Performance Analysis of a Proton Exchange Membrane Fuel Cell (PEMFC) Integrated with a Trickling Bed Bioreactor for Biological High-Rate Hydrogen Production†

ARTICLE *in* ENERGY & FUELS · NOVEMBER 2007

Impact Factor: 2.79 · DOI: 10.1021/ef700270y

Performance Analysis of a Proton Exchange Membrane Fuel Cell (PEMFC) Integrated with a Trickling Bed Bioreactor for Biological High-Rate Hydrogen Production†

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Received May 25, 2007. Revised Manuscript Received October 8, 2007

For the performance investigation of a biohydrogen reactor integrated with a proton exchange membrane fuel cell (PEMFC), mesophilic trickling bed bioreactors (TBRs) filled with hydrophobic materials (HBM) were designed and conducted for hydrogen production under the anaerobic fermentation of sucrose. The bioreactor consisted of the column packed with polymeric cubes and inoculated with heat-treated sludge obtained from an anaerobic digestion tank. A defined medium containing sucrose was fed by the different hydraulic retention time (HRT) and recycle rate. Hydrogen concentrations in the gas phase were constant, averaging 40% of biogas throughout the operation. The hydrogen production rate (HPR) was increased until 10.5 $LH_2\ L^{-1}\ h^{-1}$ of the bioreactor when influent sucrose concentrations and recycle rates were varied. No methane was detected when the reactor was under a normal operation. The trickling bed bioreactor with hydrophobic materials demonstrates the feasibility of the process to produce hydrogen gas, and PEMFC was operated with the treated biogas from the reactor as a fuel source. A likely application of this reactor technology can be hydrogen gas recovery from the pretreatment of high-carbohydrate-containing wastewaters and the electricity generation using the fuel cell system with employment of the produced biogas.

Introduction

Fossil fuels are the major global energy resource, but their combustion products lead to environmental problem. In most dark fermentation for the hydrogen product, hydrogen is an ideal and clean energy source for the future because of its high conversion, recyclability, and nonpolluting nature.[1,2] Moreover, because it has a high energy content per unit weight (122 kJ/g), hydrogen will be a promising clean energy source when it can be produced in low cost and practical development.[3] In particular, biological hydrogen production, including direct or indirect biophotolysis, photofermentation, and dark fermentation, is an environmentally friendly and efficient way of hydrogen production. Among them, dark fermentation is considered more economically feasible because it normally achieves a much higher hydrogen production rate than that obtained from other biological production methods.[2] A continuously stirred tank reactor (CSTR) was used.[7,8] However, hydrogen production in a CSTR has the following drawbacks: sensitive to operation environments, such as pH and hydraulic retention time (HRT), and easy washout of microorganisms at a short HRT.[9] To increase hydrogen production and operation stability, cell immobilization approaches, which provides the high microorganism concentration at a short HRT, were applied and resulted in stable hydrogen productions at a short HRT. The biogas transfer out of the liquid phase is limited in a CSTR without intensive stirring. While stirred reactors facilitate gas release from the liquid phase, continuous stirring of the reactor consumes considerable electric power and detaches microorganisms from the immobilization carriers. To satisfy the stable cell immobilization and easy biogas release from the liquid phase, the trickling bed bioreactor may be applied. In a trickling bed bioreactor, biofilm grows on the packing materials and a thin fluid film is created over the biofilm. This trickling bed bioreactor operation promotes high rates of gas transfer into the biofilm because of the thin fluid film and facilitates rapid hydrogen gas evolution out of the biofilm under anaerobic conditions.[10] The tricking bed bioreactors have recently been tested for biological hydrogen production under thermophilic

† Presented at the International Conference on Bioenergy Outlook 2007, Singapore, April 26−27, 2007.

