



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 50 (2014) 723 – 728

Energy

Procedia

The International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES14

Improvement of Mesophilic Biohydrogen Production from Palm Oil Mill Effluent Using Ozonation Process

Nipon Pisutpaisal^{a,b,*}, Pinanong Tanikkul^a, Wisakha Phoochinda^c

^aDepartment of Agro-Industrial, Food and Environmental Technology, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand

^bThe Biosensor and Bioelectronics Technology Centre, King Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand

^cSchool of Social and Environmental Development, National Institute of Development Administration, Bangkok, 10240, Thailand

Abstract

Biological fermentative production of hydrogen from the ozonated palm oil mill effluent (POME) was conducted in batch reactors using an anaerobic sludge as a microbial seed. Fermentation was setup at pH 4.0-6.0, varying POME concentration range of 5,000-37,000 mg L⁻¹ under mesophilic condition (37°C). The results showed that pH 6.0 is an optimum pH and the maximum hydrogen yield of 28.3 mL g⁻¹COD was obtained. Comparative results of hydrogen production from the raw POME versus the ozonated POME indicated that the ozone pretreatment of POME (mg COD: mg ozone = 102.8) elevated the biodegradability of the POME constituents and significantly enhanced yield and rate of the hydrogen production. Hydrogen production using ozonated POME concentration of 30,000 mg L⁻¹ displayed the maximum yield of 182.3 mL g⁻¹ COD, which is 49% higher than that from raw POME. Meanwhile the maximum production rate of 43.1 mL h⁻¹ was observed at COD concentration of 25,000 mg L⁻¹ ozonated POME. Maximum COD removal was 44% at COD concentration of 15,000 mg L⁻¹ ozonated POME. This work demonstrated ozonation of POME significant improved performance of hydrogen production.

© 2014 Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Selection and peer-review under responsibility of the Euro-Mediterranean Institute for Sustainable Development (EUMISD)

Keywords: Hydrogen; ozonation; palm oil mill effluent; POME; fermentation; bioenergy

1. Introduction

Palm oil industry in Thailand has been rapidly expanded. Palm oil mill effluent (POME) is an important source of water pollution when released into local rivers or lakes without proper treatment. The untreated, viscous, and

* Corresponding author. Tel.: +66 2 587 8257; fax: +66 2 587 8257.

E-mail address: npp@kmutnb.ac.th

brown liquid POME contains high content of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solids (SS). Since the viscous, brown liquid POME contains high chemical composition and concentrations of simple organic compounds (e.g. carbohydrate, protein, and lipids) and complex organic complex compounds (e.g. tannins and lignins) [1]. As a result high biodegradable organic content, anaerobic process for reduction of the pollution in the POME is advantageous before being released to the environment. Therefore, the current study is intrigued on the anaerobic process capable of reducing the pollution in the POME and generating the hydrogen at the same time. Hydrogen can also be biologically produced through the dark fermentation of renewable feedstocks (organic-rich biomass and wastewater) with no requirement of external energy input [2]. Partial ozone pretreatment is aimed to break down complex molecules of organic matters in POME to be more biodegradable. In addition, the impact of partial ozone pretreatment on the rate and yield of hydrogen production of POME was explored.

2. Materials and methods

2.1. Microbial seed

Microbial seed used throughout the study was obtained from a full-scale up-flow anaerobic sludge blanket (UASB) reactor (Malee Sampran Co., Thailand). Granular seeds with diameter >0.5 mm were washed with tap water and pre-treated at 100°C for 30 min [3] to inhibit the methane-producing bacteria prior to use into the hydrogen reactor.

2.2. Palm oil mill effluent (POME)

The raw POME was collected from the stabilization pond (Sooksomboon Palm Oil Co., Ltd. Chonburi, Thailand). Raw POME exhibits dark brown color, a temperature of $70\text{--}80^{\circ}\text{C}$, and pH 4.4–4.7. Suspended solids in the raw POME were allowed to settle down for one day (24h) before its storage in a cold room at 4°C to use. The ozonated POME was prepared by using the pre-settled POME was ozonated (Ozonator, model OZ-553, Thailand) with ozone loading rate of 300 mg h^{-1} (mg COD: mg ozone = 102.78 from separated experiment to clarify the impact of ozonation on the improved hydrogen production yield).

