



Electrochemical reforming of ethylene glycol. Influence of the operation parameters, simulation and its optimization



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ABSTRACT

A compact pure hydrogen production process was developed based on the electrochemical reforming of ethylene glycol–water mixtures by using a low temperature proton exchange membrane (PEM) electrolysis cell. A bimetallic 40% Pt–20% Ru carbon based anode and a 20% Pt carbon based cathode were used for the PEM electrochemical reforming experiments. The main operation parameters (applied current, feed stream flow rate, concentration and temperature) were experimentally studied and optimized to enhance the hydrogen production rate. As a result and based on the experimental data, a complete integrated process was proposed and simulated by Aspen HYSYS software. Considering the energy requirements of the different units of the process, an energetic evaluation of the whole system was carried out by integrating the experimental current–potential data. Thus, material and energy balances of the overall process have been calculated for each of the possible current–working conditions. Hence, the optimal operating conditions, which led to the highest energetic efficiency of the system (57%) were attained at a current density of 0.08 A/cm², leading to a total energy consumption of 17.14 kWh kg^{−1}H₂. The analysis presented in this paper also offers a better understanding of the characteristics of a PEM electrochemical plant for hydrogen production.

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1. Introduction

Nowadays, hydrogen could be considered as the most promising energy carrier, providing a clean, reliable and sustainable energy system. It could offer an answer to the threat of global climate change and avoid undesirable issues associated with the use of fossil fuels [1]. Traditional processes for hydrogen production are the catalytic steam reforming of natural gas, light hydrocarbons and naphtha, or the gasification of coal to yield syngas followed by water gas shift conversion [2,3]. However, these processes lead to the production of a mixture of H₂ and carbon derived products (CO and CO₂) under high reaction temperature conditions (above 600 °C). Further separation and purification steps are required in order to obtain high quality hydrogen for electrical energy production in fuel cells. It would complicate the design of a compact production process and increase the final price of the obtained hydrogen.

In the last years, the electrochemical reforming of water–alcohol mixtures has gained much attention vs. chemical catalytic routes for hydrogen production since it allows the quick production of pure hydrogen in a single reaction/separation step, by typically using a proton exchange membrane cell [4–9]. The electrochemical reforming process of water–alcohol mixtures is based on the use of electrical power to split the chemically-bonded species by the electro-oxidation of the

alcohol fuel to protons on the anode catalyst–electrode of the cell. The protons are then transported through the proton exchange membrane (PEM) to the cathode of the cell leading for the simultaneous production and separation of hydrogen. In fact, recent studies have shown promising results regarding the electrochemical reforming (also called electro-reforming) of water–alcohol mixtures, i.e., methanol [4–7], glycerol [8,9], ethanol [10–12] and bioethanol [13] at atmospheric pressure. These studies have allowed to establish some comparisons between the upgrading of alcohols and bio-alcohols towards the hydrogen production and the conventional catalytic routes (steam reforming or partial oxidation). In this sense, the former requires lower reaction temperatures (typically below 100 °C) and leads to the production of pure hydrogen at the cathode compartment of the cell, which is automatically separated from the other reaction products. In addition, this technique for hydrogen production presents several advantages with respect to the water electrolysis process, such as lower power electricity demands, since part of the energy required is provided by an organic molecule (alcohol). Furthermore, this process is compatible with renewable energy technologies and can be used to adjust/store electrical energy consumption and demand via H₂ production. However, most of the previous studies of electrochemical reforming [4–10,13] have only been focused from a fundamental point of view in lab scale PEM electrolyzers. In fact, a unique work aimed on developing alcohol electro-reforming beyond the lab scale using methanol PEM stacks electrolyzer could be found [14]. Then, more applied research would be required in order to critically evaluate the real interest of this kind of systems.

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The aim of the present work was to go a step forward respect to previous studies, designing, simulating and optimizing the full electrochemical reforming of a biomass derived compound, i.e., ethylene glycol process. Ethylene glycol (EG), which can be produced from biomass by acid hydrolysis, would be a promising hydrogen carrier since it is less toxic and inflammable and also possesses relatively high theoretical energy density than other alcoholic molecules such as methanol [15]. The production of hydrogen from bio-renewable organic sources coupled with renewable electrical energy (Fig. 1), being a very interesting technique to produce bio-hydrogen in a sustainable way. The influence of the main operation parameters in a 6.25 cm² PEM lab scale single electrochemical reforming cell has been experimentally investigated for the first time in this work. Moreover, taking into account its practical application of the suggested process, a compact hydrogen production plant based on this technology was proposed and simulated using the steady state Aspen HYSYS software. By coupling the experimental data with the energy requirements calculated for the different units of the process, an energetic evaluation of the whole system was also carried out.

