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Review of techniques for biohydrogen production from palm oil mill effluent

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Abstract

Due to rapid growth in population and societal development, the demand for energy is on the increase. The production of palm oil as one of the major edible oils consumed in the world has increased tremendously. Palm oil mill effluent (POME), a wastewater from the most significant agricultural industry is produced in tremendous amounts that requires proper management to mitigate its negative environmental effects. Studies have shown that Palm oil mill effluent (POME) possesses the properties of a good carbon feedstock for hydrogen generation in fermentation processes. In this study, several methods for biohydrogen production from Palm oil mill effluent (POME) were discussed. An apprehension into the different pre-treatment methods on POME including physicochemical, chemical and biological and their effects on the characteristics of POME including pH, temperature, sugar content, solid content, viscosity, nutrients and by-product toxicity on the biohydrogen production and effluent quality were reviewed. Various bioreactor designs were used for biohydrogen from POME, the modifications applied on the system design to increase the stability and productivity of POME treatment have been examined. The individual and interactive effects of pH, different temperatures of heat treatment, different inoculum sizes and substrate concentrations on biohydrogen production were discussed. Moreover, higher biohydrogen productivity could be obtained with the addition of nanoparticle nutrients and introducing genetically modified H2-producing bacteria. Finally, further investigation in the future shall focus on the development of a more inclusive and efficient POME treatment via DF process that favours biohydrogen production, environmental benign and economically viable.

Keywords: Palm oil mill effluent; Enzyme; Biohydrogen; Substrate; Reducing sugars

1. Introduction

Palm Oil production has increased tremendously in the last decade, accounting for the world largest vegetable oil production. Palm oil industries generate lignocellulosic biomass wastes such as empty fruit bunch (EFB), mesocarp fiber, shell, and palm oil mill effluent (POME) from each tonne of fresh fruit bunch (FFB) processed. More than half of the waste is turned into POME which is a liquid by-product produced from the sterilization and milling process of fresh fruit bunch (FFB). Due to its characteristic of having a high organic content, the treatment and disposal of this waste is an economic burden on the palm oil industry. Thus, creating a marketable product from this waste would reduce the treatment cost. Recovery of energy from waste might reduce the cost of wastewater treatment and contribute to reducing our dependence on fossil fuel. Hydrogen and energy production could mitigate these waste treatment problems (Karlsson et al 2008). The RS are the reactive molecules that can be converted into fuels, Chemicals, food, and animal feed via a biological or chemical process. As in the natural ecosystem, RS is often stored in the polysaccharide form of grains like corn, wheat, and rice. Palm oil mill effluent contains complex cellulose and polysaccharides, which can be further converted into RSs that favor biohydrogen production.

Studies have shown that Anaerobic systems have great potential to treat POME because of its highly organic content characteristic. The feasibility of applying anaerobic fermentation of organic waste to produce hydrogen had been

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demonstrated in literature. These systems do not require high energy for aeration, thus allowing the recovery of energy in the form of biogas. Biohydrogen is a promising clean fuel ultimately derived from renewable energy sources and it is environmental friendly. During the combustion of hydrogen, water will be produced as the sole product. It is high in energy yield and it could be produced by low-energy intensive processes (Kyazze et al 2008). Biohydrogen production is a complex process which is greatly influenced by many factors. These factors include substrate specificity, substrate concentration, reactor configuration, hydraulic retention time (HRT), organic loading rate (OLR), pH, temperature, oxidation-reduction potential and nutritional requirements (Zhang et al 2008). The AD process takes longer time with untreated POME. Pretreatment is thus needed for the isolation of polysaccharides, reduction of crystallinity, breakdown of cell wall structures, and the increase of accessibility and porosity to make the raw material consumable by the microbial group. Studies have showed that hydrogen production is strongly inhibited by pH values as low as pH 5. Other than nutrient composition, substrate concentration is found to be one of the most important factors affecting biohydrogen production. The optimization of fermentation conditions, particularly nutritional and environmental parameters are of primary importance for bioprocess development (Pan et al 2008).

