Performance of a Pilot-scale Multitube Membrane Module under Coal-Derived Syngas for Hydrogen Production and Separation

Bernardo Castro-Dominguez¹, Ivan P. Mardilovich, Rui Ma, Nikolaos K. Kazantzis, Anthony G. Dixon,

Yi Hua Ma

Center for Inorganic Membrane Studies, Department of Chemical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, USA.

Abstract

Pilot-scale tests generate information about the performance of energy systems and thus help in the deployment of new technologies. This work aims at demonstrating the pilot-scale application of palladium-based membrane technology for the purification of H₂. A multitube membrane module with a total permeable area of 1050 cm² was tested under actual coal-derived syngas. The module was composed of seven membranes with a Pd/Au/Pd layered structure supported on PSS tubes. The membranes were arranged with one membrane at the center and six equally distributed around it. The membranes had a composition of 7 μm Pd and 0.4 μm Au and a cumulative He leak of <0.01 cm³/min/bar before testing. The module was operated at 450°C, 12.6 bar and 10 lb/h of desulfurized syngas provided by a gasification unit and enriched with H₂ to 34%. The module showed a stable H₂ permeance of 16.2 Nm³m⁻²h⁻¹bar^{-0.5} throughout 840 hours. The produced H₂ purity was in the range of 99.87-98%. An H₂ production of 6 lb/day and recovery of 64% were achieved, representing a significant development in the field. The scalability and industrial applicability of this technology was successfully demonstrated. Furthermore, a CFD model illustrated different physical phenomena associated with this multitube configuration.

Keywords

Hydrogen production; Multitube membrane module; Pd-based Composite Asymmetric Membranes; Coal-derived Syngas; Computational Fluid Dynamics

¹ Author to whom correspondence should be sent; Address: 100 Institute Road, Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609-2280, USA; E-mail address: bcastr Dominguez@wpi.edu / bcastr Dominguez@gmail.com , Phone number: +1-508-8315666.

1. Introduction

As an energy carrier and as a fuel, hydrogen is a chemical that could potentially assume a key role in the design and operation of future versatile energy systems. Some of the benefits of building a hydrogen economy include: environmentally-friendly properties when oxidized as a fuel, availability of multiple H₂ transportation methods (road, rail, ship, pipeline, etc.), multiple storage configurations (unlike electricity), applicability as fuel or for electrical generation, and potential production through multiple sources/pathways [1]. Currently, the production of H₂ relies heavily on fossil fuel-based sources such as natural gas and coal, but can potentially extend to renewable sources such as biomass. According to the U.S. Office of Energy Efficiency and Renewable Energy [2], methane steam reforming accounts for 95% of the hydrogen produced in the United States; simultaneously, it is expected that coal gasification will be deployed in the mid-term time frame. To achieve the proposed hydrogen economy, the production of pure H₂ is essential whilst reducing the generation of greenhouse gases such as carbon dioxide. It is important to point out that most applications require an H₂ purity in the range of 99.99% to 99.9995% and that H₂ separation and purification account for half of the production costs [3,4]. Palladium-based membrane technology has been shown to be effective in the generation of ultrapure molecular H₂ at high fluxes, as well as facilitating the capture of CO₂ when integrated as a catalytic membrane reactor (CMR) [4,5].

Palladium membrane technology can exhibit superior economic performance compared to conventional technology options under specific market and regulatory conditions when integrated within different H₂ production and/or energy systems [6,7]. For instance, Ma et al. [6] showed that the economic performance profile of a hydrogen production plant (HP) utilizing CMR technology could not be perceived as competitive when assessed against the incumbent technology options based on pressure swing adsorption (PSA) in the absence of any regulatory action on CO₂ emissions. Nonetheless, in the presence of future regulatory action on CO₂ emissions, it was demonstrated that superior techno-economic performance characteristics emerge for CMR technology when integrated into the aforementioned process systems, namely ones associated with: i) a significant reduction (26%) of total capital investment costs compared to conventional PSA-based HP plants; and ii) an enhancement of the overall economic performance under various economic metrics and carbon prices.

