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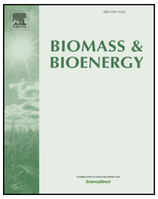

Research paper

Hydrogen production from pine-derived catalytic pyrolysis aqueous phase via microbial electrolysis

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ABSTRACT

Microbial electrolysis of an aqueous phase generated from catalytic pyrolysis of pine sawdust was investigated for renewable hydrogen production. The microbial electrolysis cell (MEC) performance was investigated at an organic loading rate ranging from 2 to 50 g/L-day. A maximum hydrogen productivity of 5.8 ± 0.18 L/L-day was obtained, however, the productivity increased linearly only up to a loading rate of 10 g/L-day. The highest current density achieved was 6.8 ± 0.1 A/m^2. The efficiency of conversion of the substrate to current in the anode decreased with increasing loading, but the initial maximum Coulombic efficiency was 98 ± 0.04%. The cathode efficiency, on the other hand, increased with loading up to a maximum of 89 ± 1.4%. Total hydrogen recovery was relatively constant for most runs at 30%, which is equivalent to an yield of 0.6 moL H_2/mole COD, except at the highest loading rate. The operation of the MEC under batch mode, however, resulted in a higher hydrogen recovery of 63 ± 4%. The conversion of a wide range of compounds, including carboxylic acids, anhydrosugars, furanic and phenolic compounds present in the aqueous phase is reported. The results demonstrate potential for hydrogen production from a waste stream which can improve the total biofuel or energy yield of the biorefinery.

1. Introduction

Microbial electrolysis is an upcoming technology which generates hydrogen from waste organic matter. The anode uses a microbial catalyst to break down the organic matter into electrons and protons, which are then combined at the cathode via application of an external voltage, to generate hydrogen. Microbial electrolysis cells (MECs) have been used to treat a number of waste streams [1–5] generating hydrogen and potentially a cleaner water stream which can be reused or recycled [6,7]. Most studies use simple waste streams or simulated streams containing acetate as the feed. However, the number of studies using complex industrial waste streams has been rising steadily. For enabling commercialization of the MEC technology, utilization of real waste streams has to be demonstrated. These streams can contain complex organic matter requiring one or more break down steps to generate the substrate for exoelectrogenesis, which is usually acetate. Typical methods such as hydrolysis and/or fermentation are necessary to break down complex organic matter into substrates for exoelectrogens. Rezaei et al. used enzymatic hydrolysis to depolymerize cellulose in the bioanode [8]. Another study used a two-step fermentation prior to exoelectrogenesis to convert recalcitrant lignocellulosic materials into hydrogen [9]. Ki et al. have used a pulsed electric field to degrade primary sludge to improve energy recovery from a sludge stream [10]. More recently, the use of integrated systems or single reactors to achieve conversion of complex organic matter into electrons has been reported [2,11,12]. The MEC technology has made steady progress in achieving high productivity and efficiency in converting simple as well as complex substrates [5,13,14]. A maximum hydrogen production rate of 50 L/L-day has been reported with acetate [15], while up to 11.7 L/L-day has been reported using complex substrate mixtures [16,17]. Maximum hydrogen recovery from acetate in MECs has been reported to be 91% [18], while that using complex substrates has ranged from 10 to 77% [11,14].

Biomass can be a potential source of complex substrates for MEC.

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One of the pathways for conversion of biomass to advanced biofuels is via catalytic pyrolysis [19]. The process generates two liquid products, an aqueous and an organic fraction. The organic phase is a bio-oil, which is hydrotreated to generate hydrocarbon fuels and the aqueous phase is typically treated as a waste, since it cannot be used for fuel production [20]. However, this catalytic pyrolysis aqueous phase (CPAP) can contain up to 20% of the carbon fed into the pyrolysis process [21]. Thus, valorization of the CPAP can lead to improved economic feasibility for the process. Use of an aqueous phase from intermediate pyrolysis has been reported previously [14], however, the use of CPAP in an MEC has not been reported in the literature to the best of our knowledge. Other reports on use of biomass and biorefinery waste streams with high chemical oxygen demand (COD) as a source of renewable hydrogen production also exist [13] [9] [14,22], [23]. The reports indicate potential for this technology to serve as an important contributor in renewable hydrogen production from biomass. For enabling use of solid biomass as a feedstock in MEC, its liquefaction or extraction into an aqueous phase is necessary. This can be achieved thermochemically or biochemically, using pyrolysis or enzymatic hydrolysis, respectively. In the latter approach, lignin is usually separated as a solid fraction and represents another waste stream, however, in the pyrolysis approach, it is transformed into a bio-oil which serves as a substrate for production of hydrocarbon fuels. The pyrolyzed carbohydrates associated with the bio-oil are highly water soluble and remain associated with the aqueous phase, either emulsified with the bio-oil or resulting in a separate aqueous phase. During catalytic pyrolysis, oxygen is partly removed from the biomass as water, which results in separation of an aqueous phase containing depolymerized carbohydrates and their degradation byproducts [24], while thermal fast pyrolysis results in a single product which is an emulsified oil containing water soluble compounds [25]. This emulsified bio-oil can be separated into aqueous and organic fractions [26] or utilized wholly for biofuel production [27]. Utilization of the separate aqueous phase generated via thermal fast pyrolysis of switchgrass in a MEC was recently demonstrated [14]. This aqueous phase contained a wide range of compounds including carboxylic acids, alcohols, aldehydes, ketones, sugar derivatives, furanic and phenolic compounds [25]. The aqueous phase generated via catalytic pyrolysis contains a larger fraction of phenolic compounds which have been reported to be inhibitory to certain exoelectrogens [28]. The concentration at which inhibition becomes a problem is relatively high (> 0.8 g/L), thus, dilute streams can be processed in MEC with minimal inhibition as demonstrated for aqueous streams derived from switchgrass within a recycle loop [11].

