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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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 H₂ 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 hours showing 100% conversion of ethanol in all conditions and producing H₂ with a purity of 99.9%.

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Keywords

Hydrogen production; Catalytic membrane reactor; Ethanol steam reforming; Palladium membrane; Computational fluid dynamics.

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 energy and environmental implications and consequently, bio-ethanol 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 [2,3,4,5,6]. For instance, Roldán [7] showed the performance of ESR in a conventional reactor for a large-scale plant operated for 500 hours. 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 CO₂ 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, CO₂ which is considered a greenhouse gas. It is important to mention that although the emission of CO₂ from bioethanol is considered carbon neutral, the application of CMR technology can significantly enhance the production of H₂.

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.

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-CeO ₂	613-753	6-10	3	17.6	100	0.3-4.8	[15]
Co/Al ₂ O ₃	673-873	1-8	1-11	-	95.3	-	[14]
Ru/Al ₂ O ₃	673-723	1.2-1.5	8.4-13	46.2	-	0.52-0.82	[16]
Pt _{0.5%} /Al ₂ O 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- Al ₂ O ₃	873-1023	7-70	3-12	2.51	100	0.4-3.9	[18]
Pd-Rh/CeO ₂	873-923	4-12	3.2-6	30.4	100	3.5	[19]
Co/Al ₂ O ₃	673	3-8	3	24.2	100	-	[20]

2. Materials and Methods

2.1 Membrane fabrication, characterization and description of the CMR rig

A membrane with a surface area of 0.015 m² 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 [21,22,23,24,25]. 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 He leak tests. Figure 1 shows the He leak characterization tests as a function of the membrane thickness at each synthesis step. The membrane was used for H_2 separation after it reached the minimal He flux located at a thickness of 13 μm . At this moment the membrane displayed a H_2 permeance of $80 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$ at 450°C. The membrane showed a He leak increase and thus, it was further plated with Pd and Au to enhance its stability and reduce the leak. The final structure and thickness presented in this membrane was Pd 6.9 μm /Au 0.2 μm /Pd 6.7 μm /Au 0.1 μm .

After synthesizing the membrane, it was arranged in a protective double-screen cage (shown in Figure 2) which held the membrane in close proximity with the catalyst. This cage was used to separate the catalytic particles from the surface of the membrane by loading the catalysts between the two screens, avoiding any defects caused by the particle-membrane interaction. The nickel-based catalyst (HiFUEL R110, from Alfa Aesar) [26] was first crushed and sieved (16/+40 mesh) before its confinement in the protective-membrane cage, which was loaded with 220 g of crushed catalyst. Notice that during the reaction, carbon deposition can occur at the surface of the catalyst, blocking the active sites. However, it has been reported that at relatively low temperatures (350°C-500 °C) the coking process is suppressed due

to the presence of H_2 [27]. The characterization of the H_2 permeance and the reaction were conducted in a large-scale module described in detail by Catalano et al. [11]. Notice that before initiating the H_2 permeation tests, pure He was fed to the system overnight in order to remove any air and moisture from the CMR. The reactions were carried out at different conditions with 65 ml/min of He on the tube side, which was used as sweep gas in order to increase the driving force of the separation.

Figure 1. Helium leak tests as a function of the different synthesized layers

Figure 2. Picture of the membrane, membrane-cage assembly and shell of the CMR module

2.2 Framework of the 1-D and 2-D simulation models

Ethanol steam reforming is a highly endothermic reversible reaction, which is favored by high temperatures, low pressures and low space velocities. The kinetic properties of ESR for different catalysts have been studied throughout the literature and different mechanisms have been proposed [15,28,29,30,31,32,33,34]. Nonetheless, it is considered that the reactions shown in Eq.1-4 are the most representative for the performance of the process [35]:

At first, a 1-D model was developed utilizing Polymath with the purpose of understanding the operating conditions needed in the experimental rig. The kinetic expressions for a Ni-based catalyst proposed by Sun et al. [35] and Xu and Froment [36] were utilized in this study and are presented in Table 2. These kinetic parameters were used to simulate ESR in conventional reactors, and the results were compared with experimental results presented in the literature [33,37]. The kinetics showed > 99% accuracy in predicting the performance of ESR.