Large-scale membrane-based separation processes require high available surface areas to achieve the desired production rates. In order to reduce costs in membrane technology while increasing the permeation rate, it is necessary to increase the ratio of the surface area of the membranes to the volume of the module holding them. Therefore, a multitube membrane unit raises the amount of membrane surface area that can be accommodated in a given volume such as in the case of hollow fiber membrane modules [8]. Only a very limited number of large-scale operating tests, however, have been conducted under

realistic conditions. Mardilovich et al. studied the performance of pilot-scale Pd and Pd-alloy membranes under actual coal-derived syngas [9]. Thirteen membranes were tested for a cumulative time of 4275 hours and classified according to their composition in four groups: pure Pd, Pd-Au, Pd-Pt and Pd-Au-Pt. The membranes produced an H₂ quality in the range of 99.95-99.00% and displayed excellent stability; nevertheless, a permeance drop occurred when the membranes were tested under syngas conditions, possibly due to the presence of sulfur present in the lines of the system. Furthermore, it was found that Au-containing membranes improved the robustness of the membranes by repairing any in-situ formation of pinholes. Adding gold to the membranes has been shown to be beneficial as their H₂ permeance recoverability improves when poisoned by H₂S and other contaminants present in syngas [10,11]. Furthermore, as reported throughout the literature [9,10,11,12], the H₂ permeabilities of Pd/Au membranes have been shown to be higher than those of pure Pd membranes.

According to Lu et al. [13], the current state of affairs for the application of Pd membranes shows only small scale applications. Indeed, few multitube membrane modules have been evaluated and the associated results presented in the literature for H₂ purification. For instance, Tosti et al [14] demonstrated the design of a finger-like permeator tube reactor useful for ethanol reforming. The module was capable of producing 6 L min⁻¹ of H₂ utilizing 19 Pd-Ag membranes with a thickness of 50-60 μm and a total surface area of 1490 cm². Diniz da Costa et al. [15] reported the design of a cobalt-based silica multitube membrane reactor. The module was used for the water-gas-shift reaction producing a H₂ purity of 98%. Notice that the produced H₂ flux and the total surface area of the module were not reported in the study. Parsley et al. [16] reported the evaluation results of a carbon molecular sieve multitube membrane module for the separation of H₂ from actual coal derived syngas under water-gas-shift reaction conditions. The module consisted of 86 tubes with a surface area of 7600 cm² and was capable of producing H₂ with 90% purity. Moreover, numerical simulations on single tube membrane units have been widely reported in the literature [17,18], but to the authors knowledge only a few multitube membrane models have been previously published. For instance, Coroneo et al. [19] studied a module containing three membranes and baffles. The purpose of the reported model was to demonstrate the effect of baffles which divided the module in sections reducing concentration polarization.

In economic terms, as described by Ma et al. [20], scaling up (increasing the surface area of the active membrane) is the next step towards the actual deployment of this membrane technology. Certainly, various techno-economic assessments have envisioned, as a key element, the use of multitube membrane modules capable of holding large membrane surface areas [6, 7]. Furthermore, these multitube membrane systems require optimization and a thorough analysis in order to maximize their technical benefits which could result in better economic performance outcomes in the presence of technological

challenges and irreducible uncertainties in fuel markets and the regulatory landscape. For instance, physical phenomena such as mass and heat transfer limitations can significantly reduce the H₂ throughput, which could significantly influence the economic performance profiles of hydrogen plants [6,7,20]. In light of the aforementioned characteristics, the present work aims at demonstrating the development, scale up and field testing of a seven-tube palladium-based membrane module operating under actual coal-derived syngas and industrial settings, and producing H₂ at purity levels above 98%. Furthermore, a thorough analysis on the physical phenomena occurring inside the multitube membrane module was performed to illustrate essential differences between single and multitube membrane systems. This work contains in Section 2 the experimental procedures for membrane synthesis, characterization of the multitube module and specifications of the numerical simulation, followed by the description of the main results in Section 3. Section 4 contains a discussion based on the results of the numerical simulation and finally, some concluding remarks are offered in Section 5.

