Using algae and other biomass for H2 production in a modified microbial fuel cell process: a bioelectrochemically assisted microbial reactor

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ABSTRACT:

Biological hydrogen production using photosynthetic algae and bacteria can result in the generation of large amounts of waste biomass. This biomass can be used to produce hydrogen gas by modifying microbial fuel cell (MFC) technologies to produce hydrogen instead of electricity. By applying a small voltage (0.25 V in practice), it is possible to generate pure hydrogen gas at the cathode in this modified MFC process known as a bioelectrochemically assisted microbial reactor (BEAMR). Using the BEAMR process we have produced ~3 mol-H2/mol-acetate. Linking this process with fermentation of sugars could produce 8-9 mol-H2/mol-glucose, at an energy equivalent of one mole of hydrogen. The process is not limited to sugars, as any biodegradable organic matter can be used, such as domestic wastewater and steam-exploded corn stover hydrolysates. Thus, it should be possible to link the BEAMR process with photosynthetic biohydrogen production in the form of algae, bacteria or crops, to create an overall sustainable biohydrogen process.

KEYWORDS: algae, electrolysis, fermentation, fuel cell, photosynthetic.

Introduction

Biological hydrogen production using photosynthetic algae and bacteria can generate large amounts of waste biomass. The disposal of this waste biomass can be an economic burden to the process. One alternative to land disposal of biomass is to generate hydrogen from fermentation of sugars in the biomass, but so far fermentation is not a viable option due to low hydrogen yields. Typically, only 2 moles of hydrogen can be produced per mole of glucose, with a maximum theoretical yield of 4 mol-H2/mol-glucose by known fermentation pathways. As a result, with glucose only 15% of the starting material could be used to make hydrogen, with 85% being potentially wasted as fermentation end products (primarily acetic and butyric acids). Moreover, only carbohydrates can be used to make hydrogen by this fermentation route as other types of organic matter (such as proteins and fats) do not yield appreciable amounts of hydrogen.

We have developed a new method of renewable electricity generation using microbial fuel cells (MFCs) [1-3]. In a MFC process bacteria oxidize organic matter, releasing electrons to the anode and protons into the solution. The electrons flow to the counter electrode (cathode), generating current. The electrons in a MFC combine with protons and oxygen, aided by a catalyst, creating water. Power can be produce by any biodegradable fuel. So far we have shown power generation from simple substrates such as glucose, acetate, butyrate, ethanol, starch, protein, ethanol, and others, as well as from complex waste materials including human wastewater, animal wastewater, and corn stover hydrolysates produced by a steam explosion process [3, 4].

By modifying the MFC process, we invented a process that can produce hydrogen from any organic matter, even acetate produced by glucose fermentation [5,6]. We refer to this new process for hydrogen production as a bio-electrochemically assisted microbial reactor (BEAMR) process as a small potential must be added into the circuit of a modified MFC to create sufficient potential to generate pure hydrogen gas at the cathode. Because this process is based on the same fuel-cell technology used to make electricity using microorganisms, it can be inferred from MFC studies that any biomass that could be used to make electricity could also be used to make hydrogen. To demonstrate this, in this study we show that hydrogen can be produced from domestic wastewater using the BEAMR process, and therefore from any biodegradable source of organic matter. By using this process to create hydrogen from waste biomass generated from photosynthetic hydrogen production using algae or bacteria, it will be possible to make the overall process more efficient and more sustainable.
Methods

In order to modify the MFC process, where bacteria oxidize organic matter and release electrons, we remove oxygen from the cathode chamber and add a small potential to generate hydrogen at the cathode instead of water. The anodic reaction in a MFC is spontaneous organic matter electrolysis that poises the electrode at \(-0.3\) V (vs a standard hydrogen electrode, or SHE). In theory, only an additional 0.11 V (room temperature, pH=7) is needed to spontaneously generate hydrogen at the cathode, but overpotentials increase the required voltage. By adding 0.25 V, it is possible to generate hydrogen from the cathode in the modified MFC using acetate and other organic matter present at sufficient concentrations to sustain anaerobic conditions in the anode chamber. In contrast, water electrolysis requires approximately 1.8 V, or over 7 times the voltage [5]. Using this process we have so far produced \(~3\) mol-H\(_2\)/mol of acetate. Linking this process with fermentation of sugars could produce \(8-9\) mol-H\(_2\)/mol-glucose, at an energy cost of one mole of hydrogen.