The H_2 flux across the membrane was simulated according to Sieverts' law and utilizing the experimental value of the permeance ($\overline{P}_{\text{H}_2}$) as shown in Eq. 27, where $P_{\text{H}_2}^{\text{shell}}$ and $P_{\text{H}_2}^{\text{tube}}$ represent the H_2 partial pressure of the shell and inside the tube, respectively. On the retentate side (reaction zone) a negative H_2 flux through the membrane boundary was defined utilizing Sieverts' law. On the permeate side of the membrane boundary, the same expression, but positive, was defined to simulate the H_2 concentration profile.

$$-n \cdot N_i = \overline{P}_{\text{H}_2} [\sqrt{P_{\text{H}_2}^{\text{shell}}} - \sqrt{P_{\text{H}_2}^{\text{tube}}}] \quad (27)$$

Table 2. Summary of the kinetic expressions used in the simulation framework

$r_1 = k_1 P X_e$	$[\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(5)
$r_2 = (k_2 P / X_h \text{den}^2) [X_{\text{co}} X_w - X_{\text{CO}_2} X_h / K_2]$	$[\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(6)
$r_3 = (k_3 / X_h^{2.5} \text{den}^2 \sqrt{P}) [X_M X_W - X_{\text{CO}} X_h^3 P^2 / K_3]$	$[\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(7)
$r_4 = (k_4 / X_h^{3.5} \text{den}^2 \sqrt{P}) [X_M X_W^2 - X_{\text{CO}_2} X_h^4 P^2 / K_4]$	$[\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(8)
$k_1 = (4.55 \times 10^{-5} / T) \exp(-2030 / T)$	$[\text{mol Pa}^{-1} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(9)
$k_2 = 5.43 \times 10^{-3} \exp(-8074.33 / T)$	$[\text{mol Pa}^{-1} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(10)
$k_3 = 3.711 \times 10^{14} \exp(-28879 / T)$	$[\text{mol Pa}^{0.5} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(11)

$k_4 = 8.960 \times 10^{13} \exp(-29336.1/T)$	$[\text{mol Pa}^{0.5} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}]$	(12)
$K_2 = \exp(4400/T - 4.036)$		(13)
$K_3 = 1 \times 10^{10} \exp(-26830/T + 30.114)$	$[\text{Pa}^2]$	(14)
$K_4 = K_2 K_3$	$[\text{Pa}^2]$	(15)
$den = 1 + P(K_{CO}X_{CO} + K_hX_h + K_MX_M) + K_WX_W/X_h$		(16)
$K_{CO} = 8.230 \times 10^{-10} \exp(8497.71/T)$	$[\text{Pa}^{-1}]$	(17)
$K_M = 6.640 \times 10^{-9} \exp(4604.28/T)$	$[\text{Pa}^{-1}]$	(18)
$K_h = 6.120 \times 10^{-14} \exp(9971.13/T)$	$[\text{Pa}^{-1}]$	(19)
$K_W = 1.770 \times 10^5 \exp(-10666.35/T)$		(20)
$R_{C_{CO}} = r_1 - r_2 + r_3$		(21)
$R_{C_{CO2}} = r_2 + r_4$		(22)
$R_{C_{H2}} = r_1 + r_2 + 3 \cdot r_3 + 4 \cdot r_4$		(23)
$R_{C_{H2O}} = -r_2 - r_3 - 2 \cdot r_4$		(24)
$R_{C_{CH4}} = r_1 - r_3 - r_4$		(25)
$R_{C_{C2H5OH}} = -r_1$		(26)

Furthermore, a 2-D computational fluid dynamics (CFD) finite element simulation model was developed in COMSOL Multiphysics 5.2 to further explore the intrinsic physics of this CMR. The geometry utilized for the development of this simulation model is shown in Figure 3. The following assumptions were included to simplify the proposed CFD framework:

- i) The effect of the protective cage used to hold the loaded catalyst is negligible and does not cause any disturbance in the flow pattern
- ii) A 2-D axisymmetric geometry with two domains (shell and tube) was used for this model

iii) The system is isothermal and under laminar flow

Notice that due to the presence of the sweep gas stream, the H_2 partial pressure of the permeate (tube side) is reduced, but it will vary as a function of the H_2 flux.

