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Experimental and simulation studies of the production of renewable hydrogen through ethanol steam reforming in a large-scale catalytic membrane reactor

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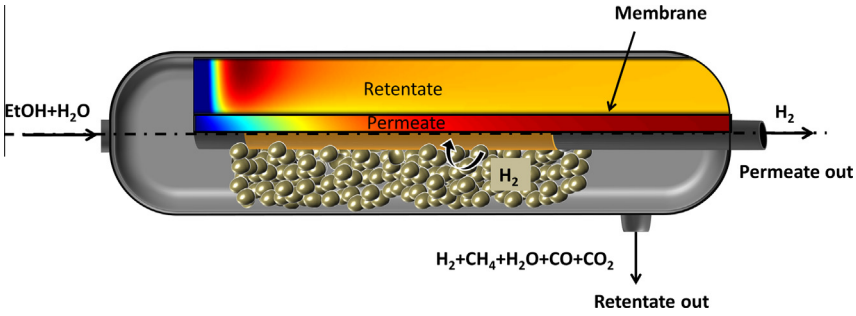
HIGHLIGHTS

- Ethanol steam reforming was studied in a catalytic membrane reactor (CMR).
- A CFD simulation model showed 91% accuracy compared to experimental data.
- An experimental hydrogen production rate of 0.38 g per hour was obtained.
- The effect of operating conditions on the reactor performance was determined.
- Hydrogen production in the CMR was enhanced by 122% over fixed bed production.

GRAPHICAL ABSTRACT



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ABSTRACT

The diversification of hydrogen production sources has tremendous energy and environmental implications, making ethanol steam reforming (ESR) an essential process that requires further investigation. Hence, the purpose of this work is to investigate the performance of a large-scale catalytic membrane reactor (CMR) used to enhance the efficiency of ESR by the in-situ removal of H_2 from the reactor module. The reactor consisted of a tubular membrane located at the center and surrounded by a commercial nickel-based catalyst. A thin, defect-free composite asymmetric membrane was prepared as a Pd/Au/Pd/Au structure, then characterized and tested under reacting conditions. Ethanol steam reforming was conducted under different conditions such as steam-to-carbon ratios, liquid hourly space velocities (LHSV), operating pressures and temperatures. A 1-D model and a 2-D computational fluid dynamics (CFD) model were developed, validated experimentally and used to explore further the features of this reaction. The CMR module was operated for 300 h showing 100% conversion of ethanol in all conditions and producing H_2 with a purity of 99.9%.

1. Introduction

Currently, hydrogen is mainly produced from nonrenewable sources; specifically, 95% of the total H_2 produced in the United States utilizes steam reforming of natural gas as the main process/source [1]. The diversification of hydrogen sources has tremendous

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energy and environmental implications and consequently, bioethanol rises as a better resource material since it is considered a renewable and carbon neutral hydrogen carrier. Ethanol steam reforming (ESR) is the process under which ethanol reacts at high temperatures with steam to generate hydrogen, carbon monoxide and carbon dioxide. This process has been widely studied in traditional reactors such as packed beds (PBR) and reported in the literature [2–6]. For instance, Roldán [7] showed the performance of ESR in a conventional reactor for a large-scale plant operated for 500 h. It was shown that the conversion of ethanol is highly favored by high temperatures and low space velocities. In this work, an ethanol conversion of 97.3 wt% and 99.7 wt% was achieved utilizing a commercial nickel-alumina catalyst at 300 °C and 450 °C with a steam to carbon ratio (S/C) of 1.5 and a weight hourly space velocity (WHSV) of 1.0 h^{-1} and 2.0 h^{-1}, respectively.

Catalytic membrane reactor (CMR) is a technology that can significantly improve chemical conversions by integrating the processes of reaction and separation in one unit [8]. In particular palladium-based membranes have been studied as a component of CMR technology since they produce high H_2 fluxes at theoretically infinite H_2 selectivities. Different Pd and Pd-alloy membranes have been tested under industrial conditions, displaying an excellent performance [9,10] suitable for their application in large-scale settings. Through the use of Pd-membranes, the constant removal of H_2 from the reaction zone is possible, altering the composition inside the system and thus allowing higher conversions. This process is called process intensification, and it has been shown for processes such as water-gas-shift (WGS) reaction [11] and methane-steam-reforming (MSR) [12]. In addition, techno-economic assessments of energy systems suggest that the application of membrane technology can be beneficial under specific market and regulatory conditions. In particular, Ma et al. [13], showed that on H_2 production plants based on coal gasification, the integration of CMRs (for the processes of WGS and H_2 purification) induced better economic traits under a carbon regulatory constraint, and that it is possible to reduce CO_2 emissions by 70% when a carbon capture and sequestration system is implemented. Indeed, the production of hydrogen from carbon-based sources generates considerable amounts of byproducts, specifically, CO_2 which is considered a greenhouse gas. It is important to mention that although the emission of CO_2 from bioethanol is considered carbon neutral, the application of CMR technology can significantly enhance the production of H_2.