2. Experimental

2.1. Design and operation of the lab scale PEM electrochemical-reforming unit

The preparation of the membrane electrode assembly (MEA) of the PEM electrochemical reforming unit as well as the experimental setup were described in our previous study [10]. A bimetallic alloy of Pt/Ru (40% Pt–20% Ru/C-Alfa Aesar) and Pt (20% Pt/C-Alfa Aesar), both supported on carbon, were used as the anode and cathode electrodes, respectively. These catalysts showed a good performance in the electro-reforming of alcohol–water solutions [10]. For the preparation of each electrode in first place a catalyst ink was prepared by mixing the commercial catalyst powder with Nafion solution and isopropanol to achieve a metal loading of 3 mg/cm² for the anode, and 0.5 mg/cm² for the cathode. The high metal loading used for the anode ensures suitable electrocatalytic activity of the system for electrochemical reforming of alcoholic molecules [4–10]. However, a further metal loading optimization should be done in view of practical applications. The geometric surface area of both electrodes was 6.25 cm². A proton conducting Sterion membrane of 185 mm thickness (Hydrogen Works) was used as the electrolyte. The MEA was prepared by hot-pressing, under 1 metric ton at 120 °C for 3 min.

The anode compartment of the cell was fed by ethylene–glycol (Panreac Synthesis) water solutions of different concentrations (1–8 M), i.e., EG/water molar ratio (0.02 to 0.26) under a constant

flow rate between 1 and 5 ml/min. Water was supplied to the cathode with the same anode flow rate in order to maintain the humidity of the membrane and the PEM operation was limited below 90 °C and atmospheric pressure [16,17]. Constant potentials and currents were applied to the cell via a DC power supply (DELTA ELEKTRONIKA POWER SUPPLY ES 015–10). The produced hydrogen flow rate was also followed by gas-volume measurements and crosschecked via Faraday's Law calculations (based on the cell current). This demonstrated that practically 100% of the applied electrical energy was used for H₂ production. At this point, it should be mentioned that H₂ was the unique gaseous product detected in the cathode compartment; i.e., no CO and/or CO₂ were found out in this cell side.

2.2. Electrochemical reforming process simulation with Aspen HYSYS

A compact hydrogen production process was proposed and simulated using the steady state Aspen HYSYS (AspenTech V.7.1) software. The simulations were performed under steady state conditions based on the experimental study developed in Section 2.1. The Peng–Robinson equation was used to calculate the thermodynamic properties of each flow stream. For the simulation and optimization of the electrochemical reforming process, the operating conditions of the electrochemical reforming unit were obtained from the previous experimental study. It is important to note that, due to the absence of an electrochemical reforming PEM reactor unit on the data base of the simulation software, it was modeled as a conversion reactor together with a split separation unit where the produced hydrogen is completely separated from the reaction mixture by the imposition of electrical energy. The electro-oxidation of EG on Pt–Ru anode can produce several two-carbon intermediates and products: glycolaldehyde, glyoxal, glyoxylic acid, oxalic acid and glycolic acid, being the latter one of the most important [18, 19]. In this work, glycolic acid (GA) was assumed to be the unique product from the EG electro-oxidation, due to the similarities in the physical and chemical properties of all these compounds, according to the following anodic reaction:



Pure H₂ was produced at the cathodic compartment of the cell as follows:



Hence the overall reaction of the process is:

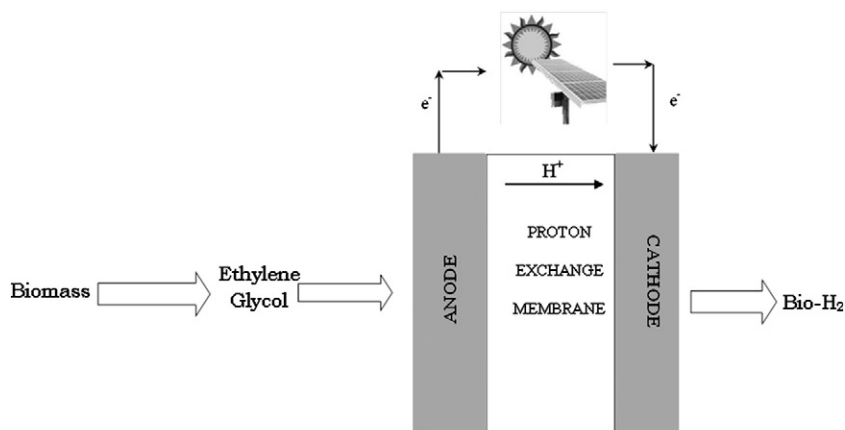


Fig. 1. Schematic representation of renewable production of hydrogen from EG.

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