Steam reforming of pyrolysis aqueous phase has been reported extensively in the literature using chemical catalysts. In comparison to microbial electrolysis which is also a form of reforming occurring at ambient temperatures, the catalytic steam reforming requires much higher temperatures in the range of 650 °C–750 °C [29,30]. Coking is a significant issue at lower temperatures (~ 600 °C) and can lead to catalyst deactivation within a few hours [24,29,31]. Single substrate studies show that levoglucosan, guaiacol and furans have high tendency to form coke [32]. Furthermore, simpler molecules such as acetic acid are also affected by the other molecules reducing conversion in the presence of the other substrates [31]. A recent study by Paasikallio et al. reported high yields of hydrogen at 650 °C using pyrolysis aqueous phase from fast pyrolysis of pine sawdust, however, the experiments only studied a short run time of 2 h [24]. Developing a catalyst capable of minimizing coking and extending half-life as well as achieving high process and energy efficiency are challenges that this technology has to overcome to enable commercialization.

The work described here investigates hydrogen production via microbial electrolysis from a catalytic pyrolysis aqueous phase (CPAP) generated from pine sawdust. The conversion of various classes of compounds, including carboxylic acids, anhydrosugars, furanic and phenolic compounds present in the CPAP was studied. In addition, characterization of effluent streams obtained from MECs treating switchgrass-derived bio-oil aqueous phase (BOAP) was also conducted to compare with the CPAP results. The performance of the MEC is reported in terms of current density, anode and cathode efficiency and hydrogen productivity. Utilization of the aqueous phase for hydrogen production can minimize the loss of carbon and energy and reduce the need for hydrogen sourcing via fossil fuels.

2. Materials and methods

2.1. Catalytic pyrolysis of pine sawdust

The feedstock for catalytic pyrolysis was pine sawdust, which was processed in VTT's 20 kg/h circulated fluid bed (CFB) pyrolysis pilot unit. The experiments generated a separate aqueous phase, which was collected and provided by VTT/Pacific Northwest National Laboratory to Oak Ridge National Laboratory. The details of the catalytic pyrolysis experiments have been reported previously [33]. Briefly, a HZSM5 catalyst was used in a catalytic fluidized bed reactor unit operating at 520 °C. The catalyst to biomass ratio was 7:1 wt basis. The aqueous product was separated from the organic phase after the experiment [33].

2.2. MEC construction and experimental setup

Two replicate MECs were constructed using Lexan and PVC enclosures with anode and cathode volumes of 16 ml each and a projected area of 12.56 cm^2. Carbon felt was used as the anode material and Pt-deposited carbon was the cathode material. Nafion 115 was used as a membrane separator between the anode and cathode chambers, with the catalytic carbon pressed on to it on the cathode side. A carbon rod and stainless steel wire were used as current collectors in the anode and cathode chambers, respectively. Additional details of the MEC construction are reported elsewhere [11].

2.3. Bioanode development

An anode biofilm developed previously using a bio-oil aqueous phase (BOAP) generated from pyrolysis of switchgrass as the substrate was used in this study [14]. It was acclimated to the CPAP for a period of three weeks with addition of substrate at an organic loading rate of 2 g/L-day. The process included a change of the nutrient medium when the MEC effluent cell density increased above an optical density of 0.05, measured at 600 nm as reported previously [34]. During the change of the anode medium, the anode chamber was flushed with freshly prepared, nitrogen-sparged nutrient medium to remove planktonic cells, and enrich an electroactive biofilm as described previously [34,35]. After the acclimation period, the experiments to determine the effect of loading rate and other parameters were conducted under continuous and batch operation conditions.

2.4. Continuous and batch MEC operation

The MEC anodes utilized a flow-through design, with the anode liquid continuously recycled via a feed reservoir [11]. Two types of substrate delivery conditions were studied: continuous substrate delivery and fed-batch addition. For the former experiments, the organic loading rate was studied over the range of 2–50 g COD/L-anode volume per day. The substrate was added via a syringe pump into the flow line entering the anode (Fig. 1). These experiments lasted from 24 to 48 h, after which liquid samples were taken from the anode reservoir to determine residual COD and individual compound concentrations via high pressure liquid chromatography (HPLC). The hydrogen gas was collected in the cathode chamber connected to an inverted cylinder filled with water, such that the water column exerted a slight negative pressure on the cathode chamber connected to the cylinder headspace to facilitate hydrogen collection. The anode liquid was recirculated at a