Figure 3. Geometry used in the 2-D CFD simulation model

In COMSOL, considering the effect of the catalytic bed, the physics used for this model was “Reacting Flow in Porous Media (Concentrated Species)” for the retentate side and “Transport of Concentrated Species” coupled with “Laminar Flow” for the permeate side. Reactions were proved to be reaction rate limited as the effectiveness factor η was calculated to be 1 [38]. The equation of motion and species continuity equations for retentate side (Eq. 28, 30) and permeate side (Eq. 29, 30) were solved simultaneously within the geometric mesh, which contained 93,152 domain elements.

$$(\rho/\varepsilon_P)((u \cdot \nabla)u/\varepsilon_P) = \nabla \cdot [-pI + \mu/\varepsilon_P(\nabla u + (\nabla u)^T) - (2\mu/3\varepsilon_P)(\nabla \cdot u)I] - (\mu k^{-1} + \beta_F|u|)u + F \quad (28)$$

$$\nabla \cdot (\rho u) = 0$$

In which ε_p is the porosity of the catalytic bed, and β_F is the Forchheimer coefficient.

$$\rho(u \cdot \nabla)u = \nabla \cdot [-pI + \mu(\nabla u + (\nabla u)^T) - (2/3)\mu(\nabla \cdot u)I] + F \quad (29)$$

$$\nabla \cdot (\rho u) = 0$$

$$\nabla \cdot j_i + \rho(u \cdot \nabla)w_i = R_i \quad (30)$$

Notice that the density (ρ) of the gas mixture was specified to be a function of composition and thus it changed as the reaction and separation proceeded. Furthermore, diffusion coefficients ($\mathfrak{D}_m$) were calculated as shown in Eq. 31:

$$\mathfrak{D}_m = 0.0018583\sqrt{T^3(1/M_A + 1/M_B)}(1/p\sigma_{AB}^2\Omega_{\mathfrak{D},AB}) \quad (31)$$

Where σ_{AB} was obtained from the Lennard-Jones parameters, T is the temperature of the gases, p the pressure and $\Omega_{\mathfrak{D},AB}$ the collision integral [39]. Longitudinal and transverse dispersion coefficient ($\mathfrak{D}_L$ and $\mathfrak{D}_T$) for fixed bed reactors were calculated using Eq. 32-Eq-36 [40]

$$Pe_m = Re \cdot Sc \quad (32)$$

$$1/Pe_L = 1/(\tau \cdot Pe_m) + 1/2 \quad (33)$$

$$\mathfrak{D}_L = ud/Pe_L \quad (34)$$

$$1/Pe_T = 1/(\tau \cdot Pe_m) + 1/12 \quad (35)$$

$$\mathfrak{D}_T = ud/Pe_T \quad (36)$$

In which Pe_L and Pe_T are the longitudinal and transverse Péclet numbers, τ is tortuosity and d is the catalyst average particle diameter.

3. Results and Discussion

3.1 Membrane Characterization

The membrane module was first flushed with He and the retentate pressure increased by 1 bar. Figure 4 shows the permeation and He leak tests of the membrane at different temperatures. The temperature (Figure 4) of the reactor was increased to 350°C at 1°C per minute under He. A leak test performed on the module showed a He flux of 0.2 sccm/bar. Hydrogen was fed to the system for 20 hours displaying a H₂ permeance of 11 Nm³m⁻²h⁻¹bar^{-0.5}. The temperature of the module was then increased to 450°C and the H₂ permeance was measured continuously for 20 hours. The membrane's permeance increased gradually reaching a steady value of 21 Nm³m⁻²h⁻¹bar^{-0.5}, or about 50% higher than at 350 °C. The He leak at this temperature increased to 1 sccm/bar. In order to test the leakage, He was introduced to the system instead of pure H₂ from 44- 46 hours as shown in Figure 4. The membrane had estimated ideal H₂/He selectivities of 10,800 and 1,139 at temperatures of 350 °C and 450 °C, respectively. Afterwards, the temperature was increased to 600 °C for 2 hours under pure H₂ in order to activate the catalyst, as specified by the provider. The membrane showed a good thermal stability since, after activation, no He leak was found on the membrane at a pressure difference of 1 bar, while the H₂ flux remained stable. This phenomenon as described by Mardilovich et al. [9] could be the result of Au acting as a patch paste on the membrane defects.

