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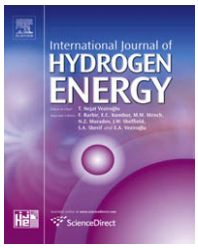

Hydrogen production from cellulose in a two-stage process combining fermentation and electrohydrogenesis

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ABSTRACT

A two-stage dark-fermentation and electrohydrogenesis process was used to convert the recalcitrant lignocellulosic materials into hydrogen gas at high yields and rates. Fermentation using *Clostridium thermocellum* produced 1.67 mol H_2/mol-glucose at a rate of 0.25 L H_2/L-d with a corn stover lignocellulose feed, and 1.64 mol H_2/mol-glucose and 1.65 L H_2/L-d with a cellobiose feed. The lignocelluose and cellobiose fermentation effluent consisted primarily of: acetic, lactic, succinic, and formic acids and ethanol. An additional 800 ± 290 mL H_2/g-COD was produced from a synthetic effluent with a wastewater inoculum (fermentation effluent inoculum; FEI) by electrohydrogensis using microbial electrolysis cells (MECs). Hydrogen yields were increased to 980 ± 110 mL H_2/g-COD with the synthetic effluent by combining in the inoculum samples from multiple microbial fuel cells (MFCs) each pre-acclimated to a single substrate (single substrate inocula; SSI). Hydrogen yields and production rates with SSI and the actual fermentation effluents were 980 ± 110 mL/g-COD and 1.11 ± 0.13 L/L-d (synthetic); 900 ± 140 mL/g-COD and 0.96 ± 0.16 L/L-d (cellobiose); and 750 ± 180 mL/g-COD and 1.00 ± 0.19 L/L-d (lignocellulose). A maximum hydrogen production rate of 1.11 ± 0.13 L H_2/L reactor/d was produced with synthetic effluent. Energy efficiencies based on electricity needed for the MEC using SSI were $270 \pm 20\%$ for the synthetic effluent, $230 \pm 50\%$ for lignocellulose effluent and $220 \pm 30\%$ for the cellobiose effluent. COD removals were ~90% for the synthetic effluents, and 70–85% based on VFA removal (65% COD removal) with the cellobiose and lignocellulose effluent. The overall hydrogen yield was 9.95 mol-H_2/mol-glucose for the cellobiose. These results show that pre-acclimation of MFCs to single substrates improves performance with a complex mixture of substrates, and that high hydrogen yields and gas production rates can be achieved using a two-stage fermentation and MEC process.

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1. Introduction

Biohydrogen production from cellulose has received considerable attention as a carbon neutral method for producing hydrogen from renewable resources and wastes. Lignocellulose is the most abundant biopolymer on earth and the main component of plant biomass. It is available in many human-created wastes such as straw, wood-chips, grass residue, and paper waste. Hydrogen has a high energy content (120 MJ/kg compared with 44 MJ/kg of gasoline) and is a useful energy carrier for transportation when produced using sustainable and renewable energy sources such as biomass. There are multiple ways of producing hydrogen from diverse feedstock using microorganisms with no external energy input necessary, such as biophotolysis, photo-fermentation, and dark-fermentation [1–5]. Dark-fermentation has a maximum hydrogen yield of 2.4–3 mol H_2/mol glucose in practice [6,7]. However, this is only 20–25% of the 12 mol of hydrogen possible based on stoichiometric conversion of glucose to hydrogen [6,7], resulting in residual organic matter containing end-products (such as acetic and butyric acids, and ethanol) that cannot be further converted by fermentation to hydrogen [3–5].

A new method was recently developed, called electrohydrogenesis, that can be used to convert biomass to hydrogen gas in a device called a microbial electrolysis cell (MEC) [8]. In an MEC, bacteria on the anode oxidize organic matter, releasing electrons through the circuit to the cathode where hydrogen can be formed from protons in the water. This reaction is endothermic, and therefore additional electrical input is needed that is provided by a power source. The MEC efficiency relative to the electrical input has reached over 400% [9], proving that the electrical energy needed (typically >0.2 V applied) is much less than that used for water electrolysis (>1.6–1.8 V applied) [9–11]. Hydrogen has been produced in MECs using many different substrates, including acetic acid, butyric acid, lactic acid, glucose, cellulose, and wastewater [10,12–15], but few tests have been conducted using complex mixtures of substrates such as wastewaters [16,17]. No test has been conducted using effluent of a bioreactor fermenting carbohydrates.