2.3. Batch fermentation

The first set of batch experiment was varied pHs 4.0–6.0 to obtain an optimal pH for the hydrogen production and second batch were varied POME concentrations of $5,000\text{--}37,000\text{ mg L}^{-1}$ under the optimal pH at 37°C . After placing POME and microbial seed in the reactor, it was capped tightly with the silicone stopper and flushed with nitrogen gas to create an anaerobic condition. All experiments were performed in duplicate. Gas sample was taken once in every 4 h, the volume of biogas was collected with measured by water displacement method. Mixed liquor samples were analyzed for pH, total chemical oxygen demand (COD_T), dissolved chemical oxygen demand (CODs), total solid (TS) and total volatile solids (TVS) according to standard methods [4].

2.3. Analytical methods

Gas composition in the batch reactor headspace was measured on a gas chromatography (Shimadzu GC 2014, Japan) equipped with thermal conductivity detectors (TCD) fitted with stainless steel column packed with Unibeads C (80/100 mesh). Helium was used as a carrier gas. The temperatures of the injection port, column and detector were 120 , 70 and 150°C , respectively. Volatile fatty acids (VFAs) and ethanol were analyzed by a gas chromatography (Shimadzu GC 2010, Japan) equipped with a flame ionization detector (FID) fitted with Stabilwax DA capillary column (Restek, USA). Hydrogen, air, nitrogen and helium were used as a carrier gas. The temperature of the injection port, column and detector were set up at 230 , 80 and 250°C , respectively.

2.4. Data analyses of batch experiment

Kinetics of hydrogen production was calculated from the cumulative hydrogen production versus time data of each batch experiment fitted with the modified Gompertz equation [5].

$$H = H_{\max} \cdot \exp \left\{ - \exp \left[\frac{R_{\max} \cdot e}{H_{\max}} (\lambda - t) + 1 \right] \right\} \quad (1)$$

where, H is the cumulative volume of hydrogen production (mL), t is time of fermentation (h), H_{\max} , is the hydrogen production potential (mL), R_{\max} , is the maximum hydrogen production rate (mL h⁻¹), λ is lag phase (h) and e is a constant (2.71828).

3. Results and discussion

3.1. Optimum pH

The first experiment was performed under varied pHs ranging from 4.0-6.0, using the raw POME and the ozonated POME with the initial concentration of 10,000 mg L⁻¹. The results showed that pH 6.0 was the optimum pH and gave the highest hydrogen production yield for both types of POME (Table 1). Hydrogen production tended to decrease when pH decreased and no hydrogen was produced at pH 4.0. pH is the most factors of hydrogen fermentation processes on the hydrogenase activity in the metabolic pathways [6]. If pH is not maintained, it may inhibit hydrogen production. Kinetics data H_{\max} , R_{\max} , λ , and yield (Table 1) were clearly indicated the significant role of pH on the hydrogen fermentation, and could be strongly concluded that pH 6.0 is the optimum pH for the current study.

Table 1. Kinetic parameters of hydrogen production under varied initial pHs

pH	H_{\max} (mL)		R_{\max} (mL h ⁻¹)		λ (h)		Yield (mL g ⁻¹ COD)	
	Raw POME	Ozonated POME	Raw POME	Ozonated POME	Raw POME	Ozonated POME	Raw POME	Ozonated POME
4.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	10.0±0.0	10.0±0.0	0.0±0.0	0.0±0.0
4.5	0.4±0.1	0.4±0.1	0.2±0.1	0.2±0.1	16.7±0.0	16.7±0.0	1.9±0.1	0.3±0.1
5.0	27.1±0.4	39.7±1.0	4.2±1.2	6.2±1.0	8.5±0.5	18.2±0.4	21.6±1.5	21.9±0.3
5.5	37.6±2.5	51.7±4.9	4.1±0.9	5.1±1.3	7.7±0.1	7.6±0.2	23.6±1.6	24.5±2.9
6.0	58.0±2.4	100.5±8.7	5.0±0.7	12.9±1.3	7.6±0.4	8.5±0.4	28.3±2.1	30.9±2.2