Fan et al (2004) employed thermal pretreatment at 120 °C on POME, which increased methane yield by as much as 9 times. The maximum biogas production of 1471 mL was achieved using thermal pretreatment at a 20:80 solid/liquid sample ratio. The ratio was calculated after the pretreated samples were allowed to settle, where the solid part is the settled suspension and the liquid part is the clear liquor phase. Chaiprapat and Laklam observed that the pretreatment of POME by ozone yielded higher COD removal in an anaerobic sequencing batch reactor. Mahmod et al. Fan et al (2004) studied acid pretreatment, which yielded increases in hydrogen yield by as much as 97% and 65% using phosphoric and nitric acids, respectively. At 0.8% w/v of phosphoric acid and 18.47 g/L of the initial RS, they achieved a hydrogen yield of 1.24 mol H2/mol glucose, which corresponded to the maximum hydrogen production of 0.181 mmol/L/h. Thermophilic biohydrogen is suitable to treat POME since the latter is discharged at a high temperature ranging between 70 and 80 °C (Pan et al 2008). The thermophilic process can facilitate a higher biogas production and higher substrate degradation relative to the mesophilic process (Kyazze et al 2008). The most common enzymes used in the pretreatment of lignocellulosic materials are cellulase, xylanase, lipase, vinasse and laccase. Conventional techniques such as a one-factor-at-a-time method is time consuming and laborious to perform. Enzymatic pretreatment has been recognized as a useful pretreatment for POME, since it does not corrode equipment but uses less energy. Besides, the concentration of volatile fatty acids (VFAs) as the main inhibitor of biohydrogen production remains low under the thermophilic condition. Therefore, this study aimed to optimize the RS recovery from POME as a platform to enhance the biohydrogen production. The main objective of this study was to optimize the parameters for hydrogen production by natural microflora by using the Response surface methodology (RSM) approach. The individual and the interactive effects of pH, different temperatures of heat treatment, different inoculum sizes and substrate concentrations on biohydrogen production are investigated in this study.

2. Biohydrogen production from POME in an anaerobic sludge reactor

Chong et al (2009) conducted a lab-scale up-flow anaerobic sludge blanket fixed-film reactor (UASFF) to produce biohydrogen from palm oil mill effluent (POME). The reactor was fed with POME at different hydraulic retention time (HRT) and organic loading rate (OLR) to obtain the optimum fermentation time for maximum hydrogen yield (HY). The results showed the HY, volumetric hydrogen production rate (VHPR), and COD removal of 0.5–1.1 L H_2/g $COD_{consumed}$, 1.98–4.1 L H_2 L^{-1} day^{-1}, and 33.4–38.5%, respectively. The characteristic study on POME particles was analyzed by particle size distribution (PSD), Scanning electron microscopy (SEM), and Energy-dispersive X-ray spectroscopy (EDX). The microbial Shannon and Simpson diversity indices and Principal Component Analysis assessed the alpha and beta diversity, respectively. The results indicated the change of bacterial community diversity over the operation, in which *Clostridium sensu stricto 1 and Lactobacillus* species were contributed to hydrogen fermentation.

3. Biohydrogen production from POME by two stage anaerobic sequencing batch reactor

Hawkes et al (2007) evaluated the production of biohydrogen through dark fermentation of palm oil mill effluent (POME) in two-stages of biohydrogen in an anaerobic sequencing batch reactor (ASBR) system using enriched mixed culture for the first time. This study attempts to examine the effect of HRT and its interaction behavior with the solid retention time (SRT), and the sugar consumption. The effluent after discharged from the thermophilic reactor contained 7.61 g/L TC and 22.87 g/L TSS was fed to the secondary mesophilic reactor system. Results indicated that the overall sugar consumption reached 88.62% at the optimum HRT of 12 h with the SRT set to 20 h. The optimum hydrogen yield and HPR in the thermophilic stage were 2.99 mol H_2/mol-sugar and 8.54 mmol H_2/L·h respectively, while for the mesophilic stage were 1.19 mol H_2/mol-sugar and 1.47 mmolH_2/L·h respectively. The overall HPR showed an improvement and increase from 8.54 mmol H_2/L·h to 10.34 mmol H_2/L.h. Microbial community analysis of mixed culture in the two-stage thermophilic (55.0 °C) and mesophilic (37.0 °C) ASBR reactor was dominated by *Thermoanaerobacterium* sp. based on the PCR-DGGE technique.

