

## Electrochemical reforming vs. catalytic reforming of ethanol: A process energy analysis for hydrogen production



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### ARTICLE INFO

#### Article history:

Received 11 February 2015

Received in revised form 11 May 2015

Accepted 13 May 2015

Available online 15 May 2015

#### Keywords:

H<sub>2</sub> production

Ethanol

Electrochemical reforming

Catalytic steam reforming

Simulation

### ABSTRACT

This work reports an energetic analysis for hydrogen production via catalytic steam and electrochemical ethanol reforming processes. For both systems, a complete flow diagram process was proposed and simulated by Aspen HYSYS according to literature data. Besides hydrogen, other byproducts such as acetaldehyde (electrochemical reforming) and ethylene and methane (catalytic reforming) were also considered. The energy requirement of the different process units was calculated according to the operating parameters. Just process energy (thermal energy and electrical energy) consumption was considered in the study of the steam reforming whereas both energy process and electrical energy consumption were considered in the study of the electrochemical reforming. Material balances revealed electrochemical reforming to present higher hydrogen yields. (0.0436 vs. 0.0304 kg H<sub>2</sub>/kg C<sub>2</sub>H<sub>5</sub>OH of the classical catalytic reforming). In addition to its higher simplicity, simulation results showed a lower energy consumption in the H<sub>2</sub> production by the electrochemical approach (29.2 vs. 32.70 k Wh/Kg of H<sub>2</sub>). These results demonstrated the interest of the electrochemical reforming of ethanol to obtain high purity hydrogen in a single reaction/separation step, thereby representing an interesting alternative to classical catalytic reforming.

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### 1. Introduction

Hydrogen is one of the most important raw materials in the chemical and petrochemical industries. Furthermore, it could also be considered as an attractive energy carrier with a reduced environmental impact [1]. Then, it can offer an answer to the threat of global climate change and avoid undesirable issues associated with the use of fossil fuels [2]. Hydrogen does not exist in nature in a form that can be collected and consumed but it can be currently produced by a number of processes such as natural gas or biogas reforming [3], gasification of coal and biomass [4,5], water electrolysis [6], photoelectrolysis [7] and biological processes [8]. Traditionally, large-scale production of hydrogen is mainly based on the methane reforming process. However, this pathway has a non-renewable nature as methane is mainly obtained from natural gas. Furthermore, together with hydrogen, other carbon derived products such as carbon monoxide and carbon dioxide are formed as side products. In this sense, there is a growing interest in

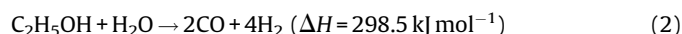
the search for effective alternatives to produce hydrogen from renewable sources. In this regard, ethanol is very attractive because of its relatively high hydrogen content, broad availability, non-toxicity, secure storage and handling. In addition, it can be obtained from the fermentation of biomass [9].

The catalytic steam reforming of ethanol is an endothermic process that requires external heat input:



which could be supplied from external sources in order to maintain the system at a steady reaction temperature. Heat can also be supplied externally by the combustion of part of the feed, by burning combustible off gases or by a combination of both processes.

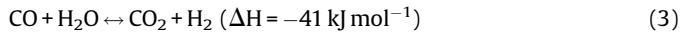
Additionally, the ethanol-steam mixture is catalytically converted to carbon monoxide according to the following reaction:



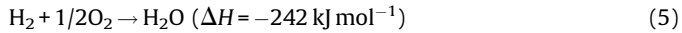
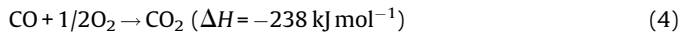
Hydrogen production via catalytic reforming of ethanol involves two more additional steps aimed at reducing the concentration of CO below the stringent levels required by hydrogen fuel cells operating downstream: the water gas shift

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reaction (WGS, Reaction (3)) and CO preferential oxidation reaction (COPROX, Reaction (4) and Reaction (5)). WGS (Reaction (3)) is an important step in which CO is generally oxidized to CO<sub>2</sub> in excess steam:

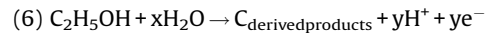


In the COPROX process, the following reactions occurs in the gas phase:

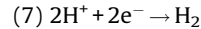


The final step is the purification of the hydrogen from the gas stream exiting the COPROX process, which can be accomplished using several techniques. The most common methods are: pressure-swing-adsorption (PSA) to separate CO<sub>2</sub> followed by the condensation of the remaining H<sub>2</sub>O, PSA to separate H<sub>2</sub>, and membrane separation of H<sub>2</sub> [10]. Consequently, production of high purity hydrogen by catalytic ethanol reforming is a complicated process including several reaction and separation steps. A novel process based on ethanol electrooxidation (also called electrochemical reforming of ethanol) has recently attracted great interest since it allows the simultaneous production of pure hydrogen and accomplished its separation in a single step. In addition, the separation in a single-step of the reaction product from the reaction chamber shifts the reaction equilibrium to the right and thus, higher yields are achieved. This process is based on a low temperature proton exchange membrane (PEM) reactor configuration, consisting on a membrane electrode assembly (MEA) formed by an anode/membrane/cathode, which allows simultaneous production and separation of hydrogen. Consequently, this technology allows to produce pure hydrogen in a quick and convenient way. In addition, this process can be used to store electrical energy via H<sub>2</sub> production [11]. Recent studies have shown very promising results when the electrolysis of water-alcohols mixtures proceeds. Thus, methanol [12–15], ethanol and bio-ethanol [11,16], glycerol [17,18] and ethylene glycol [19] have been successfully tested at lab scale. When compared to water electrolysis, the electrochemical reforming of organics can be carried out at significantly lower voltages, thus leading to a reduction of electricity consumptions. In the electrochemical reforming process, an ethanol–water mixture is supplied to the

anode cell. The electro-oxidation of ethanol is carried out by applying an electrical power, turning into the production of protons on the anode catalyst-electrode according to the following reaction:



The produced protons are selectively transported through the PEM membrane to the cathode compartment, which leads to the production of hydrogen:



This study aims to compare the energetic performance of two technologies for renewable hydrogen production via reforming of ethanol–water mixtures: electrochemical and catalytic ones. The performance of both processes was evaluated by material and energy balances performed using conditions reported in the literature. The energetic analysis was carried out by simulating these processes with Aspen HYSYS (Aspen Tech V.7.1). Finally, a comparative study of the two processes was performed in order to evaluate the yield and energy consumption in the production of hydrogen.

## 2. Methodology

The simulation of the catalytic steam reforming and electrochemical reforming of ethanol–water mixtures processes was performed under stationary conditions using the flowsheeting simulator Aspen HYSYS (AspenTech V.7.1). Peng–Robinson equation was used to calculate the thermodynamic properties of each flow stream. This equation of state is widely used in reforming processes of ethanol and thus, it was used in this work for comparison purposes [19,20]. The component list was restricted to C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>O, H<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> for the catalytic steam reforming [21–24] and C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>O, H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>O for the electrochemical reforming as experimentally confirmed [16]. The reaction conditions for the catalytic steam reforming of ethanol were taken from literature data for a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (1 wt.% metal loading) [21]. In the case of the electrochemical reforming of ethanol, catalysts based on Pt–Ru (40 wt.% Pt–20 wt.% Ru) and Pt (20 wt.% Pt), both supported on carbon, were used. The metal loading was of 1.5 mg cm<sup>-2</sup> and 0.5 mg cm<sup>-2</sup> for the Pt–Ru and Pt catalysts, respectively. As reported in literature, these metals have been typically used as the anode (Pt–Ru) and cathode (Pt) electrodes in electrochemical reforming reactors [19]. The

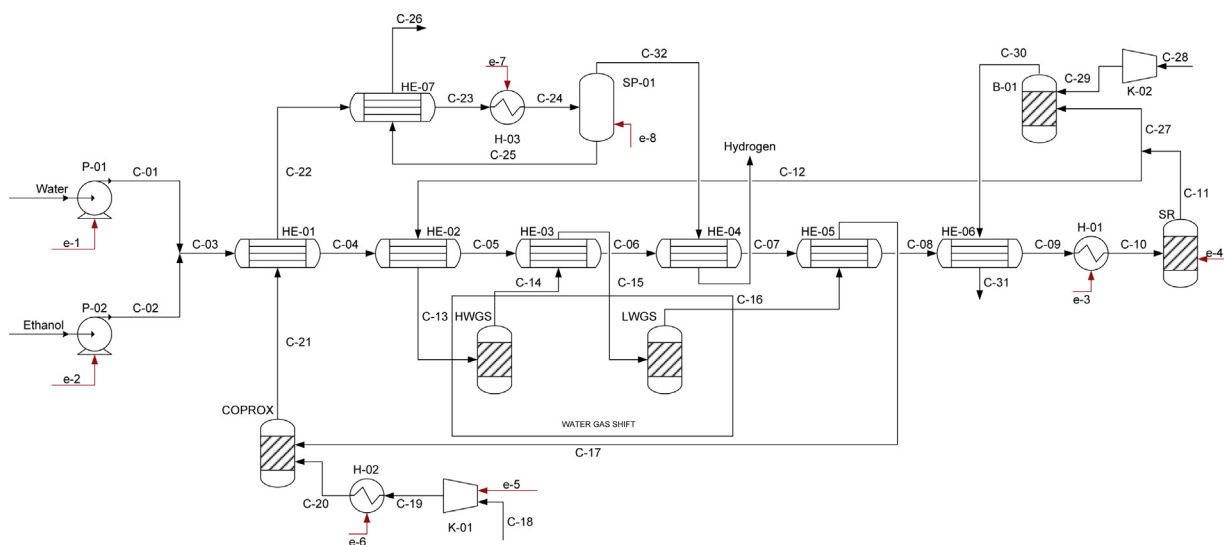


Fig. 1. Flow diagram of the catalytic steam reforming process of ethanol.

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