In order to examine hydrogen production from other sources of organic matter, we developed a specially constructed reactor to provide high surface areas at the anode for bacterial growth (Figure 1). The reactor had the anode and cathode chambers directly adjacent to each other, separated by a proton exchange membrane (PEM; Nafion\textsuperscript{TM} 117; Dupont Co., USA; projected surface area of 11.4 cm\(^2\)). Each chamber (292 mL capacity) contained an electrode (projected surface area of 26.5 cm\(^2\)) placed 1.8 cm from the PEM. The anode was filled with graphite granules (total volume of 131 mL; Product 100, Graphite Sales, Inc., Chagrin Falls, OH) to increase the surface area of the anode and proximity of the anode to the PEM. The cathode was carbon paper with a Pt loading on one side of 0.5 mg/cm\(^2\) (A-3 EFCG; De Nora North America, Somerset, NJ). Copper wire was attached to the electrodes and all exposed metal surfaces were sealed with a nonconductive epoxy (Dexter Corp., NJ).

To demonstrate that electricity production is possible from any biodegradable organic matter, we tested the system using domestic wastewater. During start up, the system was operated as a MFC (with oxygen at the cathode) before it was switched over to BEAMR mode by flushing the cathode chamber with nitrogen gas, and then adding voltage using an external power source. Wastewater was obtained from the effluent of the primary clarifier of the Pennsylvania State University Wastewater Treatment plant, and amended with phosphate buffer solution (PBS) containing: 4.09 g/L Na\(_2\)HPO\(_4\) and 2.54 g/L NaH\(_2\)PO\(_4\), (pH = 7.1).

![Figure 1. Two-chambered acrylic BEAMR reactor shown with the anode chamber filled with granules.](image-url)
Results and Discussion

Hydrogen was successfully produced using the BEAMR process even with a complex waste organic matter source such as domestic wastewater. The minimum applied potential required for hydrogen production in the cathode chamber was found to be 0.23 V. Current density was variable and low with only a plain carbon electrode in the anode chamber. However, by adding graphite granules into the anode chamber we were able to increase the current density produced in proportion to the applied voltage. We achieved a maximum Coulombic efficiency of 26% (i.e. this is the percent recovery of all possible electrons based on the COD of the wastewater) and a hydrogen recovery of 42% (recovery of hydrogen based on the measured current).

The system successfully removed organic matter, as shown by removal efficiencies evaluated in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and dissolved organic carbon (DOC) in the range of 87 to 100%. The final BOD of the treated wastewater was always reduced to less than 7.0±0.2 mg/L at detention times (fed batch mode) between 26 and 116 hr (depending on applied voltage).

The overall hydrogen production based on COD removal was a maximum of 0.019 mg-H₂/mg-COD, with an energy requirement of 0.012 mg-H₂/mg-COD. In Table 1, we compare the hydrogen recovery performance with that previously obtained in another reactor system using acetate as the substrate [5]. As can be seen in this table, the overall yield with wastewater is lower than that obtained with acetate. However, this is consistent with our findings for electricity generation with pure compounds versus more complex substrate such as human and animal wastewaters. We have found greater Coulombic efficiencies and power densities with these pure compounds than with wastewaters, likely as a result of the presence of soluble electron acceptors in the wastewaters.

Table 1. Comparison of hydrogen production yields obtained using wastewater, with those previously obtained using acetate as reported by Liu et al. [5].

<table>
<thead>
<tr>
<th>Factor</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetate</td>
</tr>
<tr>
<td>Yield- mol-H₂/mol-S</td>
<td>2.9</td>
</tr>
<tr>
<td>- mg-H₂/mg-COD</td>
<td>0.091</td>
</tr>
<tr>
<td>Energy need: mol-H₂</td>
<td>0.5</td>
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<tr>
<td>mg-H₂</td>
<td>1</td>
</tr>
<tr>
<td>Efficiency:</td>
<td></td>
</tr>
<tr>
<td>mg-H₂ produced / mg-H₂-required</td>
<td>5.8</td>
</tr>
</tbody>
</table>

*Based on maximum yield

These results demonstrate that it is possible to generate hydrogen from waste biodegradable organic matter. However, a comparison of the yields produced using acetate and domestic wastewater suggest that specific waste streams will need to be examined to evaluate their potential for hydrogen production. In addition, the current hydrogen yields from wastewaters are low, and therefore need to be improved to make this BEAMR process feasible for converting algae or photosynthetic bacterial biomass into hydrogen gas. However, these results do show that this organic matter electrolysis process is not limited to sugars or fermentation end products.

It is important to note that waste biomass from agricultural operations can also be used in this process to generate hydrogen. Our group has recently shown that MFCs can be used to generate electricity from the steam-exploded corn stover hydrolysates [4]. Thus, it should be possible to generate hydrogen gas from this agricultural waste material as well as from other materials. Taken together, these results demonstrate a route for hydrogen production using bacteria and biomass in a manner that could allow for distributed hydrogen production from a variety of organic matter sources.
References