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10.1021/ef700270y CCC: $40.75
Published on Web 11/16/2007

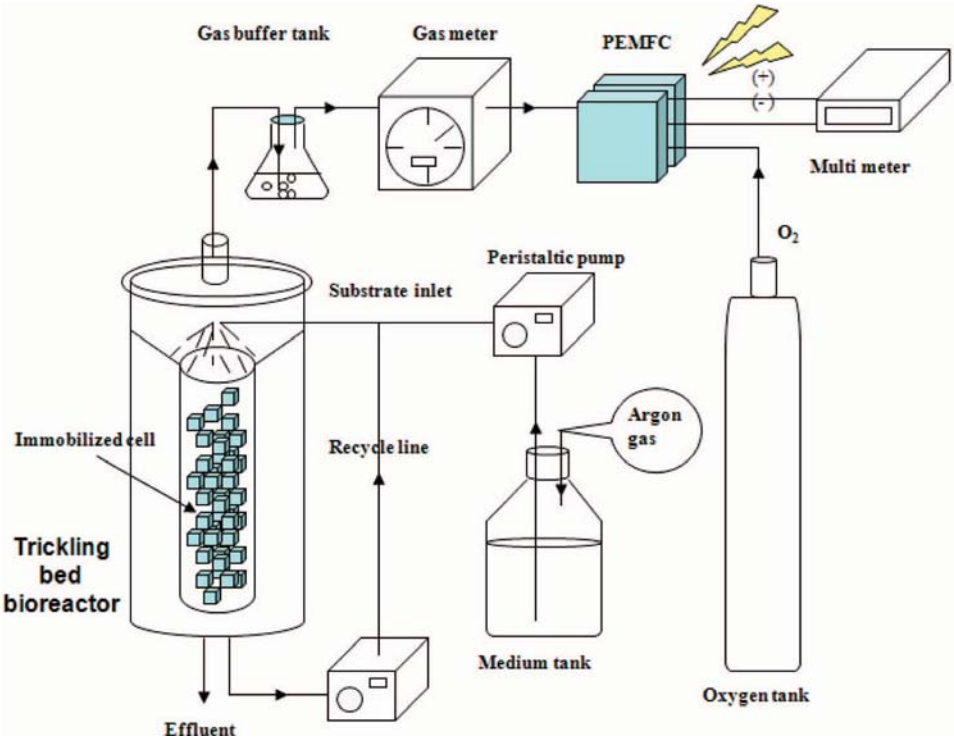

Figure 1. Schematic diagram of the trickling bed bioreactor.

conditions[7,11] and under mesophilic conditions using pure culture.[10] However, thus far, no reactors have been tested under mesophilic conditions using mixed microorganisms.

If this bioreactor is efficient and stable in hydrogen production, it seems feasible to apply the hydrogen production from the trickling bed bioreactor for electricity generation using a fuel cell. In a recent study, a dark hydrogen fermentation process using a continuously stirred anaerobic bioreactor (CSABR) seeded with silicone-immobilized sludge was integrated with a proton exchange membrane fuel cell (PEMFC) system for online electricity generation.[9] We therefore tested the feasibility of these concepts for hydrogen production using a tricking bed bioreactor with easy hydrogen release from the liquid phase and for electricity generation using PEMFC. Although studies of hydrogen production by mixed cultures have also attracted research attention, little information is available on the integration with biohydrogen production and electricity generation. Thus, the purpose of this study was to investigate the performance of the continuous hydrogen production by mixed microorganisms in a trickling bed bioreactor (TBR) and the electricity generation by a PEMFC with treated biogas from the reactor as a fuel.

