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An analytical and experimental investigation of high-pressure catalytic steam reforming of ethanol in a hydrogen selective membrane reactor[☆]

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ABSTRACT

The objective of this work was to explore the benefits of high-pressure steam reforming of ethanol for the production of hydrogen needed to refuel the high-pressure tanks of fuel cell (polymer electrolyte) vehicles. This paper reports on the potential efficiency benefits and challenges of pressurized reforming and options for dealing with the challenges; it reports the results from experiments in a micro-reactor, followed by a modeling study of the reactor to project the dependence of the hydrogen yields on process parameters. The experiments were conducted in the range of approximately 7–70 atm, 600–750 °C, steam-to-carbon molar ratios of 3–12, and gas hourly space velocities of 8500–83,000 per hour. By placing a hydrogen-transporting palladium-alloy membrane within the catalyst zone, this study quantified the beneficial effect of hydrogen extraction from the reforming zone. The model was used to explore the parameter space to define the reactor and conditions that would be needed to approach the efficiency targets for distributed hydrogen production plants. The results indicate that the tested catalyst was sufficiently active, and the hydrogen yield achieved with the experimental membrane reactor was limited by the low hydrogen flux of the tested membrane. The reactor model predicts that a membrane with at least 20 times higher flux than currently evaluated would be sufficient to generate hydrogen yields to match efficiency targets of 72%.

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1. Introduction

Light-duty fuel cell vehicles are being developed by many automobile manufacturers. One of the strategies for refueling these vehicles is to set up distributed hydrogen production facilities – small plants located at the refueling stations – that convert bio-derived liquid fuels, such as ethanol, to high-purity hydrogen. The hydrogen would then

be compressed and delivered to the fuel cell vehicle. Several hydrogen refueling facilities have already been set up to gather data and experience on their operation [1,2]. A popular hydrogen production pathway for the near-term is via the steam reforming of natural gas followed by pressure swing adsorption (PSA). These processes typically produce high-purity hydrogen at pressures of 10–20 atm (150–300 psi), which is subsequently compressed to 425 atm

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(6250 psi) and higher for filling the on-board vehicle storage tanks.

Compressing the hydrogen to the high pressures requires a considerable amount of electrical energy. Depending on the initial pressure at which the hydrogen is available for compression, and the efficiency of the process for producing the needed electrical energy, the compression energy requirement can represent a significant percentage of the lower heating value (LHV) of the delivered hydrogen. Fig. 1 shows the effect of the initial pressure of the available hydrogen on the energy required to compress the hydrogen to a dispensing pressure of 425 atm (~6250 psi). The compression energy, expressed as a percentage of the LHV of hydrogen, factors in a production and transmission grid electricity efficiency of 32.5% [3]. If the high-purity hydrogen exits the production plant at 1 atm, then its compression to 425 atm can consume close to 40% of the fuel's heating value. The non-linear slope of the curve reflects the fact that the energy requirement is a function of the ratio of final to initial pressure.

The energy requirement of compressing H₂ can be significantly reduced if the hydrogen can be produced at a high pressure. Unfortunately, processes that require compression of the initial feed are not good candidates for this argument, since the compression of the feed itself requires energy. Examples of such processes include systems where the fuel is gaseous (e.g., natural gas, biogas, etc.), or where air is needed for the reforming step (e.g., partial oxidation, autothermal reforming). However, the steam reforming of a liquid fuel, such as ethanol, offers promise since the energy required to pump in incompressible feeds – liquid fuel and water – into a heated and pressurized chamber is negligible and the reformat is then available at the high pressure.

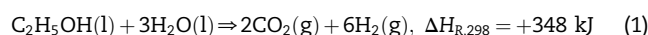
This work was undertaken to study the steam reforming of ethanol at elevated pressures. There is considerable information available in the literature on the steam reforming of ethanol, but these are mostly limited to ambient and low-pressure operations [4–13]. This paper investigates the effect of temperature, pressure, steam-to-carbon molar ratios (S/C) and the gas hourly space velocity (GHSV) on product yields in a membrane reactor where the hydrogen is extracted from the

reforming zone through a palladium-alloy membrane tube. The removal of hydrogen through a hydrogen transport membrane in the reforming zone will favor the equilibrium product distribution towards higher hydrocarbon conversion and hydrogen yields [13,14].