2. Methodology

2.1 Membrane Preparation and Module Design

The palladium membranes developed at Worcester Polytechnic Institute (WPI) and previously reported in the literature [9,10,11,21,22,23] were scaled up and replicated in order to synthesize eight new membranes. Eight porous stainless steel (PSS) tubes purchased from Mott Metallurgical Corp. were used for the synthesis of the membranes. Each porous tube had a surface area of 150 cm² and dimensions of 15 in. in length and 0.5 in. OD. Each porous support had a Media Grade of 0.5 μm and was welded to a capped end on one side and to a stainless steel tube on the other. All supports were cleaned in an ultrasonic bath utilizing propanol followed by an oxidation step at 600 °C for 12 hours in air [23,24,25].

The pre-oxidized supports were subject to grading using two types of slurries composed of pre-activated alumina particles. The first grading step consisted of coarse particles with sizes in the range of 1-3 μm; while fine grading introduced particles of 0.6 μm. The grading layers were glued with palladium as previously described [22,24,25]. The membranes were then activated and electroless plated to create a dense Pd layer of the graded supports; for further reference on this procedure please refer to the pertinent literature [25,26]. Afterwards, a gold layer was deposited on top of the palladium in order to improve the stability and recoverability of the membranes, as reported by Chen et al. [11]. An additional layer of Pd was finally plated on top of Au to create a multilayered composite membrane. The thickness of the Pd and Au layers was estimated through gravimetric measurements and each step of the synthesis was characterized by an He leak test. Figure 1 shows the different thickness of the stages in the synthesis of

the composite membranes; on average the membranes had a thickness layer of 5.4 μm Pd, 0.4 μm Au and 1.6 μm Pd, with an intermediate grading layer of 2.5 μm .

Figure 3 shows the average He leak at each step of the synthesis. As purchased, each support had an He flux of 200 L/min at one bar ΔP and it was reduced to a cumulative (all seven membranes) He flux of $< 0.01 \text{ cm}^3/\text{min}$. The supports showed half the He flux after oxidation and further reduction to 56 cm^3/min after grading. Grading is a critical step in the formation of a defect-free Pd membrane since it reduces the uneven pore size distribution of the support and smooths its surface, allowing the formation of an even Pd thickness after plating [22,26]. The total permeable surface area of the seven membranes is 1050 cm^2 . The additional synthesized membrane was tested at WPI under controlled conditions with pure H_2 for comparison purposes. Moreover, it is important to mention that the membranes were synthesized layer-by-layer, creating well defined Pd and Au layers. Nonetheless, as shown in previous studies [9,11], alloying occurs in-situ when the temperature is increased under the operating conditions considered in this work

Figure 1. Composition of the multilayered composite membranes used in the present study.

Figure 3. Average He leak through the Pd/Au/Pd membranes throughout each synthesis step.

2.2 Coal Derived Syngas

The multitube membrane module containing the seven Pd/Au/Pd membranes was installed in the WPI-MTR (Worcester Polytechnic Institute - Membrane Technology Research) skid at the National Carbon Capture Center in Wilsonville, AL [27] and it is shown in Figure S1 (Supplementary Materials). The module was purged with pure N₂ and its operating pressure was increased to > 12 bar and the temperature was increased to 450°C. It is important to mention that the module showed no leak while testing the module seal. After reaching the operating temperature, a mixture of 35:65 H₂/N₂ was fed to the system, followed by the actual coal-derived syngas.