Materials and Methods

Seed Sludge and Medium Composition. Anaerobically digested sludge obtained from a wastewater treatment plant located in Seoul, Korea, was used as inoculums. The collected sludge was incubated at 30 °C during 48 h and was sieved using a 200 μm mesh. Prior to use, the seed sludge was pretreated at 100 °C for 30 min to inhibit the methane-producing bacteria activity and enrich the hydrogen-producing bacteria forming spore.[4] The heat-treated sludge was inoculated with 10 v/v % in the reactors. The characteristics of seed sludge were a chemical oxygen demand (COD) of 11 900 mg/L, suspended solid (SS) of 8100 mg/L, and volatile suspended solid (VSS, to express the biomass) of 5400 mg/L. The medium used for hydrogen production consisted of sucrose as a sole carbon substrate and sufficient inorganic supplements, including 5240 mg/L NH_4HCO_3, 10 080 mg/L $NaHCO_3$, 187.5 mg/L K_2HPO_4, 150 mg/L $MgCl_2 \cdot 6H_2O$, 22.5 mg/L $MnSO_4 \cdot 6H_2O$, 37.5 mg/L $FeSO_4 \cdot 7H_2O$, 7.5 mg/L $CuSO_4 \cdot 5H_2O$, 150 mg/L $CaCl_2 \cdot 2H_2O$, and 0.188 mg/L $CoCl_2 \cdot 5H_2O$.

Experimental Setup and Conditions. A schematic description of the trickling bed bioreactor and PEMFC is shown in Figure 1. Hydrogen production experiments were conducted in a trickling-bed reactor, 40 cm in length, 4 cm inside diameter, total volume of 0.8 L, and head space of 1000 mL, filled with cube-type media, hydrophobic media (HBM) in the size of 0.5 × 0.5 cm. The reactor was operated at 40 °C as the mesophilic temperature. The pH of the mixed liquor was at around 5.5 without any feeding NaOH and HCl solutions. The anaerobic condition in both the head space and mixed liquor was attained by flushing with Ar gas immediately before start-up. The variable sucrose concentration (5, 15, 25, and 40 g/L) and HRT were applied. In some test, flocculation and clogging by biomass occurred in a high sucrose concentration condition. Excess biomass was removed from a reactor via the backwashing process by blowing Ar gas from the bottom of the reactor for 5 min. The biogas was pumped into a CO_2 absorber that was composed of a bottle containing 2 L of 6.0 M NaOH solution, trapping the entering CO_2 gas via a quick reaction of NaOH and CO_2 to form $NaHCO_3/Na_2CO_3$ precipitates. The effluent stream containing H_2 and water vapor was then introduced into a column packed with silica-gel beads for water vapor removal. Finally, the purified H_2 (at >99% purity) was fed to the PEMFC device to generate electricity. PEMFC, catalyst-coated membrane type, with the catalyst of 40 wt % Pt and the electrodes of 0.4 mg of Pt/cm^2, was made by our laboratory and used for the electricity generation with the biogas supply from the bioreactor.

Analytical Methods. Gas samples of 100 μL were withdrawn daily from the gas sampling port, which connected with the reactor using a gastight (Hamilton, Reno, NV) syringe. The compositions of hydrogen, carbon dioxide, and methane in the biogas were determined using a gas chromatograph (Agilent Technologies, Model 6890N) equipped with a thermal conductivity detector (TCD). Argon gas was used as a carrier gas at a flow rate of 20 mL/min. The operational temperatures of the injector port, the oven,