The H₂ permeance of the membrane was tested when its composition and thickness was 6.9 μm Pd/ 0.2 μm Au/ 3.2 μm Pd; its permeance was 80 Nm³m⁻²h⁻¹bar^{-0.5} at 450°C. There was a 70% reduction in H₂ permeance after the membrane was replated. The decline in H₂ permeance occurred as the thickness of the membrane was increased, inferring higher resistance to the diffusion of protons through the Pd lattice. Furthermore, there is an overall increase in the gold content of the membrane, which can significantly influence the solubility of H₂ in the active sites of the membrane, as reported by Sonwane et al. [41]. Nonetheless, the H₂ permeance of the membrane is in agreement with the values presented in the literature for Pd and Pd/Au membranes [9,10,42] and with 20 μm free standing foils, which have a theoretical permeance of 15 and 23 Nm³m⁻²h⁻¹bar^{-0.5} at 350 °C and 450 °C, respectively. Notice that the resistance of the support is not taken into consideration for the theoretical calculation of the free standing

foils, suggesting that the selective layer of the membrane presented in this work has enhanced properties and/or the resistance of the support is negligible.

Figure 4. Hydrogen permeance at different times and temperatures: Permeance (—), Temperature (—)

3.2 Performance of the 1-D and 2-D simulation models

The 1-D and 2-D simulation models were compared to the experiments carried out in the large-scale catalytic membrane reactor presented in this work. In Figure 5 only the experimental results for the H₂ mole fraction at the retentate were compared against those found through the simulation models, in order to avoid unnecessary and repetitive information; nonetheless, both simulations predicted accurately the tendency of the reaction. The result of the 2-D model shows a higher accuracy than that of the 1-D simulation. While the 1-D model showed 85% accuracy; the 2-D improved its performance to 91%. The 2-D model takes into consideration the effect of radial mass transfer limitations as well as the features of porous media, which can affect the performance of CMRs.

Figure 5. Comparison of the simulation and experimental results found in the present study:

1D Simulation-Experiment (◆), 1D Simulation-Experiment trendline (—); 2D Simulation-Experiment (■), 2D Simulation-Experiment trendline (—)

The discrepancies found between the simulation results and the experiments could be triggered by four main effects or a combination of them:

- i) The permeance of the membrane is assumed to be constant under reacting conditions. Experimentally, the permeance of the membrane has been shown to be affected by components such as CO and steam [43], which are unevenly distributed along the reactor.
- ii) Carbon deposition in the catalytic bed is neglected in the simulation models. The possibility of coking can lead to a decrease in the activity of the catalyst as well as in the permeance of the membrane. Nonetheless, operating at mild temperatures (350-450°C) significantly reduces the possibility of coking for MSR and WGS reactions [44].
- iii) Potential temperature gradients along the catalytic bed are neglected. The CMR used in this study had a length of 1 m and its temperature was supplied by a furnace (Watlow 1.6 kW) with a length of 0.8 m. Although the connections and auxiliary equipment were thermally insulated to avoid cold spots, temperature gradients were observed, as reported previously by Catalano et al. [11].

iv) The simulation model inputs are based on lab-scale parameters. The current CMR study was performed on a large-scale bench, which can induce changes in the operational and modelling properties of the system [45].

3.3 Performance of the catalytic membrane reactor

The CMR module was tested continuously for 300 hours, generating H₂ with a purity of 99.9%. The conversion of ethanol was 100% for every condition, in agreement with the results reported by Kumar et al. [46], where it was shown that noble metal catalysts achieve 100% ethanol conversion with a selectivity near to 99% depending on the type of support and loading metal. A hydrogen flux of 0.38 grams of H₂ per hour was achieved by the module. Each experimental point was measured at least 5 times to ensure consistency. The average error bars of this work were estimated to be ± 0.1 , ± 0.3 and ± 0.2 for H₂, CO₂ and CH₄, respectively. The following subsections describe in detail the performance of the CMR when the operational variables were modified.