Syngas was produced by an air-blown transport-integrated gasification (TRIG™) system that used powder river basin (PRB) coal. The raw syngas was treated to reduce particulates to 0.1 ppv, CO to < 1% and H₂S to < 1ppm, followed by H₂ enrichment of 30–40% to increase the H₂ partial pressure in the module and thus improve the driving force for permeation. The feed had an average composition of H₂: 34%, N₂: 55%, CO < 1%, CO₂: 10%, H₂O: balance as described previously in the pertinent literature [27]. The composition of the feed, permeate and retentate was monitored by a gas chromatograph (model Siemens Maxum II, columns: HysepN and HA-MS for H₂, N₂, CO, and CH₄; HysepN and HysepQ for CO₂ and H₂S; detector was a TCD), while the flow rates were measured periodically using a rotameter. Notice that the syngas at 160-180°C was additionally heated through a pipe-coil that surrounds the module as shown in Figure S1 (Supplementary Materials). For further information about the configuration of the rig and the gasifier, please refer to previously reported work [9,10,27]. Finally, it is

important to mention that postmortem membrane characterization was not performed due to logistic issues with the membrane module.

2.3 Computational Fluid Dynamics Model

A simplified computational fluid dynamics (CFD) model for the multitube membrane module was developed, to study the physics of the system under similar conditions to those presented in the experiment. The model consisted of a 3-D representative geometry subject to the continuity equation (Eq. 1) and the equation of motion (Eq. 6). COMSOL Multiphysics 5.0 was used to solve the equations within the proposed geometry and "Transport of Concentrated Species" was utilized as the physics of this system.

$$\nabla \cdot \mathbf{j}_i + \rho \mathbf{u} \cdot \nabla w_i = R_i \quad (1)$$

where $\mathbf{j}_i$ represents the diffusion of species i , $\rho \mathbf{u} \cdot \nabla w_i$ convection and R_i the rate of H_2 flux across the membrane. Diffusion of species i is assumed as:

$$\mathbf{j}_i = - \rho D_{im} \nabla w_i + \rho w_i D_{im} \nabla M_n / M_n \quad (2)$$

$$D_{im} = 1 - w_i \neq i x k D_{ik} \quad (3)$$

$$M_n = i w_i M_i - 1 \quad (4)$$

The mass flux of the system was defined by Equation 5:

$$N_i = \mathbf{j}_i + \rho \mathbf{u} w_i \quad (5)$$

The equation of motion (Eq. 6 and Eq. 7) was used to describe the flow of syngas inside the module:

$$\rho \mathbf{u} \cdot \nabla \mathbf{u} = \nabla \cdot (-p \mathbf{I} + \mu \nabla \mathbf{u} + \nabla \mathbf{u} T + \mathbf{F}) \quad (6)$$

$$\nabla \cdot \rho \mathbf{u} = 0 \quad (7)$$

The change in density as a function of the mass fractions in the module was defined as:

$$\rho = p R T i w_i M_i - 1 \quad (8)$$

In contrast with previous models which applied source and sink terms to simulate transport across the membrane, this model used a reacting boundary flux based on Sieverts' Law (Eq. 9):

$$-n \cdot \mathbf{N}_i = P_{H_2} p_{H_2}^{shell} - p_{H_2}^{tube} \quad (9)$$

Where $n \cdot N_i$ represents the H_2 flux across the membrane, P_{H_2} the permeance of the membrane, and $p_{H_2}^{shell}$ and $p_{H_2}^{tube}$ the H_2 partial pressure at the shell and at the tube, respectively.

The simulation model used in this work has the following assumptions:

- 1) Laminar flow
- 2) Isothermal system
- 3) Gas flow was symmetrical along the membranes
- 4) Outlet had a pressure of 12.6 bar with no viscous stress

A fine mesh was defined containing 2,000,000 elements (Figure 5). A direct solver with two segregated groups was adopted for the calculation. A super computer with 130 GB RAM memory was used in this work.

Figure 5. Geometry of the model and mesh.