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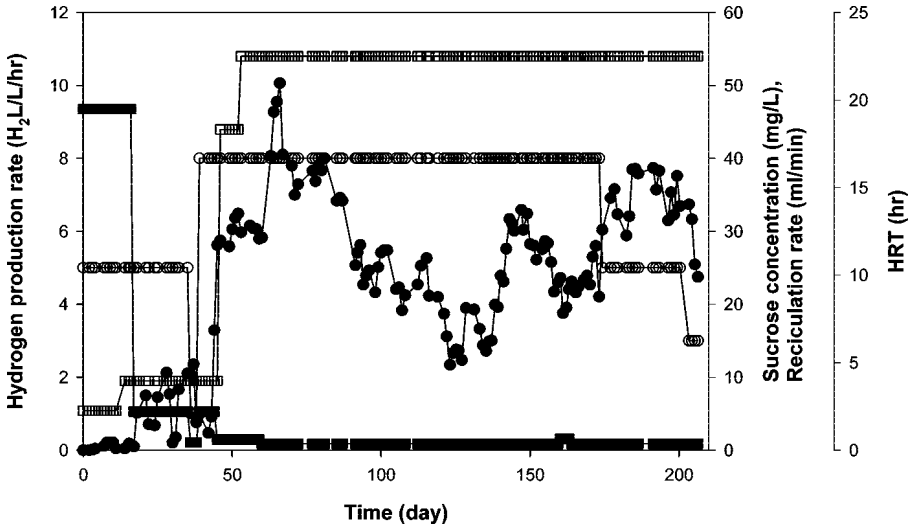

Figure 2. HPR in the trickling-bed bioreactor: HPR (●), sucrose concentration (○), HRT (■), and recirculation rate (□).

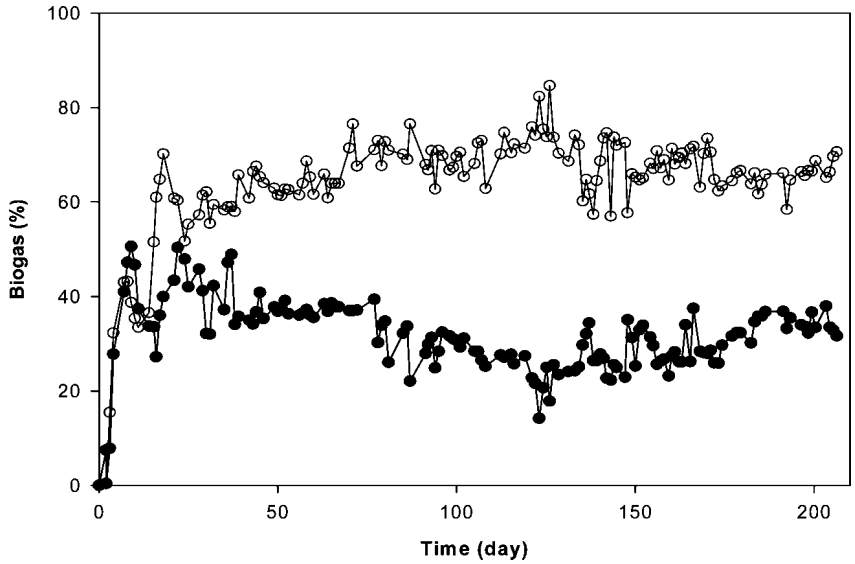

Figure 3. Hydrogen contents in biogas from the trickling-bed reactor. H_2 content (●) and CO_2 content (○) in biogas.

and the detector were 100, 50, and 200 °C, respectively. Liquid samples were collected and filtered using a 0.22 μm pore diameter filter (Whatman, PP) before analysis. Volatile fatty acids (VFAs) were analyzed using a gas chromatograph (Agilent Technologies, Model 6890) equipped with a flame ionization detector (FID) and a 30 m × 0.25 mm × 0.25 μm HP-INNOWax polyethylene glycol column. A pH was measured using a pH meter (Orion, A 490) in the effluent line. Residual sucrose was measured with a sucrose test kit (Merck, reflectoquant plus). Samples were stored sealed in a refrigerator (4 °C) prior to analysis. The morphology of hydrogen-producing bacteria in this study was analyzed using a scanning electron microscope (SEM) (FEI XL-30 FEG).