3.3.1 Effect of space velocity

At first, the effect of space velocity in the performance of the CMR for ESR was explored at 450°C and a S/E ratio of 3. Figure 6 shows the mole fraction on a dry basis at the retentate outlet as a function of the space velocity for the experiments performed (scattered points), the 1-D model (solid line) and the 2-D CFD simulation (dashed line). Notice that one experimental point was outside range and therefore it was considered an error; Figure 6 neglects this point in the graph. It can be observed that in most cases H₂ appears to grow as the space velocity increases, this is the result of decreasing the H₂ contact time with the membrane surface, which causes an accumulation of H₂ at the retentate side. Although at higher space velocity the membrane recovery decreases by the lack of contact time with the membrane, more H₂ is observed at the permeate side. This effect occurs since as the space velocity increases, more reactant is fed to the reactor, leading to an overall higher H₂ production.

The mole fraction of methane in the retentate appears to have a slight decrease at higher velocities for the 2-D simulation and for the experimental results. The 1-D model showed a steady performance where CH_4 appeared constant at all velocities. The 2-D model considers radial mass transfer limitations, while the 1-D model assumes perfect mixing; therefore, discrepancies between the different models can be observed. In CMRs, the process of MSR is expected to proceed further when operating at reduced feed flow rates, assuming that the reaction is not kinetically limited but rather controlled by the permeation rate of the membrane. This phenomenon has been previously reported in the literature [42,47], where methane conversion reduces as the space velocity is increased. In Figure 6, CH_4 appears to decrease rather than increase, indicating that the reaction is being hindered by the presence of H_2 in the reaction zone. In other words, higher velocities influence the rate of H_2 removal more strongly than the reaction rate. A similar performance is observed with carbon dioxide, where it appears to have a slight decrease towards higher velocities. A reduction in CO_2 can be caused by a reduced conversion of ethanol and/or methane. As mentioned before, the total conversion of ethanol was achieved and since CH_4 is reduced, it is suggested that the lower CH_4 conversions caused the reduction in CO_2 at higher flow rates.

Figure 6. Retentate composition at different LHSV and 450°C, 3 bar and a S/E = 3: H₂ Experiment (▲), H₂ 1D Simulation (—), H₂ 2D Simulation (— ·); CH₄ Experiment (◆), CH₄ 1D Simulation (—), CH₄ 2D Simulation (— ·); CO₂ Experiment (■), CO₂ 1D Simulation (—), CO₂ 2D Simulation (— ·)

3.3.2 Effect of pressure and steam content

After the analysis of the space velocity, the liquid feed flow rate was fixed at 2.48 cm³/min or a LHSV of 3.77 h⁻¹. The CMR module was tested at different pressures and S/E ratios as shown in Figure 7. At first, the S/E was fixed to 3 and the pressure was varied from 2 to 10 bar. It can be observed that as the operating pressure increases, the H₂ mole fraction of retentate decreases implying that the H₂ removal through the membrane is intensified as the driving force for permeation is increased. Moreover, higher pressures enlarged the mole fraction of CH₄ at the retentate. This effect does not indicate that the content of CH₄ increases, but rather that, due to the removal of H₂, the mole fraction of methane appears higher. This hypothesis is valid in all conditions, since no ethanol was detected at the retentate outlet. The same effect appears to occur for CO₂, where as the pressure increases, the CO₂ mole fraction of the retentate increases (Notice that the accuracy of the 1-D and 2-D models with respect to CO₂ is of 79% and 95% respectively). In conventional reactors, ESR [2] and MSR [42] show a negative response to pressure as it is thermodynamically unfavorable, as described by Le Chatelier's principle. Nonetheless, the removal of H₂ from the reaction zone changes the composition of the reaction zone, improving the overall performance of the reactions. The effect of pressure at different S/E ratios did not seem to influence the aforementioned trend. Indeed, as pressure increased the H₂ mole fraction of the retentate decreased, CH₄ increased and CO₂ increased.

