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Hydrogen production from switchgrass via an integrated pyrolysis–microbial electrolysis process

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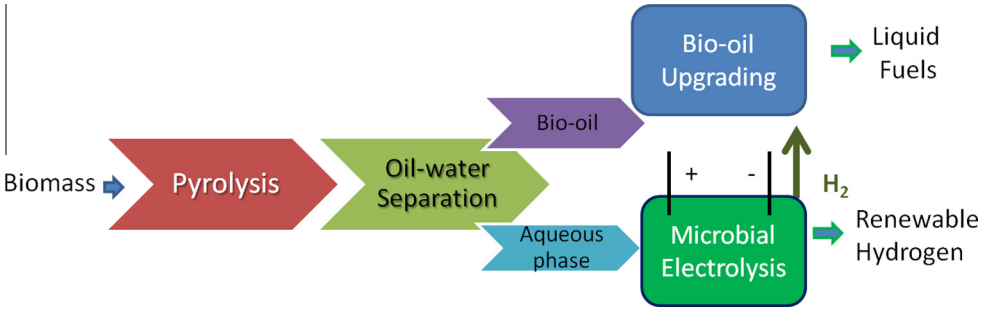
HIGHLIGHTS

- Demonstrated conversion of switchgrass-derived bio-oil aqueous phase to hydrogen.
- Enriched anode community capable of simultaneously converting inhibitory compounds.
- Achieved hydrogen production rate of 4.3 L H_2/L-day using biomass-derived liquids.
- Long-term operation with high Coulombic, conversion and overall energy efficiencies.

GRAPHICAL ABSTRACT



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ABSTRACT

A new approach to hydrogen production using an integrated pyrolysis–microbial electrolysis process is described. The aqueous stream generated during pyrolysis of switchgrass was used as a substrate for hydrogen production in a microbial electrolysis cell, achieving a maximum hydrogen production rate of 4.3 L H_2/L anode-day at a loading of 10 g COD/L-anode-day. Hydrogen yields ranged from 50 ± 3.2% to 76 ± 0.5% while anode Coulombic efficiency ranged from 54 ± 6.5% to 96 ± 0.21%, respectively. Significant conversion of furfural, organic acids and phenolic molecules was observed under both batch and continuous conditions. The electrical and overall energy efficiency ranged from 149–175% and 48–63%, respectively. The results demonstrate the potential of the pyrolysis–microbial electrolysis process as a sustainable and efficient route for production of renewable hydrogen with significant implications for hydrocarbon production from biomass.

1. Introduction

Sustainable hydrogen supply and water management are the two most significant sustainability issues facing biorefinery development. Production of transportation fuels from biomass via pyrolysis enables production of hydrocarbon fuels, making it a high priority alternative for biorefineries. However, due to the high oxygen content of biomass, significant amount of hydrogen is needed for deoxygenation and generation of fuel hydrocarbons. The ability to produce hydrogen from biomass or biomass-derived streams can significantly reduce the greenhouse gas emissions released by use of natural gas as a hydrogen source. Production of hydrogen from natural gas contributes 18% to capital costs via the thermochemical route converting biomass to fuels (Jones et al., 2013). Biomass used for pyrolysis typically contains 20% moisture or more resulting in a water-rich bio-oil from the

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pyrolysis process. Fast pyrolysis and intermediate pyrolysis generate a bio-oil product which is essentially a mixture of aqueous and organic phases. Separation of the bio-oil for fuel production produces large amounts of aqueous phase containing organic carbon from biomass. A bio-oil derived from switchgrass was reported to contain over 70% aqueous phase (Imam and Capareda, 2012). If the carbon from the aqueous phase is not recovered, a significant fraction of biomass and energy is lost to the water phase, decreasing the overall efficiency of the process.

Production of renewable hydrogen from biomass is a long-sought technology for moving away from fossil fuels and towards a low-carbon economy. Microbial electrolysis is a versatile technology capable of addressing the issue of hydrogen production as well as water management (Logan et al., 2008). By extracting energy from the aqueous stream in the form of hydrogen and treating water, the efficiency of biomass to fuel production can be increased by minimizing external hydrogen requirement and enabling water recycling (Borole, 2011). Previous work on bioanode development has resulted in a highly enriched anode consortium using the waste stream from ethanol fermentation, capable of converting furan aldehydes, phenolics, and other normally inhibitory compounds (Borole et al., 2009d, 2013). Optimization of electroactive biofilms to handle complex wastewater streams requires a multipronged approach that includes process, system design and biology parameters (Borole et al., 2011b; Sleutels et al., 2012). Recent advancements in understanding of the electrochemical performance of anode biofilms and the dependence of the enrichment process on organic loading, continuous vs. batch substrate delivery and other parameters have led to current densities reaching above 20 A/m^2 (Ichihashi et al., 2014; Sleutels et al., 2012).

