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Kinetic analysis of biohydrogen production from anaerobically treated POME in bioreactor under optimized condition

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ABSTRACT

In this study, the biohydrogen production from POME was performed under mesophillic conditions by mixed culture in a 2 L bioreactor using the optimized conditions obtained previously. The effect of controlling pH initially or throughout the fermentation was also examined. The fermentation performance was monitored by comparing P, R_m, λ, and P_s in both systems. In this present study, the reactor system showed higher hydrogen production potential values with the utilization of pH control. Hydrogen production potential was increased two folds when the reactor system was equipped with pH control rather than just fixed the initial pH at 5.8. The biohydrogen production under controlled pH occurred after 7 h fermentation resulting in maximum Ps and Rm of 1.32 L/L POME and 0.144 L/L.h, respectively.

1. Introduction

Considering that the hydrogen gas is one of the alternatives to fossil fuels, there are numerous ways to produce hydrogen [1]. Hydrogen must be made from renewable resources if its use to impact global CO_2 levels. The carbohydrate-rich crops and food industry wastes are considered as suitable substrates for dark fermentative hydrogen production [2]. Palm oil mill effluent (POME) has a good potential for biohydrogen production when being treated anaerobically. Utilization of biohydrogen gas, produced from anaerobic treatment of POME can be beneficial to the palm oil industry and the nation due to the energy availability. Besides, methane gas which is known to be greenhouse gases could be minimized and thereby reduce the environmental impact.

Biohydrogen production is a complex process and is greatly influenced by many factors such as substrate specificity, substrate concentration, reactor configuration, hydraulic retention time (HRT), organic loading rate (OLR), pH, temperature, oxidation-reduction potential and nutritional requirement [3]. Moreover, the optimization of fermentation conditions, particularly nutritional and environmental parameters are of primary importance for bioprocess development [4]. Previously, factors affecting hydrogen production from POME during anaerobic digestion in batch fermentation by anaerobic mixed cultures were optimized using Response

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Surface Methodology with Central Composite Design [5]. The experiments were conducted in 160 mL serum bottles containing 100 mL POME (medium). Investigated parameters included pH, heat treatment temperature, inoculum size and substrate concentration [5]. It was found that, using POME sludge as inocula, the initial pH and substrate concentration had impact on fermentative biohydrogen production individually and interactively. The maximum P_s and R_m of 282 mL H_2/g carbohydrate and 137 mL/h, respectively, were achieved at initial pH 5.86 and substrate concentration of 80 g/L. The predicted and experimental results obtained were closely related indicating that the data were reproducible.

Among several parameters, culture pH has been regarded as one of the most important factor affecting the biohydrogen production [2,6–9]. Vijayaraghavan and Ahmad [10] found that controlling pH is crucial in order to produce biohydrogen. Therefore, to further improve the productivity of biohydrogen from POME, we attempted to conduct batch fermentation in 2 L bioreactor using the optimized conditions obtained previously. Biohydrogen production in batch mode under uncontrolled (initial pH fixed at 5.8) and controlled pH were compared on the basis of hydrogen gas content, hydrogen yield (P_s) and hydrogen production rate (R_m).

2. Materials and methods

2.1. Palm oil mill effluent

Palm Oil Mill Effluent (POME) was obtained from FELDA Serting Hilir Palm Oil Mill located at Serting, Negeri Sembilan, Malaysia. The fresh hot POME (80–90 °C) was collected and kept in a cold room at temperature 4 °C to avoid degradation of the wastewater. The POME used within a week and fresh POME will be collected again from the same mill and characterized based on COD, BOD, TS and SS measurements to ensure consistency in its characteristics. The POME used in terms of COD was 40–80 g/L.

2.2. Inoculum preparation and preservation

Inoculum used for this project was obtained from bottom reactor part of 500 m^3 digester tank from wastewater treatment at the same mill. The sludge was preserved in a cold room at 4 °C without further treatment.

For production in bioreactor, the POME sludge was pretreated at 85 °C for 20 min as the optimized parameter determined by design software. Then, the heat-treated sludge was mixed with POME in ratio 1:1 in 160 mL serum bottle and incubated at 37 °C for 24 h. The incubated sludge was then used as inoculum for fermentation in 2 L bioreactor.

2.3. Reactor operation and monitoring

A laboratory scale bioreactor was used. The bioreactor was equipped with an internal diameter of 10 cm, external diameter of 15 cm and height of 20.5 cm. Total volume of reactor was 2000 mL and the working volume was 1000 mL. A biogas tube was used to trap the biogas to a gas collection bag. The temperature was maintained by circulating hot water through thermomix and operated at a temperature of 36 ± 1 °C. Fixed or an initial pH of 5.8 was set for all the experiments. The bioreactor was routinely monitored for the pH changes, biogas generation and composition, and VSS distributions. The gas volumes were corrected to a standard temperature (0 °C) and pressure (760 mmHg) (STP). In this operation, the fermentation process was carried out at COD of 80 g/L for 1 day in batch mode.

2.4. Analytical methods

Acetic, propionic, butyric and other organic acids were analysed using High Performance Liquid Chromatography (HPLC). HPLC SPD-10A, UV–VIS detector, LC-10 AS Liquid Chromatography (Shimadzu, Japan) with a cation exchange resin column (Aminex HPX-87H column, 300 mm × 7.8 mm) and 4 mM sulphuric acid was used as mobile phase. The fermentation broth in eppendorf tube was spinned down at 12,000 rpm for 10 min in Mikro 22 K Hettich Zentrifugen centrifuge to remove suspended solids and biomass. The supernatant was then filtered through an acrodisc filter with 0.45 μm pore size. The mobile phase was filtered prior to use by using cellulose nitrate membrane filter (Millipore) with a pore size 0.45 μm using an aspirator pump (JEIO TECH, model VE-11). Standard curve of the VFAs (acetic, propionic, lactic, butyric) were prepared at 2, 4, 6, 8 and 10 g/L. The samples were analysed for VFAs in triplicates after every three hours.

The biogas content was analysed using a gas chromatograph equipped with a thermal conductivity detector and the column was packed with Porapack Q (80/100 mesh). The temperatures of the injector and the column were kept at 0 °C and 50 °C, respectively. Nitrogen was used as the carrier gas with a flow rate of 30 mL/min. The COD, total solid (TS) of the samples were measured according to the standard methods (APHA 1985). Total suspended solids (TSS) was determined by filtration method. The total sugar in terms of carbohydrate was determined using phenol-sulphuric methods. Hydrogen and carbon dioxide were detected using a Shimadzu GC-8A gas chromatograph (Shimadzu Corp., Japan), equipped with a thermo-conductivity detector. The temperatures at stainless steel column and injection point were 50 °C and 100 °C, respectively. The carrier gas was nitrogen and the column was packed with Porapack Q (80/100 mesh, Wayers Corp, Mildford, MA, U.S.A). The gas produced was also quantified using Kitagawa Hydrogen test kit and methane detector. The hydrogen yields were measured at 2 h interval.

2.5. Kinetic analysis

In this study, a modified Gompertz equation was employed to model the kinetics of biohydrogen production [3]. The Gompertz model is a three-parameter model which is simpler and easier to use and the three-parameter solution is more stable, as the parameters are less correlated. The three parameters of the modified Gompertz equation were hydrogen production potential (P), maximum hydrogen production rate (R_m) and duration of the lag phase (λ). In addition, when a three-parameter model is used, the parameter estimates have more degrees of freedom and can be given a biological