An increase in the driving force of H₂ transport certainly has an important contribution in the performance of CMR technology. Based on simulation data, Figure 8 shows how much H₂ is generated in CMRs when compared to traditional packed bed reactors (PBR) at different membrane permeances and pressures and thus the term (σ) was used to describe this effect (Eq. 37). A similar study has been done by

Helmi et al. [48], in which the benefit of fluidized bed membrane reactor (FBMR) compare with traditional fluidized bed reactor (FBR) was observed by analyzing the improvement of CO conversion in WGS reaction operating in the two reactors.

$$\sigma[\%] = [(F_{H_2}^{per} + F_{H_2}^{ret})_{CMR} - (F_{H_2}^{ret})_{PBR}] / (F_{H_2}^{ret})_{PBR} \cdot 100 \quad (37)$$

The effectiveness of CMR technology in generating H_2 directly depends on the total amount of H_2 removed from the reaction zone. One method to improve this rate of removal is by increasing the driving force for H_2 transport or the H_2 partial pressure difference between the retentate and the permeate. Therefore, higher retentate pressures significantly improved the generation of H_2 (Figure 8). In Figure 8, an increase in pressure not only made the CMR more efficient, but simultaneously reduced the performance of conventional PBRs. Therefore, the term (σ) appears to increase significantly as pressure was increased.

Another factor that influences the rate of H_2 removal from the reactor is the permeance of the membrane. Low permeances in CMRs imply analogous features with conventional PBRs; however, as the permeance increases, the generation of H_2 is enhanced. This boost, shown in Figure 8, reaches a plateau which occurs when the permeance of the membrane is hindered by a low driving force for H_2 transport. In other words, as more hydrogen is depleted from the retentate and collected on the permeate side, the hydrogen partial pressure on each side becomes equal, making the driving force close or equal to zero. After reaching this condition, an increase in H_2 permeance does not reflect the effect of process intensification. This phenomenon can be confirmed when analyzing the point where the plateau is reached. The plateau appears at higher permeance values when the operating pressure is increased (Figure 8); this effect will continue until the driving force becomes limited by the kinetics of the reaction.

Steam showed an enhancing effect on the production of H_2 and the reaction overall. As the S/E ratio increased, the H_2 mole fraction at the retentate increased as shown in Figure 7. This outcome indicates that the rate of H_2 removal is the limiting process within the CMR, and that an increase in

pressure will generate more H_2 . On the other hand, the mole fractions of CH_4 and CO_2 in the retentate decreased and increased, respectively, as the S/E increased. This trend indicates that the conversion of CH_4 in the process improves in the presence of higher steam content. Although the presence of steam appears to be beneficial to the overall production of H_2 , Li et al. [43] reported that steam significantly affects the permeability of Pd membranes as it has shown strong adsorption ability on Pd surfaces. This suggests that there is a tradeoff between operating at high S/E ratios to improve the kinetics of the reaction while maintaining high permeability properties in the membrane.

Figure 7. Composition of the retentate at different pressures at 450°C, LHSV=3.77 h⁻¹ and a) S/E= 3, b) S/E= 5 and c) S/E= 7: H₂ Experiment (▲), H₂ 1D Simulation (—), H₂ 2D Simulation (---); CH₄ Experiment (◆), CH₄ 1D Simulation (—), CH₄ 2D Simulation (---); CO₂ Experiment (■), CO₂ 1D Simulation (—), CO₂ 2D Simulation (---)

Figure 8. Hydrogen production improvement at different membrane permeances and retentate pressures:
11 bar (—), 8.5 bar (—), 6 bar (—), 3 bar (—)

3.3.3 Effect of temperature

The highly endothermic characteristic of ESR indicates that the process is thermodynamically favored by high temperatures. In CMR technology, temperature is a critical factor since it strongly relates to the H-diffusion through the Pd lattice and the activation energy for solution. To analyze the influence of temperature, the experiment was carried out under a fixed LHSV of 3.77 h^{-1} , a S/E ratio of 5 and a retentate pressure of 6 bar. The temperature was varied in the range of 350°C - 500°C . As shown in Figure 9, as the temperature increased, the H_2 mole fraction in the retentate side increased, as a consequence of different elements. The first one relates to an increase in the kinetic properties of the catalyst, which induces higher CH_4 conversions, as previously shown in the literature [49]. Another factor is the membrane's H_2 permeance, which is enhanced by high temperatures (Eq. 38). Nonetheless, the generation of H_2 overcame the rate of removal and therefore an accumulation of H_2 is observed at the retentate.

$$Q = Q_0 e^{-E_p/(R \cdot T)} \quad (38)$$

In which Q_0 is the membrane permeability constant ($\text{m}^3 \mu\text{m}/[\text{m}^2 \text{h atm}^{0.5}]$), E_p represents activation energy of H_2 diffusion (kJ/mol) and R is the gas constant.