Results and Discussions

After 10 days of the start-up, hydrogen production from the reactor started. While changing several operation conditions, the HRT, sucrose concentration, and recirculation rate, the hydrogen production rate (HPR) reached up to 10.5 $LH_2\ L^{-1}\ h^{-1}$ at around 70 days in the HBM reactor after the start-up as shown in Figure 2. However, HPR decreased after showing the maximum HPR. The main reason was the clogging because of the excessive microbial growth on the surface of the medium. The clogging lead the limitation of the nutrient supply, and thus, the pH in the reactor, especially near the biofilm, was in the range below pH 4.5. Too low of pH inhibited the growth of hydrogen-producing bacteria and their performances on hydrogen production. Produced hydrogen stayed for a longer time in the reactor because of the clogging, and the higher hydrogen partial pressure also inhibited the hydrogen production. A decrease of the hydrogen partial pressure could be considered as an approach toward improvement of hydrogen productivity. To enhance the biogas transfer to the gaseous phase, the excessive biofilm from the surface of immobilization media was detached by forced agitation of the stationary packed media at about 125 days after the start-up. HPR increased to about 7 $LH_2\ L^{-1}\ h^{-1}$ after the forced agitation and to about 8 $LH_2\ L^{-1}\ h^{-1}$ by changing the sucrose concentration from 40 to 25 g/L in the HBM reactor.

As shown in Figures 3 and 4, hydrogen contents in the produced biogas from the reactor were in the range of 20−55% and the main volatile fatty acids were butyric and acetic acid.

The amount of acetic and butyric acid produced during hydrogen fermentation is a very important factor in hydrogen production. It is the reason that the hydrogen-production mechanism by anaerobic bacteria follows eqs 1 and 2. When acetic acid is the end product, a theoretical maximum product of 4 mol of hydrogen per 1 mol of glucose is obtained as follows in eq 1. When butyric acid is produced according to eq 2, a

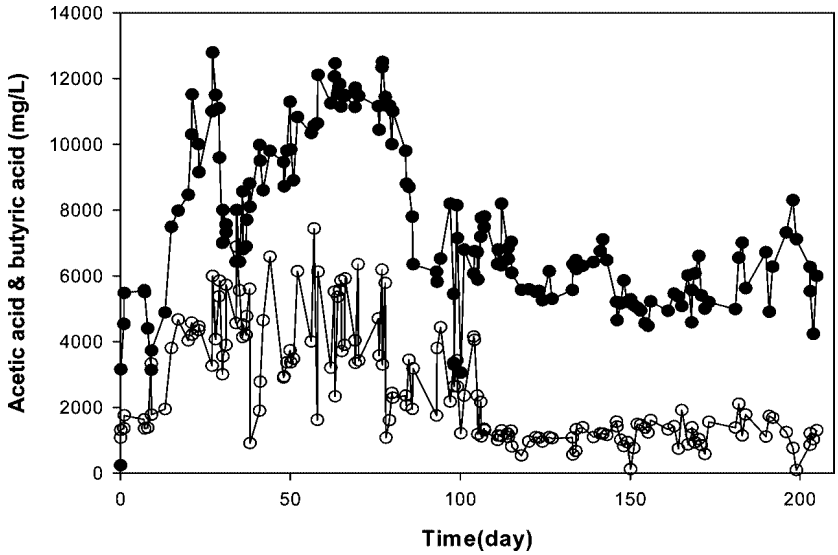

Figure 4. Concentration of VFAs during the hydrogen production. Acetic acid (○) and butyric acid (●).

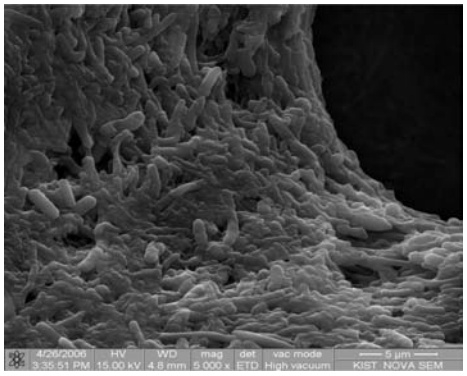

Figure 5. Microorganisms on the surface of hydrophobic media in the trickling-bed bioreactor.