In this study we examined the use of a two-stage process for converting lignocellulose into hydrogen. This process consists of a dark-fermentation process to optimize the conversion of pre-treated lignocellulosic biomass into hydrogen, carbon dioxide, acetic, formic, succinic, and lactic acids, and ethanol, followed by electrohydrogenesis to convert the residual volatile fatty acids (VFAs) and alcohols into hydrogen gas. MECs have previously been used to produce hydrogen directly from cellulose, but the process efficiency and hydrogen production rates were low compared to those achieved with single VFAs [12]. Thus we reasoned that a more efficient process could be developed by optimizing the fermentation and electrohydrogenesis processes in separate reactors. For the fermentation process, we used a pure culture of *Clostridium thermocellum*, a gram-positive, acetogenic, and thermophilic microbe. It produces an active extracellular cellulase system [18] called the cellulosome [19], and it has one of the highest known growth rates on crystalline cellulose [20,21]. The influent to the fermentor was either the dilute-acid pre-treated lignocellulose feed from corn stover [22] or a cellobiose solution. Inocula for the MEC were developed from wastewater and acclimated either to a synthetic feed containing the primary constituents in the fermentation effluent (acetic acid, ethanol, succinic acid, lactic acid, and formic acid) or the individual substrates.

2. Materials and methods

2.1. Biomass pre-treatment

Corn stover biomass was pretreated at 20% (w/w) solid concentration by dilute-acid hydrolysis (H_2SO_4; 1.08%, w/w) at 190 °C for 90 s in a pilot scale reactor at NREL's Alternative Fuel User Facility [22]. The solid lignocellulose fraction (containing mostly cellulose and lignin) was separated from the aqueous hemicellulose by centrifugation, followed by washing in water at 3800 × *g* for 25 min. After pressing to remove excess water, the final material (45% moisture content) was analyzed according to NREL's Laboratory Analytical Procedure [27] and contained on a dry weight basis: 59.1% cellulose, 25.3% lignin, 5.1% xylan, 0.7% arabinan, 0.4% galactan, 0.2% mannan, 0.1% acetic acid, 1.9% protein, and 3.7% ash.

2.2. Fermentation

Clostridium thermocellum 27405 (from David Levin, Univ. of Manitoba) was maintained at 55 °C by routinely transferring 10% (v/v) inocula into fresh ATCC 1191 medium [23], supplemented with avicel cellulose (0.5%, w/v) as the sole carbon substrate. Fermentation experiments were carried out in a fermentor (Electrolab 2400, Gloucestershire, UK) containing 600 ml of 1191 medium continuously sparged with N_2 gas (10 ml/min) at 50 °C (Electrolab 240 Temperature Control). Approximately 0.25% (dry w/v) of either pre-treated corn stover lignocellulose or cellobiose was added to the fermentor, followed by inoculation with 100 mL of *C. thermocellum*. The stirring rate was maintained at 120 rpm, and pH at 6.8 (Electrolab 260 pH Control Module) using an anaerobic NaOH solution (1 N). Hydrogen, CO_2, and N_2 gas measurements were recorded every hour in triplicate according to Datar et al. [6] using an online GC (Varian, Palo Alto, CA) connected to the fermenter. Concentrations of H_2 and CO_2 were calculated based on the continuous flow rate of N_2 gas (10 ml/min) and its content in the sample gas, after correcting for the altitude (0.82 atmosphere at 5280 ft) and the laboratory and reactor temperatures. At the end of fermentation, the supernatant was collected by centrifugation at 3800 × *g* for 10 min to remove the cells along with any residual solid biomass.

2.3. MECs

Anodes used in MEC tests were initially enriched by operating reactors as microbial fuel cells (MFCs) as previously described [24]. Both reactors consisted of a 4-cm long cylindrical chamber formed in a solid block of Lexan, with a liquid volume of 28 mL. The anodes were graphite fiber brush electrodes pretreated using an ammonia gas process. Cathodes

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