It is important to mention that the trend was accurately depicted by the 1-D and 2-D simulation models; but the experimental H_2 mole fraction appeared to be underestimated in Figure 9. This difference in the performance of the simulation and experimental results could be caused by the inhibition of the H_2 permeance, caused by the presence of components such as CO , steam, CO_2 and ethanol [50]. The simulation model did not consider variances in H_2 permeance; in other words, the model assumes that all gas species, excluding H_2 , act as inert components.

Figure 9. Composition of the retentate at different temperatures, a retentate pressure of 6 bar and S/E=5:
 H_2 Experiment ($\blacktriangle$), H_2 1D Simulation (—), H_2 2D Simulation (- -); CH_4 Experiment ($\blacklozenge$), CH_4 1D Simulation (—), CH_4 2D Simulation (- -); CO_2 Experiment ($\blacksquare$), CO_2 1D Simulation (—), CO_2 2D Simulation (- -)

The mole fraction of methane decreased as temperature increased since the methane steam reforming reactions (Eqs.3-4) are enhanced with temperature. The effect of temperature on methane during ESR (Eq.1-4) was studied in Figure 10, where the molar flow rate of CH₄ is computed at different membrane reactor lengths. It can be seen, at first, that CH₄ is generated early in the catalytic bed by breaking down ethanol (Eq.1); once ethanol is completely consumed, the process of MSR limits the generation of H₂. In Figure 10, the conversion of CH₄ (X_{CH_4}) was defined as:

$$X_{CH_4}[\%] = (F_{CH_4}^{max} - F_{CH_4}^{ret})/F_{CH_4}^{max} \cdot 100 \quad (39)$$

Where $F_{CH_4}^{max}$ and $F_{CH_4}^{ret}$ are the maximum CH₄ molar flow rate identified and the CH₄ molar flow rate at the outlet of the retentate, respectively. Figure 10 shows that the conversion of the generated methane, during the ESR process, improves as temperature increases.

Methane steam reforming was studied in simulation under “MSR conditions only” (CH₄ and steam) and labelled as MSR-CMR and “ESR conditions” and labelled ESR-CMR. The purpose was to compare the performance of the MSR-CMR and the ESR-CMR. Notice that the maximum CH₄ molar flow rate identified in the ESR-CMR was used as the feed stream for the MSR-CMR. Table 3 shows the theoretical methane conversion of the ESR-CMR and MSR-CMR which agrees with the result previously reported by Medrano et al. [51]. Under MSR conditions, the CH₄ conversion is higher than under ESR conditions. The reason is that the pseudo-composition formed in the reaction zone is different in both cases. For instance, in ESR, when ethanol reacts, it produces CH₄, CO and H₂; at this moment, CO immediately reacts in the WGS process (Eq. 2) to generate more H₂ and CO₂. Meanwhile, CH₄ reacts, at a slower rate, in the MSR process (Eqs. 3-4); nonetheless, the presence of CO, CO₂ generated from the other reactions, thermodynamically inhibits the conversion of CH₄. In contrast, under MSR conditions only, when CH₄ starts reacting, no products are present and that the generated compounds are in stoichiometric balance, allowing higher CH₄ conversions. It is important to mention that the presence of a H₂ selective membrane in the reactor improves the generation of H₂ for ESR; however, when compared to MSR, the effect of “process intensification” is reduced.