Few studies of ESR carried out in Pd-based membrane reactors have been reported. Table 1 shows the different studies of ESR reported in the literature, along with their specific operating conditions. Some of these studies include the work presented by Gallucci et al. [14] which compared a simulation study of ESR in a Pd-Ag membrane reactor (MR) within a traditional reactor (TR), using a Co-based catalyst kinetic expression. In this study, the ESR reaction taking place in the CMR shows both higher ethanol conversions and higher hydrogen selectivities when compared to the traditional reactor. High temperatures between 673 K and 873 K had a positive influence on ethanol conversion, and it was concluded the effect of process intensification became significant because of the positive influence of temperature on the permeance of the membrane. Additionally, it was found that ethanol conversion increases constantly as pressure increases due to the positive effect of pressure on the hydrogen flux across the membrane. Recently, Murmura et al. [15] developed a one dimensional simulation work along with a lab scale experiment under low steam to ethanol (S/E) ratios (S/E = 3). It is well known that higher S/E ratio benefits the conversion of ethanol; nonetheless, by utilizing a sweep gas stream in the permeate side, 100% ethanol conversion was achieved under a stoichiometric steam-to-ethanol ratio. In this work, the 1-D heat and mass transfer simulation was based on three main reactions: ethanol decomposition (ESR), water-gas-shift (WGS) and methane steam reforming (MSR).

The present research work presents a combination of simulation and experimental results to demonstrate the performance of a large-scale CMR for hydrogen generation via ethanol steam reforming. To the authors' knowledge, results for a membrane at this large scale are presented for the first time in the literature. This work shows in Section 2 the methodology used to synthesize the membrane and carry out the reactions, along with the theoretical framework used to develop the presented 1-D and 2-D models. In Section 3, the results of the simulation and experiments are presented with a thorough discussion. Finally, Section 4 presents a summary of the findings along with some concluding remarks.

2. Materials and methods

2.1. Membrane fabrication, characterization and description of the CMR rig

A membrane with a surface area of 0.015 m^2 was synthesized on a porous stainless steel (PSS) support from Mott Metallurgical Corp. The porous support had a 0.0127 m OD and a 0.381 m length with a porous media grade of 5×10^{-7} m. The porous tube was capped at one end and welded to stainless steel tube at the other. The synthesis of the membrane was carried out using previously reported procedures [21–25]. At first, the support was cleaned utilizing isopropanol in an ultrasonic bath followed by its oxidation in air for 12 h at 600 °C. The support was graded with two types of pre-activated 2 wt% Pd-alumina particles obtained from Johnson Matthey (UK). The first type consisted of coarse particles with an average size of 1–3 μm, followed by fine 0.6 μm particles. The grading layer was cemented via electroless plating of palladium. After grading, the membrane was activated with $SnCl_2$ and $PdCl_2$ [21] and a layer of Pd was subsequently plated. In addition, gold was deposited on the surface of the membrane through conventional electroplating. Gold was chosen as the alloy of the membrane since it has been shown to improve the stability and lifetime of Pd membranes under harsh conditions [9]. The thickness of the Pd and Au layers were estimated through gravimetric measurements while its effectiveness was determined through

Table 1
Summary of previous experimental and simulation studies of ESR.

Catalyst	T [K]	P [bar]	Steam to ethanol ratio	Membrane surface area [$*10^{-4}$ m^2]	Ethanol conversion [%]	H_2 yield	Ref.
$Pt/Ni\text{-}CeO_2$	613–753	6–10	3	17.6	100	0.3–4.8	[15]
Co/Al_2O_3	673–873	1–8	1–11	–	95.3	–	[14]
Ru/Al_2O_3	673–723	1.2–1.5	8.4–13	46.2	–	0.52–0.82	[16]
$Pt_{0.5\%}/Al_2O_3$	623–723	1.1–2.0	8.4–13	46.2	–	0.2–0.6	[17]
$NiO_{25\%}/SiO_2$	623–723	1.1–2.0	8.4–13	4.62	–	0.1–0.6	[17]
$Rh/La\text{-}Al_2O_3$	873–1023	7–70	3–12	2.51	100	0.4–3.9	[18]
$Pd\text{-}Rh/CeO_2$	873–923	4–12	3.2–6	30.4	100	3.5	[19]
Co/Al_2O_3	673	3–8	3	24.2	100	–	[20]