2. Theoretical basis

2.1. Stoichiometry, efficiency, and hydrogen yields

The steam reforming reaction for ethanol can be represented by the equation,

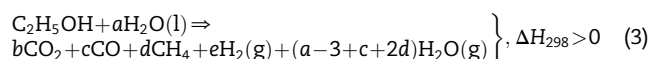


where the stoichiometry indicates that a maximum of 6 mol of hydrogen can be derived from the endothermic reaction that requires 348 kJ at 298 K. The efficiency (η) for the production of hydrogen from the above reaction can be defined as,

$$\eta = \frac{6 \Delta H_{\text{c,H}_2}}{\Delta H_{\text{c,C}_2\text{H}_5\text{OH}} + \Delta H_{\text{R}}} \times 100 \quad (2)$$

where, ΔH_{c} is the heat of combustion or lower heating value of hydrogen or ethanol (kJ/mol), and ΔH_{R} is the heat of reaction for the reforming reaction. The efficiency for this stoichiometric reaction equation, which also represents the theoretical maximum, is 91.7%. The efficiency loss, 8.3% or 132 kJ, is equal to the latent heat of vaporization of the feed water.

Practical reformers operate with excess steam to shift the chemical equilibrium of the products in favor of higher hydrogen yields and to reduce the tendency to form coke. Generation of this additional steam requires more heat, which shows up as a higher ΔH_{R} in the denominator in Eq. (2), and thus reducing the efficiency of the process. Practical reformers, where the maximum temperature exceeds 650 °C, also generate by-products like methane and carbon monoxide, and can be represented by,



At lower temperatures a variety of other species, such as aldehydes, ketones, acids, olefins, and carbonaceous solids (coke) are also formed [7,12]. In order to avoid coke formation, the steam reforming reaction is usually conducted with excess steam ($a > 3$). The higher steam content changes the kinetics of the reaction and eventually the equilibrium product distribution. The energy need for the process is affected because the water enters the system as a liquid, while the excess/unreacted water leaves as a gaseous product or the latent heat of steam condensation is not recovered for process use.

For any targeted process efficiency value¹ [15] it is possible to calculate the minimum moles of hydrogen that must be produced (per mole of ethanol feed) by the process, as a function of the steam-to-carbon molar ratio (S/C) in the reaction feed. These are plotted in Fig. 2 as a function of the S/C ratio. Thus, at the stoichiometric ratio, S/C = 1.5, a target of 72%

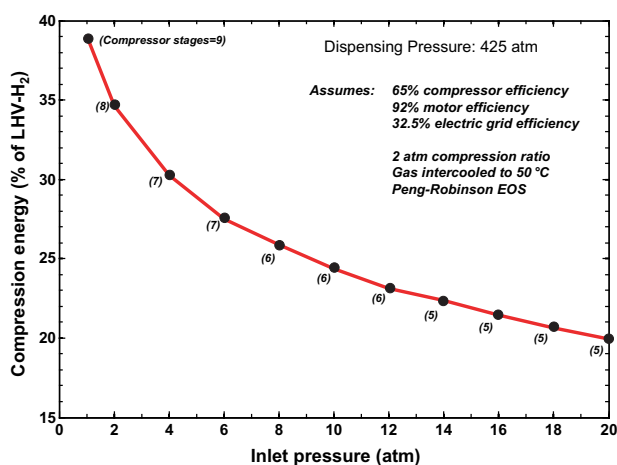


Fig. 1 – Energy required to compress hydrogen for delivery to a fuel cell vehicle.

¹ The US Department of Energy has set an efficiency target of 72% for the distributed production of hydrogen from bio-derived renewable liquids for the year 2012.

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