Biohydrogen Production under Thermophilic condition from Ozonated Palm Oil Mill Effluent

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Abstract

Palm oil mill effluent (POME) contains high organic compounds and nutrients suitable for microorganisms in anaerobic processes. The biological hydrogen production using raw POME and ozonated POME in thermophilic batch fermentation at varying POME concentration in the range of 5,000 to 35,000 mg COD L⁻¹ was examined. Hydrogen production using the ozonated POME achieved the maximum yield of 77.1 mL g⁻¹COD at 35,000 mg COD L⁻¹, which higher than that from the raw POME by 20%. Meanwhile the hydrogen production rate of 10.8 mL h⁻¹ was observed at the ozonated POME concentration of 25,000 mg COD L⁻¹. Greater COD removal in the ozonated POME by 25% compared to that in the raw POME. The main acetate and butyric acids were accumulated in the raw POME fermentation which is lower than the ozonated POME fermentation. This work demonstrated ozonation of POME significant improved performance of the thermophilic biohydrogen production.

Keywords: biohydrogen; palm oil mill effluent; ozonated POME; thermophilic

1. Introduction

Hydrogen can be biologically produced through the dark fermentation in anaerobic process of renewable feed stocks (biomass and wastewaters) with no requirement of external energy input [1] and it

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is known that as a clean energy. Anaerobic digestion is one of the most common technology for treatment of high strength of wastewater since energy can be recovered from the process. POME contains high biodegradable organic compositions (50,000 mg COD L⁻¹ and 25,000 mg BOD L⁻¹) of both simple and complex structures including carbohydrate, protein, nitrogenous, long chain fatty acids compounds, and minerals [2], which are hardly biodegraded. Ozonation of POME was hypothetically to break down complex organic constituents into simpler molecules that can be easily biodegraded, and to enhance the hydrogen production. The current work applied partial ozonation pretreatment on POME, to break down complex organic into simpler and more biodegradable structures prior to thermophilic hydrogen fermentation. The comparative performance of raw and ozonated POME fermentation was evaluated based on kinetics data.

2. Materials and Methods

2.1. Microbial seed

Microbial seed 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 fermentation reactor. The total volatile solid (TVS) of pre-treated seed was 57.4 g L⁻¹.

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 70-80°C, and pH 4.4-4.7. Suspended solids in 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 from the pre-settled POME with ozone loading rate of 300 mg h⁻¹ (mg COD: mg ozone = 102.78).

2.3. Experiment setup

The batch hydrogen fermentation was set up in 500 mL Scott Duran bottles. All experiments were fixed 25% of microbial seed of each reactor and varied 75% POME concentrations of 5,000 to 35,000 mg COD L⁻¹. After placing POME and microbial seed in the reactor, it was adjusted the pH 6.0 by 6 M NaOH or conc. H₃PO₄ and then capped tightly with the silicone stopper and flushed with nitrogen gas to create an anaerobic condition. The batch fermentation was conducted at 55°C with incubator shaking 150 rpm. All experiments were performed in duplicate. Gas samples were taken once in every 4 h and the total volume of gas was measured using water displacement method. Mixed liquor samples were analyzed for pH, chemical oxygen demand (COD), according to the Standard Methods [4] and VFAs.

2.4. Analytical methods

Gas composition (H₂, CH₄, and CO₂) in the headspace of batch reactor was measured on a gas chromatograph (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 chromatograph (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.

2.5. Kinetics of batch hydrogen production

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].

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

(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\(^{-1}\)), \( \lambda \) is lag phase (h) and \( e \) is a constant (2.71828). Hydrogen yield is calculated by dividing the hydrogen production potential by the amount of total COD removed.