4. Cell immobilization techniques for Biohydrogen production from POME

Ruggeri et al (2009) employed cell immobilization techniques to produce biohydrogen production from POME in the presence of an immobilized anaerobic sludge as the seed culture. Palm oil mill effluent (POME) was used as the substrate carbon source. The result showed that with a POME concentration of 20 g COD/l in the feed, the suspended-cell containing reactor was able to produce hydrogen at an optimal rate of 0.348 l H_2/(l POME h) at HRT 6 h. However, the immobilized-cell containing reactor exhibited a better hydrogen production rate of 0.589 l H_2/(l POME h), which occurred at HRT 2 h. When the immobilized-cell containing reactor was scaled up to 5l, the hydrogen production rate was 0.500–0.588 l H_2/(l POME h) for HRT 2–10 h, but after a thermal treatment (60 °C, 1 h) the rate increase to 0.632 l H_2/(l POME h) at HRT 2 h. The main soluble metabolites were butyric acid and acetic acid, followed by propionic acid and ethanol.

5. Biohydrogen production from POME in a pilot-scale up-flow anaerobic sludge reactor

Wang et al (2008) analysed the life-cycle of biohydrogen production from palm oil mill effluent (POME) in a pilot-scale up-flow anaerobic sludge blanket fixed-film reactor. The SimaPro LCA software and ReCiPe 2016 impact assessment method were used. Electricity usage was found to be a significant source of environmental impacts, with 50–98% of the total impacts. Furthermore, an improvement analysis was conducted, resulted in a reduction in all impacts, especially global warming impact with 77% reduction from 818 to 189 kg CO_2-eq per kg biohydrogen. While shifting the pilot reactor to Sarawak may further lessen the impact to 142 kg CO_2-eq due to cleaner grid in that region. Besides, if the environmental burden avoided due to usage of POME is considered, the global warming impact can be further reduced to 54.9 kg CO_2-eq. Thus, the pilot reactor has huge potential, especially in utilizing waste to produce bioenergy.

6. Biohydrogen production from POME via microflora

Venkata et al (2007) investigated the treatment of POME under anaerobic fermentation process to produce biohydrogen via microflora. Raw palm oil mill effluent (POME) from a cooling pond and sludge from anaerobic pond of the POME treatment plant at Labu palm oil mill were collected for the study. The experiments were conducted in 500 mL bioreactor under mesophilic operation at 37 °C with different pH (4.5, 5.0, 5.5, and 6.0) and sludge percentage values (2.5, 5, 7.5, and 10% (w/v)). The source of inoculum was used in POME sludge as hydrogen producing bacteria. From batch experiments, the maximum hydrogen production yield obtained was 5.988 ± 0.5 L H_2/L-med at 10% POME sludge (w/v) with an optimum pH of 5.5 and mesophilic temperature of 37 °C. Methane free biogas consist of 36% maximum hydrogen and 64% carbon dioxide was produced during the process.

7. Biohydrogen production from POME by anaerobic consortia and *Clostridium beijerinckii*

Rodrigues et al (2006) experimentally analyzed the use of Palm oil mill effluent (POME) as a substrate to produce hydrogen by dark fermentation. Two microbial consortia and a pure culture of *Clostridium beijerinckii* (ATCC 8260) were cultured anaerobically in raw, diluted and hydrolyzed POME to compare biohydrogen production yields in all three media. Experiments were done in 15 mL Hungate tubes containing 5 mL of medium and 1 mL of inoculum. When *Clostridium beijerinckii* was cultivated at 30 °C in the hydrolyzed POME (P003), containing 7.5 g/L of sucrose, during 8 days of fermentation and 20 % of the inoculum, the maximum biohydrogen production yield was 4.62 LH2/Lmed. Consortium C3 also showed the best production in hydrolyzed POME while consortium C6 achieved its maximum production in raw POME. This effluent is a potential substrate for biohydrogen production.