3.2. Impact of ozone pretreatment on hydrogen fermentation

The experiment was setup with varied POME concentrations and fixed pH 6.0. pH drop after 72 h incubation was observed in the narrow ranges of 5.38-5.97 for the raw POME and 5.46 to 5.98 for the ozonated POME. The result suggested that organic acid by-products from the hydrogen fermentation were accumulated in the reactor content. The biogas was free of methane at all tested POME concentrations and tend of hydrogen content was increased with increased POME concentration. The cumulative hydrogen production trends to increase with POME concentration from 5,000-30,000 mg L⁻¹, and decreased with high concentration was 37,000 mg L⁻¹ (Fig. 1). All cumulative hydrogen fermentation profile data were fitted to the modified Gompertz equation ($r^2 > 0.99$).

Table 2 summarized the kinetic parameters for the hydrogen production with varied POME concentrations. The regression results showed that H_{\max} and Yield were all dependent on the POME concentrations. The H_{\max} , R_{\max} , λ and Yield trends to increase as POME concentration. While R_{\max} increased and then decreased at the POME concentration higher than 25,000 mg L⁻¹. The highest R_{\max} was 43.1 mL h⁻¹ of 25,000 mg L⁻¹ ozonated POME. At the POME concentration from 25,000-37,000 mg L⁻¹, the λ ranged was increased because POME contained very