theoretical maximum product of 2 mol of hydrogen per 1 mol of glucose is obtained as follows in eq 2.[5]

$$C_6H_{12}O_6 \rightarrow CH_3CH_3COOH + 4H_2 + 2CO_2 \quad (1)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2 \quad (2)$$

Thus, as shown in Figures 2 and 4, HPR showed the maximum values according to an increase of acetic and butyric acid. After 70 days of the start-up, HPR decreased with a decrease of acetic and butyric acid. However, the amount of lactic acid increased after 70 days, rapidly. The influent sucrose concentration maintained 40 g/L from 70 to 170 days. The high sucrose concentration increased the biomass amount in the reactors. From the clogging because of the excess biomass, a higher partial pressure and lower pH were observed in both reactors. At low pH, anaerobic fermentation usually produces lactic acid. Generally, the metabolic pathway leading to lactate is not related to hydrogen production, and the accumulation of lactate severely inhibits hydrogen production. Bacteriocins excreted by lactic-acid-producing bacteria may inhibit the growth of hydrogen-producing bacteria and their hydrogen production.[6] In general, the fatty acid composition at around 5.5–6.6 was almost constant, and the percentage of butyric acid was comparatively higher than acetic acid, which indicate that the hydrogen fermentation condition was favorably maintained by pH control in the reactors.

For the hydrogen production, several polymeric materials were tested as the packing materials in the trickling-bed bioreactor. Hydrophobic media showed the excellent HPR among the other materials as shown in Figure 2. As shown in Figure 5, hydrophobic media was good for the growth supporter of HPR and, during the reactor operation over 200 days, showed the good and stable performances for hydrogen production. Over 200 days of the reactor operation, no methane was observed. Over 95% of the microorganisms in the biofilm were *Clostridium* sp.

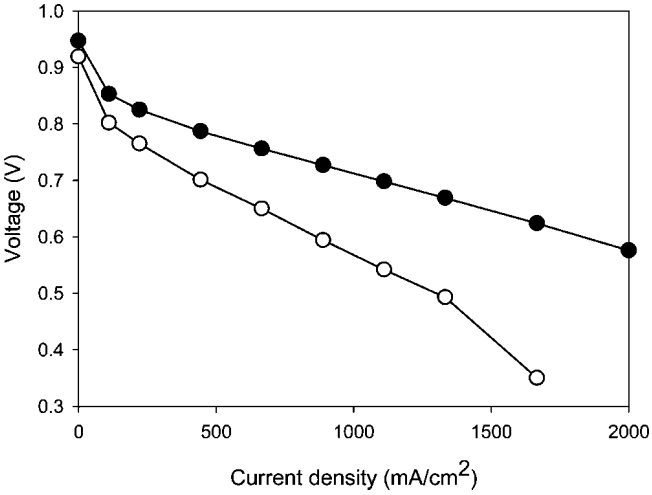

Figure 6. PEMPC performance using the treated and untreated biogas as a fuel source. Treated biogas (●) and untreated biogas (○).

Figure 6 showed the performance of PEMFC connected with the trickling-bed bioreactor. Two different type of biogas, treated with NaOH solution to purify the hydrogen gas to >99% and untreated biogas, were supplied to PEMFC as a fuel source. To remove the carbon dioxide and trace elements, the scrubbing process was used, and the biogas after the process was called "treated biogas". The PEMFC using the treated biogas showed a similar performance when pure hydrogen was used as a fuel source for the PEMFC. Because a small size of PEMFC was used for the electricity generation, no serious problems on the PEMFC operation were observed. However, for the practical application of the PEMFC integrated with the biohydrogen fermentation process, a stable hydrogen supply system, a hydrogen purification process, and optimized fuel cell operating conditions may be needed.

Acknowledgment. This work was supported by the Korea Research Council of Fundamental Science and Technology of the Korean Ministry of Science and Technology.

EF700270Y