Figure 10. Methane molar flow rate along the length of the membrane at different temperatures, a retentate pressure of 3 bar and S/E=5: 450 °C (—), 525 °C (—), 600 °C (—), 700 °C (—)

Table 3. Comparison of CH₄ conversion under ESR and MSR conditions

Temperature (°C)	X _{CH₄} in ESR-CMR (%)	X _{CH₄} in MSR-CMR(%)
450	0	28
525	3	60
600	32	95
700	74	100

For the case of CO₂, Figure 9 shows a stable performance as a function of temperature, possibly due to the integrated effect of WGS reaction and MSR. In Figure 9, CO₂ appears to deviate more experimentally, but this data has an estimated average standard deviation of 0.4. At different temperatures

CO₂ shows a rather constant mole fraction, as previously reported in the literature [15,18,29,52]. The 2-D model shows this stable CO₂ trend and also it shows a higher accuracy with respect to the experimental points than the 1-D model, possibly due to radial mass transfer effects. At high temperatures, the reaction rate of MSR increases, but the activity of WGS decreases. In contrast, at low temperatures, the WGS reaction improves while the MSR deteriorates, as reported by Sahoo et al. [53] and Murmura et al. [15]. It is important to mention that CO was not detected in the present work; nonetheless, to further explain the phenomenon observed in Figure 9, the tradeoff between MSR/WGS during the process of ESR in CMRs is presented in Figure 11. The selectivity of CO₂/CO, defined in Eq. 40, was computed at different temperatures and a retentate pressure of 3 bar.

$$S_{\text{CO}_2/\text{CO}} = F_{\text{CO}_2}^{\text{ret}}/F_{\text{CO}}^{\text{ret}} \quad (40)$$

At high temperatures (Figure 11), the generation of CO is expected to rise, as WGS is a moderately exothermic reaction, which is suppressed at high temperatures (>450°C). As the temperature decreases, the selectivity towards CO₂ increases exponentially, since the activity of the WGS reaction increases. The maximum CO₂/CO selectivity is presented at a temperature of 320°C; lower temperatures, showed a sharp decrease in selectivity. The reduction in selectivity at the lower temperatures can be attributed to i) the reduction in permeance of the membrane and ii) a slower ESR reaction rate. The reaction of ethanol is expected to proceed further down in the catalytic bed, as the ESR reaction rate is decreased; consequently, WGS will proceed under lower residence times. This reduction in residence time potentially affects the total CO concentration. Furthermore, as the permeance of the membrane decreases with reduced temperatures, it is expected to have a higher H₂ concentration in the reaction zone. The presence of H₂ allows the system to reach thermodynamic equilibrium faster, hindering the WGS reaction and thus resulting in higher CO levels.

Figure 11. Selectivity of CO₂/CO of the Ni-based reforming catalyst under ESR-CMR conditions

4. Concluding Remarks

The performance of a large-scale catalytic membrane reactor (CMR) used for ethanol steam reforming (ESR) was demonstrated through a comprehensive experimental and computational analysis. In this work, the CMR used a Pd/Au/Pd/Au composite asymmetric membrane that displayed a H₂ permeance of 11 and 21 Nm³m⁻²h⁻¹bar^{-0.5} at 350 °C and 450°C, respectively. The performance of the CMR was tested under a range of liquid hourly space velocities (LHSV), operating pressures, temperatures and S/E ratios. The CMR module was operated for 300 hours showing 100% conversion of ethanol for all conditions and producing H₂ with a purity of 99.9% at a rate of 0.38 grams per hour at 5 bar, 500°C, a S/E ratio of 5 and a LHSV of 3.77 h⁻¹. The reactor showed higher H₂ production rates when the CMR was operated at high temperatures, high pressures and high S/E ratio. Furthermore, the 1-D and 2-D simulation models were generated using Polymath and Comsol, respectively. These models were validated first with kinetic data available from conventional reactors. In this work, the models presented an accuracy of 85% and 91%, respectively, when compared to the experimental results. The simulation models suggested that the production of H₂ can be enhanced by up to 122% when operating a higher pressures and membrane

permeances. The results presented in this paper clearly show that ethanol can be used as an alternative H₂ carrier source and the application of membrane technology significantly enhances its dehydrogenation process. Finally, it is possible to conclude that in order to apply this CMR technology at industrial proportions more pilot-scale prototypes are needed to overcome the current “demonstration-stage” and move to commercialization “deployment-stage” [13, 54].

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