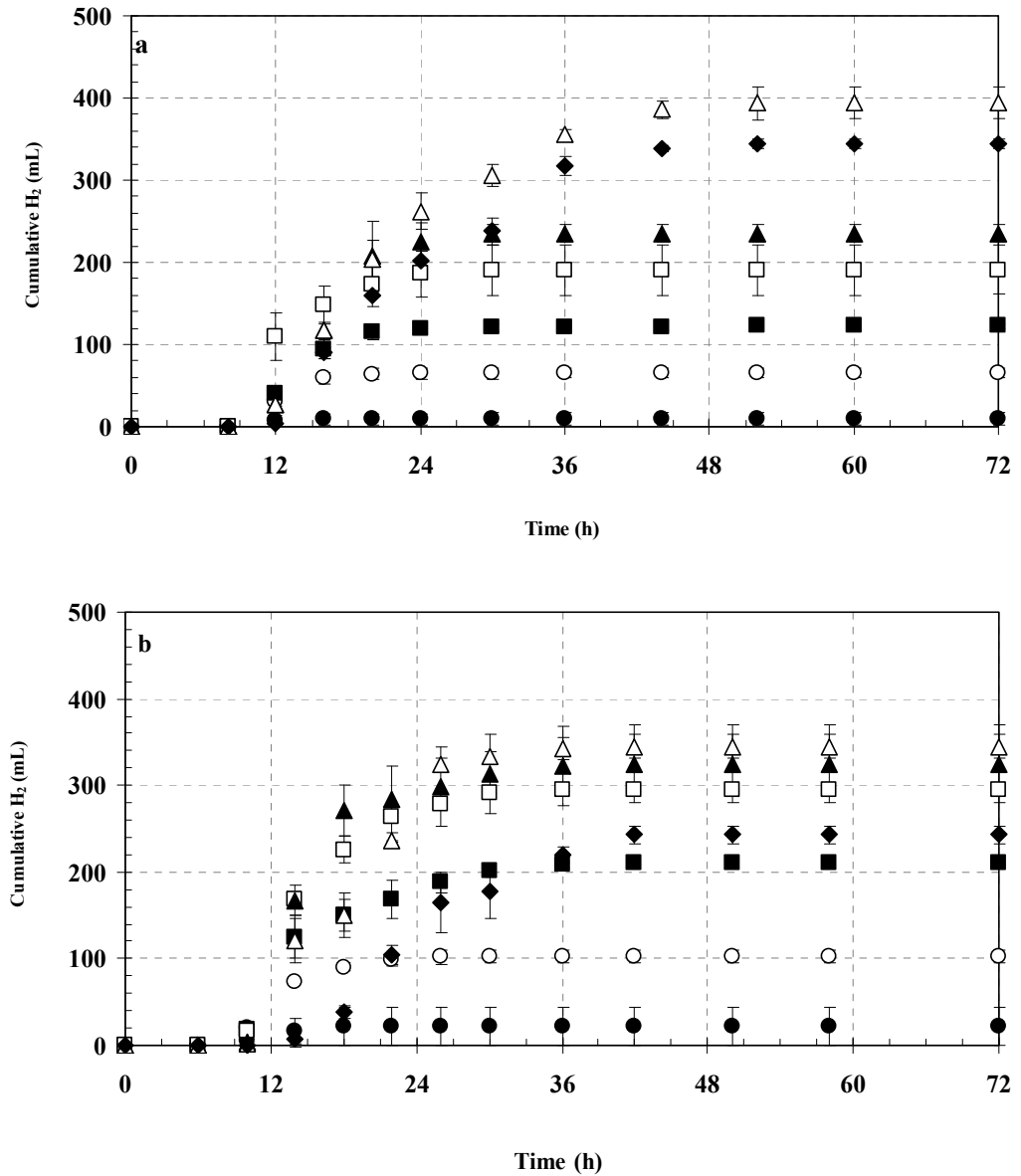


Fig. 1. Cumulative hydrogen production of raw POME (a); ozonated POME (b) with the initial concentrations of 5,000(●); 10,000 (○); 15,000(■); 20,000(□); 25,000(▲); 30,000 (△); and 37,000 (◆) mg L⁻¹. The data represent mean values and I-bars represent standard deviation of duplicate experiments.

high particulates which required long hydrolysis time. The ozonated POME concentration of 30,000 mg L⁻¹ gave the highest yield of 182.3 mL g⁻¹COD. Yield was directly related to the elevated POME concentrations, except that the yield was dropped at the highest concentration of 37,000 mg L⁻¹ for both POMEs. At the corresponding concentration, the yield from the ozonated POME was higher than that from the raw POME in most cases. The results strongly indicated that the partial ozonation of POME enhance the hydrogen fermentation of POME under mesophilic condition.

Table 2. Kinetic parameters of hydrogen production at pH 6.0 and varied POME concentrations

[COD] (mg L ⁻¹)	H _{max} (mL)		R _{max} (mL h ⁻¹)		λ (h)	Yield (mL g ⁻¹ COD)		
	Raw POME	Ozonated POME	Raw POME	Ozonated POME		Raw POME	Ozonated POME	
5,000	9.2±7.3	22.3±22.5	2.0±1.6	3.3±3.7	7.7±0.5	5.5±4.7	6.3±4.7	15.0±14.7
10,000	65.5±5.8	102.0±7.9	14.7±0.3	13.7±1.1	9.9±0.0	8.5±0.7	30.7±3.7	32.2±0.8
15,000	121.7±4.3	207.4±0.4	17.1±3.9	19.6±8.8	9.6±0.5	8.3±0.8	35.8±2.4	43.3±1.2
20,000	188.5±29.6	291.6±0.8	24.5±5.3	33.3±7.2	8.0±0.1	9.4±0.4	51.7±10.0	70.1±2.0
25,000	228.6±22.5	317.2±45.9	30.1±4.9	43.1±2.5	12.2±1.3	10.3±0.1	70.8±8.4	124.6±8.4
30,000	391.3±16.1	349.7±13.9	20.0±1.0	23.4±1.2	10.5±0.3	10.3±1.1	122.0±1.4	182.3±7.2
37,000	346.5±9.2	243.9±7.0	16.1±1.1	15.1±3.0	11.1±0.3	15.3±0.1	78.8±0.9	85.9±9.9

3.3 COD reduction

The COD_t removal efficiencies trends to increase with the increased of POME concentration from 5,000-15,000 mg L⁻¹, and then was decreased at concentrations increased from 15,000 - 30,000 mg L⁻¹. The POME concentration of 30,000 mg L⁻¹ gave the lowest COD_t removal efficiencies in both studied and the raw POME showed higher COD_t reduction than the ozonated POME. The COD_t and COD_s removal efficiencies for both POME exhibited similar trends but the COD_s removal efficiencies were dropped at the concentration of 37,000 mg L⁻¹ for both types of POME. Higher COD_s removal in ozonated POME in the corresponding concentrations suggested that partial ozonation of POME improved the biodegradability of soluble substrate in the POME.

