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Improvement of energy recovery from cellobiose by thermophillic dark fermentative hydrogen production followed by microbial fuel cell

*Jhansi L. Varanasi, Shantonu Roy, Soumya Pandit, Debabrata Das**

Department of Biotechnology, Indian Institute of Technology, Kharagpur 721302, India

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ABSTRACT

The present study demonstrated the feasibility of using an integrated approach of combining dark fermentation with MFCs to maximize the energy recovery from cellulosic substrate. Thermophillic dark-H_2 fermentation exhibited maximum H_2 production yield of 2.92 mol mol^{-1} hexose equivalent with an energy recovery of 28% which was highest reported till date. The total cumulative hydrogen potential of 3799 mL L^{-1} with maximum rate of hydrogen production of 865 mL h^{-1}, and lag time of 1.84 h were determined by using modified Gompertz equation. Subsequent use of acid rich effluents in two chamber MFCs generated maximum power density of 85.05 mW m^{-2} with an energy recovery of 2.49%. Moreover, a 75% COD removal was also achieved with a coulombic efficiency of 13% illustrating its ability for wastewater treatment. By using this integrated approach, an overall energy recovery of 30.49% was achieved demonstrating both environmental and economic sustainability of the process.

Introduction

Lignocellulosic feedstock such as rice straw, paper waste, wood chips, grass residues etc. appears to be most abundant biomass on earth's crust [1]. Extracting energy from such cellulosic substrates in the form of biohydrogen proves to be a carbon neutral method for renewable energy production. Hydrogen has high calorific value and does not evolve greenhouse gases when it is used as a fuel. Dark fermentation (fermentation process that proceeds in the presence or absence of light) has emerged to be the most feasible method for biohydrogen production as compared to other biohydrogen production processes [2]. During cellulose fermentation, the complex molecule is first hydrolysed to hexoses, which on further reaction with acidogenic fermentative bacteria, is converted to hydrogen and acetate [3]. High hydrogen yields have been reported from dark fermentation at thermophillic temperatures (60 °C) as compared to mesophilic temperatures (37 °C) due to the lower risk of contamination and higher rate of hydrolysis [4]. However, due to the thermodynamic constraints, maximum reported yields range from 2.5 to 3.5 mol H_2, which corresponds to only 20–25% of

Abbreviations: CD, current density (A m^{-2}); CE, coulombic efficiency; CEM, cation exchange membrane; COD, chemical oxidation demand (g L^{-1}); CV, cyclic voltammetry; GC, gas chromatograph; MFC, microbial fuel cell; OCV, open circuit voltage (V); OV, operating voltage (V); PD, power density (W m^{-2}); R_p, polarization resistance (Ω); VFA, volatile fatty acids.

* *Corresponding author*. Tel.: +91 3222 283758; fax: +91 3222 255303.
E-mail address: ddas.iitkgp@gmail.com (D. Das).

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the possible 12 mol of hydrogen that can be obtained from glucose based on stoichiometric conversions [5]. The residual organic matter from fermentation effluents comprise of fatty acids and alcohols such as acetic and butyric acids and ethanol. To make dark fermentation industrially viable for biofuel production, post processing of VFAs by integration with a secondary stage treatment process is desired [6].

Recently, microbial fuel cell technology has proven to be a suitable secondary stage process to fully recover the energy embedded in the metabolites and improve treatment efficiency [7]. In MFCs, the anode-respiring bacteria (ARB) oxidize the organic substrates and transfer the liberated electrons to an electrode (anode) which further travel to cathode via an external circuit and generate power in the process. Several studies have reported enhancement in bio-electricity generation with the use of pre-fermented wastewaters in MFCs [8]. An integrated system for biohydrogen production with concomitant electricity generation has received renewed attention as it creates a wider scope of developing a sustainable energy processes for biofuel production. Oh and Logan [5] investigated the applicability of combined dark fermentation – microbial fuel cell for energy recovery from food processing wastewater. Mohanakrishna et al. [9] reported an integrated approach towards biohydrogen production using composite vegetable waste and harnessing the electric current using acid rich effluent in MFC. Wang et al. [10] described integrated hydrogen production process from cellulose by combining dark fermentation, microbial fuel cell and microbial electrolysis cell. Pandit et al. [11] reported improved energy recovery from dark fermented cane molasses using microbial fuel cells. Pant et al. employed integrated conversion of food waste diluted with sewage by combining fermentation with microbial fuel cells [12]. Recently, a two stage conversion of crude glycerol to energy by linking dark fermentation with microbial fuel cell was reported [13].