3. Results

3.1 Synthesis of the membrane module and set-up

After Au deposition, the membranes were stored at 40°C for 6 months under air. The He leak of the membranes after this period changed as shown in Figure 7. Notice that some membranes presented an increased He leak while others decreased. It is suspected that overall, all membranes had an He leak increase and that the membranes which showed a reduction in He permeation were mainly affected by moisture blocking the defects present on the surface of the membranes. Due to the change in the He leak, a topmost layer was formed on top of the Pd before the module was assembled with seven of the eight membranes and subsequently shipped to the NCCC facilities. Notice that the replicability of synthesizing these membranes is effectively demonstrated, having a standard deviation in the Pd layer thickness of 0.9 μm or about 10%.

Figure 7. He leak of each membrane as fresh Pd/Au, after storage and final leak.

The multitube membrane module was designed to hold seven Pd/Au/Pd membranes. The module had one membrane located at the center of the module and six equally spaced membranes surrounding it. The surrounding membranes were kept at 1.31 in. from the central membrane and were distributed in a hexagonal arrangement; the membrane module was designed to have a length of 38 in., as shown in Figure S2 (Supplementary Materials). The axial positions of the membranes varied in order to allow Swagelok connections within the confinement of the 4.5 in. OD shell of the module. For instance, the connection of the central membrane was at a longer position than the surrounding ones; while the position of the remaining connections was alternated between shorter and medium lengths, as shown in Figure S2 (Supplementary Materials). A holder was placed on the tip of the membranes to maintain the configuration of the membranes and potentially act as a baffle for better mixing of the gases. The multitube membrane module had a shell-and-tube configuration and was sealed utilizing an assembly consisting of flanges, studs and clamps (Grazyloc 4 in.) which can be seen in Figure S2 (Supplementary Materials).

3.2 Permeation Test Results

As in previously reported gasification runs at NCCC [9,10], approximately 10 lb/h of gas with a variable composition was fed to the module as shown in Figure 9. At first, the module was tested under a 35:65 H₂/N₂ mixture for 100 h followed by flowing coal-derived syngas which was composed mainly of H₂, CO₂, N₂ and CH₄ for ~700 h.

The initial evaluation of the performance of the membrane module was based on its H_2 permeance or pressure normalized flux (PH_2), produced H_2 purity and H_2 recovery (R) as defined in Equations 10-12:

$$PH_2 = FH_{2, permout} A pH_{2ave} - pH_{2perm} \quad (10)$$

$$Purity = \frac{FH_{2, permout}}{FH_{2, permout} + F_{i, permout}} \cdot 100 \quad (11)$$

$$R = \frac{FH_{2, permout}}{FH_{2, feed}} \cdot 100 \quad (12)$$

Here $FH_{2, feed}$ and $FH_{2, permout}$ are the H_2 flow rates for the feed and the permeate outlet streams, respectively. A is the permeable surface area of the membranes, pH_{2ave} and pH_{2perm} are the H_2 partial pressures inside the module shell and in the permeate side, respectively. Given the number of data points, pH_{2ave} was approximated as the average of the H_2 partial pressure of the feed ($pH_{2, feed}$) and the retentate ($pH_{2, ret}$).

Figure 9. Composition of the gas mixture fed to the module as a function of time.

The H_2 permeance and purity of the module are displayed as functions of time as shown in Figure 11. At first, the membrane module showed a permeance in the range of $7\text{--}10 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$ when tested under H_2/N_2 mixture as depicted in Figure 11 in solid black data points. When syngas was fed into the module, a slight oscillation in permeance was observed during the first 100 h, followed by a steady performance. Notice that the average permeance under H_2/N_2 mixture and syngas were found to be of 8.8 and $8.2 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$, respectively indicating a 7% reduction in permeance under syngas conditions. The maximum flux achieved by these membranes was 6 lb/day of H_2 . It is important to mention that the module displayed constant properties (Figure 11) even though the continuous changes in the feed stream were present.

