatment efficiencies	
COD removal	42%	
Hydrogen yield (mL/L med)	5988	

CONCLUSION

This paper as preliminary study on small scale bioreactor 500mL to observe an optimum condition based on pH and inoculum percentage feed affect bio-hydrogen production from POME by micro flora. The pH value plays a vital role towards the metabolic reaction while the optimized pH is 5.5 produced highest hydrogen production 5988 mL H_2/L med at 37°C without iron supplemented as biological processes. Experimental results show that hydrogen production was inhibited at pH 4.5 with low hydrogen produced 77.62mL H_2/L med. Moreover, highest hydrogen production by inoculum feed factor at 10% POME sludge (%w/v) of 2262mL H_2/L med while at 2.5% POME sludge (%w/v) produced the lowest hydrogen of 8.08mL H_2/L med. This clearly shows that microbial activity into biomass of seed sludge consuming hydrogen producing bacteria to growth in hydrogen generation. Based on optimized value, at pH 5.5 and 10% POME sludge (%w/v) the results was obtained a maximum COD removal, biogas generation and hydrogen produced simultaneously treating the palm oil mill effluent (POME). The COD removal concentrations of influents COD at 76800mg/L till the end of processes, effluent COD concentrations of 44520mg/. Therefore, the COD concentration ranging between 40000-80000mg/L and note as previous report.

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