3. Results and discussions

3.1. Kinetics of hydrogen production

The hydrogen was successfully obtained in all experiments, and no methane was detected in all batch experiment. The final pH trends to decrease in the range of 4.5-5.8 for raw POME and 5.46-5.98 for ozonated POME. Total cumulative hydrogen fermentation trended to increase of both POME and ozonated POME reached the higher value than that from raw POME in most cases. The trends of \( H_{max} \) were similar to that of the cumulative hydrogen (Table 1). While \( R_{max} \) was also increased with concentration increased, but dropped at the concentration greater than 25,000 mg L\(^{-1}\) for both POME (Fig. 1a and b). The results illustrated \( H_{max} \) and \( R_{max} \) of ozonated POME were greater than those of the raw POME in most cases. Maximum hydrogen production yield was observed at the concentration of 35,000 mg L\(^{-1}\), for both POME and the yield of ozonated POME was higher than that of raw POME in most cases. Ozonated POME reached the highest yield of 77.1 mL g\(^{-1}\) COD was achieved (Fig. 1a and b). The results indicated that the POME concentrations have strongly effect on the hydrogen yield, and the partial ozonation effectively enhanced the hydrogen yield. Therefore, the application of the partial ozonation on POME is advantageous prior to fermentation process.

<table>
<thead>
<tr>
<th>[COD] (mg L(^{-1}))</th>
<th>( H_{max} ) (mL)</th>
<th>( R_{max} ) (mL h(^{-1}))</th>
<th>Yield (mL g(^{-1})COD)</th>
<th>( H_2 ) (%)</th>
<th>COD removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw POME</td>
<td>Ozonated POME</td>
<td>Raw POME</td>
<td>Ozonated POME</td>
<td>Raw POME</td>
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<tr>
<td>5,000</td>
<td>4.2±2.2</td>
<td>5.9±3.0</td>
<td>0.7±0.3</td>
<td>1.1±0.8</td>
<td>7.0±1.3</td>
</tr>
<tr>
<td>10,000</td>
<td>29.1±1.3</td>
<td>53.6±0.6</td>
<td>3.5±0.6</td>
<td>4.7±0.5</td>
<td>3.5±0.2</td>
</tr>
<tr>
<td>15,000</td>
<td>48.2±2.7</td>
<td>82.8±2.3</td>
<td>5.7±0.8</td>
<td>7.0±0.3</td>
<td>17.4±1.6</td>
</tr>
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<td>20,000</td>
<td>90.2±2.7</td>
<td>120.1±6.7</td>
<td>7.3±1.6</td>
<td>9.1±1.6</td>
<td>21.2±1.5</td>
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<tr>
<td>25,000</td>
<td>70.3±10.2</td>
<td>143.3±7.6</td>
<td>10.8±0.6</td>
<td>10.2±1.1</td>
<td>22.4±1.5</td>
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<tr>
<td>30,000</td>
<td>103.1±8.4</td>
<td>206.1±3.0</td>
<td>7.3±1.3</td>
<td>7.0±0.8</td>
<td>37.3±1.4</td>
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<tr>
<td>35,000</td>
<td>171.0±0.5</td>
<td>239.9±1.1</td>
<td>3.4±0.4</td>
<td>5.5±0.4</td>
<td>51.5±5.0</td>
</tr>
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Acetate and butyrate were dominant in all batches, little amount of valerate, propionate, and ethanol were detected in all the reactors. This research was successful demonstrated that the partial ozonation enhanced the hydrogen production.

Fig. 1. (a) hydrogen production yield (\(\text{Yield}\)) and maximum hydrogen production rate (\(R_{\text{max}}\)) (\(\bullet\)) of raw POME; (b) ozonated POME with the initial concentrations of 5,000 to 35,000 mg L\(^{-1}\) after 96 h fermentation. The data and I-bars represent mean values and standard deviation of duplicate experiments.

4. Conclusion

This study demonstrated that the ozonation pretreatment of the POME enhanced the biodegradability of POME constituents and also hydrogen production yields and rates under the thermophilic condition in most cases. The POME was pretreated by partial ozonation gave the hydrogen yield was increased by 60% which higher than raw POME.

Acknowledgement

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References


Biography

Asst. Prof. Nipon Pisutpaisal is a lecturer of Department of Agro-Industrial, Food and Environmental Technology, Faculty of Applied Science, King Mongkut’s University of Technology North Bangkok. He is also an affiliate staff at the Joint Graduate School of Environment and Energy (JGSEE), King Mongkut’s University of Technology Thonburi. He obtained his Ph.D. degree (Environmental Engineering) from The Pennsylvania State University, USA in 2003. Asst. Prof. Nipon Pisutpaisal is specialized in Biological Wastewater Treatment, Anaerobic Digestion, Bio-hydrogen Energy, and Fermentative Bioenergy Technology.