The present research work deals with the feasibility of two-stage energy recovery from cellulosic substrates by connecting dark fermentation with MFCs. Due to the complexity of insoluble cellulosic feedstock, the experiments were conducted with cellobiose, a soluble cellodextrin released during cellulose hydrolysis. The spent medium obtained from thermophillic dark fermentation was subsequently used in microbial fuel cells for power generation. Electroactive mixed consortia was developed from fly ash leachate and was used as anodic inoculum in MFCs. Reproducibility of the enriched culture was examined by inoculating its pre-formed biofilm into a fresh non-inoculated anode. The performance was evaluated in terms of power generation, coulombic efficiency (CE) and chemical oxygen demand (COD) removal efficiencies. The efficiency of the combined process (thermophillic dark fermentation + MFC) was investigated by calculating energy recoveries for the individual as well as integrated processes.

Materials and methods

Inoculum and media for thermophillic dark fermentation

An enriched thermophillic mixed culture capable of H_2 production (developed in the laboratory previously) was used in present study [4]. Fresh cultures were regularly maintained anaerobically in serum bottles by subculturing in a medium (DSMZ medium of No141, German Collection of Microorganisms and Cell Cultures) comprised of glucose (10 g L^{-1}), yeast extract (4 g L^{-1}), tryptone (10 g L^{-1}), $FeSO_4$ (20 mM) and Cysteine HCl (1 g L^{-1}) which were acknowledged to be suitable nutrient substrates for present culture [4]. Anaerobic condition inside serum bottles was maintained by purging with nitrogen for 5 min. The production media consisted of cellobiose (10 g L^{-1}) as carbon source and remaining media components was same as mentioned above with inoculum size of 10% (v/v) and inoculum age of 4 h.

Hydrogen production using batch fermentation

Batch fermentation was carried out (in duplicates) with cellobiose as substrate in customized double jacketed reactors with 500 mL working volume and kept on a magnetic stirrer (shown in the graphical abstract). Water was circulated in the outer jacket to maintain the temperature at 60 °C. The fermentation media was adjusted to an initial pH of 6.5. Anaerobic conditions were maintained by sparging nitrogen gas for a fixed amount of time after the inoculation. The gas mixture was allowed to pass through a 40% (w/v) KOH solution in order to absorb the carbon dioxide. The remaining gas (containing mostly H_2) was collected in a gas collector under downward water displacement method. Samples were withdrawn from the reactor at regular intervals for the analysis of pH, VFA (g L^{-1}), carbohydrates (g L^{-1}) and enzyme activity (U mL^{-1}).The batch experiment was continued until hydrogen production ceased.

Inoculum and anolyte for microbial fuel cell

Two identical double-chambered MFCs were used for the experiments. One of the MFC (R_1) was inoculated with mixed electroactive consortia (10%, v/v) from fresh fly ash leachate collected from a thermal power plant. The electroactive mixed consortia was enriched by suspending the fly ash leachate in acetate media ($NaHCO_3$ – 2.5 g L^{-1}; KCl – 0.1 g L^{-1}; NH_4Cl – 1.5 g L^{-1}; NaH_2PO_4 – 0.6 g L^{-1}; CH_3COONa – 6.8 g L^{-1}; vitamins and trace elements; pH adjusted to 7) with sodium acetate as electron donor. The culture media was incubated at 30 °C for 7 d in the dark. A small portion of the biofilm formed on the electrode material of R_1 after 30 d of operation was scrapped off aseptically, grown in suspension and re-inoculated to the other MFC (R_2).

R_1 was operated with acetate media as described for 30 days prior to the experiment. Once the R_1 showed reproducible voltages for at least 5 cycles with an external resistance of 1000 Ω, the nutrient solution in the anode chamber was replaced with the effluent from dark fermentation as sole substrate. Before adding the effluent to the anode chamber, it was pre-treated by removing microbial biomass through centrifugation at 6000 rpm for 15 min and pH was adjusted to 7.0 by suitable alkali addition (Na_2CO_3). R_2 was directly operated with the pre-treated effluent as described above. Both MFCs were flushed with nitrogen gas for 10 min before each multiple-batch cycle to minimise measurement errors and the experiments were conducted at room temperature.