3.4 Volatile fatty acids

Acetic and butyric acids were dominant soluble by-products of both types POME in all batches. The concentrations of acetic and butyric acids were increased as the increased of the POME concentration. Little amount of valeric and propionic acids were constant although the concentration of POME was increased. Ethanol accumulation was detected when the POME concentration of 25,000 mg L⁻¹ and then increased at the POME concentration higher than 25,000 mg L⁻¹ for both POME. The ozonated POME concentration of 30,000 mg L⁻¹ showed the highest hydrogen production yield, in which acetate (56.4 mM) and butyrate (37.6 mM) were dominant end products. Propionate and ethanol were negligible.

4. Conclusion

This study successfully demonstrated the optimum pH for the hydrogen production using the UASB granular seed reactor at mesophilic conditions was 6.0. The comparative kinetic parameters of hydrogen production from two types of POME, raw POME and ozonated POME (102.78 mg COD mg⁻¹ ozone) in the concentration ranging from 5,000-37,000 mg L⁻¹, the ozonated POME concentrations of 30,000 mg L⁻¹ gave the maximal hydrogen production potential of 349.8 mL and the maximal hydrogen production yield of 182.3 mL g⁻¹ COD. The maximal hydrogen production rate (R_{max}) was 43.1 mL h⁻¹ was observed of 25,000 mg L⁻¹. The maximum COD_t removal was 44% at POME concentration of 15,000 mg L⁻¹. Ozonation pretreatment of POME was significantly enhanced the biodegradability of POME constituents, hydrogen production yield, and rate.

Acknowledgements

The authors would like to express their gratitude to National Institute of Development Administration (NIDA) for the 2010 post doc fellowship.

References

- [1] Habib MAB, Yusoff FM, Phang SM., Ang KJ. Nutritional values of chironomid larvae grown in palm oil mill effluent and algal culture. *Aquaculture* 1997;158:95-105.
- [2] Chen WH, Chen SY, Khanal SK, Sung S. Kinetic study of biological hydrogen production by anaerobic fermentation. *International Journal of Hydrogen Energy*, 2006; 31(15), 2170-2178.
- [3] Fang HP, Li C, Zhang T. Acidophilic biohydrogen production from rice slurry. *International Journal of Hydrogen Energy* 2006;31:683-692.
- [4] American Public Health Association, American Water Works Association, Water Pollution Control Federation Standard methods for the examination of water and wastewater, 20th edn. Washington DC, USA;1998.
- [5] Nathao C, Sirisukpoca U, Pisutpaisal N. Production of hydrogen and methane by one and two stage fermentation of food waste, *International Journal of Hydrogen Energy*, 2013; 38(35):15764-15769
- [6] Bailey J E, Ollis DF. *Biochemical Engineering Fundamentals*, second ed. New York: McGraw-Hill; 1986.
- [7] Ginkel SV, Logan BE. Inhibition of biohydrogen production by undissociated acetic and butyric acids. *Environmental Science Technology* 2005;39:9351-56.
- [8] Wang J, Wan W. Factors influencing fermentative hydrogen production:A review. *International Journal of Hydrogen Energy* 2009;34:799-11.
- [9] Gujer W, Gunten VU. A stochastic model of an ozonation reactor. *Water Research* 2003;37:1667-1677.
- [10] William AP, Giuseppe LS, Mitchell F. The cascade mechanism to explain ozone toxicity: the role of lipid ozonation products. *Free Radical Biology & Medicine* 1995;19:935-41.
- [11] Das D, Nejat VT. Hydrogen production by biological processes: a survey of literature. *International Journal of Hydrogen Energy* 2001;26: 13-28.
- [12] Das D, Nejat VT. Advances in biological hydrogen production processes. *International Journal of Hydrogen Energy* 2008; 33(21):6046-6057.
- [13] Jeremy T, Kraemer D, Bagley M. Improving the yield from fermentative hydrogen production. *Biotechnology Letters* 2007;29: 685-695.