In this study, we report conversion of the complex mixture of organics present in the bio-oil aqueous phase (boap) derived from biomass pyrolysis containing phenolic compounds, furan aldehydes, organic acids and sugar derivatives in an MEC to produce hydrogen. This mixture is overall more recalcitrant than the fermentation stream previously utilized in bioanode (Borole et al., 2013). The development of an electroactive microbial community capable of handling the toxic compounds and generating hydrogen using a switchgrass pyrolysis-derived aqueous phase is reported. The composition of the microbial community developed for treatment of boap is described. The efficiency of conversion in the anode as well as cathode, and overall hydrogen production efficiency and productivity and their reproducibility in replicate experiments in two different MECs is reported.

2. Methods

2.1. Biomass pyrolysis

The feedstock used in the study was air-dried switchgrass with particle sizes less than 2 mm and a moisture content of 7–8 wt%, which was obtained from Genera Energy Inc. (Vonore, TN). A semi pilot auger pyrolysis system was used in this study to carry out intermediate pyrolysis. The system was equipped with a feeding system, an auger pyrolysis reactor, a biochar collector, a particle-precipitating chamber, and a condensation section (Supplemental Fig. S1). A detailed description of the pyrolysis system used in this study, (located at the Center for Renewable Carbon, University of Tennessee), is provided elsewhere (Kim et al., 2011). In brief, the bio-oil used in this study was produced under the following operation conditions. The feedstock was transferred from the feeding hopper to the pyrolysis reactor by a single auger with feeding rate of approximately 8.5 kg/h. The pyrolysis reactor (10 W × 10 H × 250 L cm) contains internal dual augers. The auger speed controlled the residence time of feedstock at 72 s. The heated zone comprised of a 200 cm long electrical resistance furnace operating at 500 °C. The sweeping gas (nitrogen gas, 20 L/min) was introduced into the front of the auger reactor and moved with the evolved vapors to the condensation section. Before the vapors enter the condensers from the auger reactor, the particle chamber (20 cm in diameter and 100 cm long) precipitated fine particles from the vapors. The biochar produced from the feedstock was collected into the biochar drum. The condensation section comprised of three condensers in series (10 cm in diameter and 200 cm long, each). Before the pyrolysis operation, all condensers were cooled to 10–15 °C using a circulation water cooling system. The bio-oils collected from three condensers were immediately combined and mixed for homogeneity and stored in the walk-in freezer until used for characterization. The pyrolysis operation was performed in duplicate.

2.2. Bio-oil separation and characterization

The crude bio-oil obtained from the pyrolysis reactor was mixed with distilled water in a ratio of 1:4 (wt.%) to separate bio-oil aqueous phase (boap: water soluble fraction) and an organic phase (water insoluble fraction). The mixture was shaken vigorously and placed at 4 °C overnight. Then the mixture was centrifuged in an IEC Clinical centrifuge (model 120) at 5000 rpm for 30 min to ensure the phase separation. The boap was collected and weighed to determine the amount of bio-oil dissolved in the water. The separated aqueous phase (boap) was used for hydrogen production in the MEC system.

The chemical compounds in boap were identified by gas chromatography-mass spectrometry (GC–MS) and quantified by GC-flame ionization detector and high performance liquid chromatography (HPLC). A Shimadzu GC–MS (QP2010S) with a Restek Rtx-5MS capillary column was used. The column was programmed at 45 °C for 3 min, then at 5 °C/min to 150 °C without holding, then 10 °C/min to 260 °C and a hold time of 7 min. The inlet was set at 240 °C, and sample injection was made in split mode (1:20). The compounds were identified by comparing their mass spectra with those from the National Institute of Standards and Technology (NIST) mass spectral data library. Due to the very high water content in the boap, organic compounds were first extracted by ethyl lactate and chloroform and then analyzed by GC–MS. The crude bio-oil was diluted a factor 20 times before being injected into the GC–MS.

GC–FID with a HP-5 column was used for quantifying volatile compounds in boap. The same program with the GC–MS was used in GC–FID. A HPLC system (Jasco 2000Plus, Jasco analytical instruments) equipped with PU-2089S Plus pump, a MD-2018 Plus Photodiode Array detector (PDA), a RI-2031 Plus intelligent RI detector, and an AS-2055 Plus auto sampler was used to analyze boap for non-volatile compounds. The liquid chromatography was conducted at 50 °C using Bio-rad HPX-87H (300 × 8 mm) column. The volume of injected sample was 20 μl. The mobile phase was 5 mM H_2SO_4 with or without 15% acetonitrile (v/v) with a flow rate of 0.6 mL/min. The method using 15% acetonitrile was used primarily to ascertain elution of all peaks from the column and to determine appropriate run time. The use of acetonitrile posed a problem with quantification of organic acids; therefore a method without acetonitrile was used with a longer run time of 120 min.

2.3. MFC and MEC construction

The bioelectrochemical system used in this study consisted of a two-chamber cell that was convertible between MFC and MEC. The anode consisted of a carbon felt (projected surface