8. Thermophilic biohydrogen production from optimized enzymatic pretreatment of POME

Sim et al (2006) studied the improvement of bioenergy production from biological pretreatment process to degrade the lignocellulose biomass in the anaerobic digestion system. This technique involves the use of enzymes. Enzymatic pretreatment was applied to POME to determine the optimum process parameters for producing reducing sugars (RS) to be used as a substrate in biohydrogen production. The Box-Behnken design (BBD) was used to construct an experiment to optimize the pretreatment variables, such as reaction time (h), enzyme concentration (% w/v), and pH. The optimum experimental conditions were found to be 12hr of reaction time, an enzyme concentration of 3.76% w/v, and pH 5. The result showed that POME treated with the optimal enzymatic pretreatment increased the RS content by

182%. Next, thermophilic biohydrogen production using a pretreated substrate was carried out at a temperature of 55 °C, mixing speed of 150 rpm, Chemical Oxygen Demand (COD) concentration of 29,100 mg/L, seed content of 18.2%, and initial pH 7.14. The biohydrogen production potential (Hmax) was significantly increased by 145% (177 mL H2/g reducing sugar) by using enzymatically pretreated POME as a substrate. This result indicated that the recovery of RS from recalcitrant POME via enzymatic pretreatment could enhance biohydrogen production. Hence, it is a useful proposal for further application in bioenergy conversion from organic waste.

9. Statistical Optimization of Biohydrogen from POME by Natural Mechanism

Atif et al (2005) investigated the used of palm oil mill effluent (POME) as substrate for biohydrogen production. Heat-treated POME sludge acclimated with POME incubated at 37°C for 24 hours was used as seed culture. Preliminary screening on the effects of inocula sizes, heat treatment, substrate concentration and pH of incubation by using a factorial design (FD) were conducted under mesophilic condition (37°C) using a serum vial (160 mL). The experimental results from two-level FD showed that pH and Chemical Oxygen Demand (COD) of POME significantly affected biohydrogen production. Optimizations of the specific hydrogen production (P_s) and the hydrogen production rate (Rm) were achieved by using a central composite design (CCD). The maximum Ps of 272 mL H_2/g carbohydrate was obtained under optimum conditions of pH 5.75 and substrate concentration of 80 g/L. The maximum Rm of 98 mL H_2/h was calculated under the optimum conditions of pH 5.98 and substrate concentration of 80 g/L. The optimized conditions obtained were subjected to a confirmation run and it showed reproducible data with a P_s of 226 mL H_2/g carbohydrate and R_m of 72 mL H_2/h.

10. Conclusion

The initial pH and substrate concentration had impacts on fermentative biohydrogen production from POME individually and interactively. Experimentally studies have shown that the enzymatic pretreatment of POME using cellulase (Novozym 50199) could significantly improve biohydrogen production efficiency. The optimized process parameters via the response surface methodology were able to improve RS content in the substrate and hence improve the thermophilic biohydrogen production. POME showed to be a good substrate for the biohydrogen production. Higher yield of H2 was obtained with *Clostridium beijerinckii* (ATCC 8260) cultivated in hydrolyzed POME (P003). Other bacteria and consortia are good producers of hydrogen, such as C3 and C6, but they depend on an adequate control of the parameters that most interfere in the fermentation. In addition, POME has a potential producer of hydrogen in various forms (raw, diluted and hydrolyzed). The most important consequences of biohydrogen production from POME can be related to the electricity usage, which found to be as the highest contributor to global warming potential. The improvement analysis was done, which caused a significant reduction in global warming potential. Further, the credit of environmental burden avoided due to POME treatment showed an impressive impact in all categories.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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