Furthermore, the additional synthesized membrane MTM-8 with the same dimensions and characteristics was tested in the facilities of Worcester Polytechnic Institute under clean and pure H_2 . The H_2 permeation test is shown at 350 and 450°C in Figure 13, displaying permeances of 75 and $80 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$, respectively. In terms of flux the membrane showed a maximum productivity of 1.03 lb/day at a pressure difference of 0.35 bar. Moreover, a hypothetical multitube model composed of pure free-standing Pd membranes with a thickness of $7.4 \text{ }\mu\text{m}$, and tested under pure H_2 at 450°C was calculated to have a theoretical H_2 permeance of $63 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$. In addition, the single tube membranes previously tested under similar syngas conditions at NCCC [9], showed H_2 permeances between $5\text{--}15 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$ and under pure H_2 at WPI permeances between $10\text{--}29 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$. The reduction of the cumulative H_2 flux across this multitube membrane is attributed to i) the fast depletion of H_2 along the membrane module; ii) the mass transfer resistance caused by the boundary layer formed at the surface of the membrane; iii) the permeance inhibition caused by CO, CO_2 and steam [28]; and finally iv) the potential sulfur content on the feed lines of the system at NCCC as previously reported [10]. At these operating conditions, the module presented a depletion of H_2 along the membrane module hindering the actual value of the permeance. For instance, the feed stream presented an average H_2 partial pressure of 4.3 bar and it was reduced to 2.5 bar at the retentate outlet or by a factor of about 1.7. This reduction in driving force is not linear, as assumed in the present estimation of the permeance shown in Figure 11. Furthermore, radial mass transfer limitations cause concentration polarization which occurs when H_2 diffusion is slower than the permeation rate. Indeed, the presence of a H_2 depleted boundary layer can significantly reduce the displayed H_2 flux across the membranes [29].

Figure 11. Hydrogen permeance and purity profiles of the multitube membrane module at NCCC under H_2/N_2 and syngas at 450°C and 12.6 bar.

Figure 13. Hydrogen permeance of membrane MTM-8 at WPI under pure H_2 at 450°C and 1 bar.

A non-linear mathematical analysis was performed in order to approximate more accurately the permeance of this module. By neglecting the presence of uneven radial mass distribution and mass

transfer resistances, but including the nonlinearity of the H_2 partial pressure within the module, the permeance of the membrane module was estimated by solving the differential equation shown in Eq. 13. FH_2 is the local H_2 flow rate across the membrane module, A the total permeable surface area, and pH_2 is the local H_2 partial pressure, which is defined as the product of the total operating pressure and the local H_2 mole fraction in the retentate (Eq. 14). The initial conditions of this ODE were specified as the given average experimental values such as feed gas composition and flow rate.

The permeance was adjusted accordingly in order to match the displayed H_2 recovery, retentate composition and total H_2 flow rate at the outlet of the permeate stream. Notice that given the complexity of this calculation, the permeance estimate was shown only for the average properties rather than for every single point through time as the data shown in Figure 11. The H_2 permeance of the membrane module was estimated to be $16.2 \text{ Nm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-0.5}$, which is considered to be a more accurate value than that obtained using Eq. 13, because p_{H_2} on the retentate side was allowed to vary nonlinearly, as shown in Figure 15.

$$dFH_2/dA = pH_2 \cdot p_{H_2} - p_{H_2,perm} \quad (13)$$

$$p_{H_2} = p_{total} F_{H_2,ret} / F_{i,ret} \quad (14)$$

Figure 15. Axial distribution of the retentate H_2 flow rate, showing the difference between the linear and refined mathematical approximation

The presence of CO is well known to affect the permeance of Pd membranes [28]. Competitive absorption of CO within the active sites available reduces the potential solution of more H₂ molecules and consequently inhibits their performance under ideal conditions. It is important to mention that other contaminants present in syngas such as sulfur have been shown to reduce the permeance of Pd membranes. Our group [9,10] showed in single tube Pd and Pd-Alloy membranes that even traces of sulfur can significantly reduce the H₂ permeance; nevertheless, the presence of the Au aids in the recovery of the lost permeance by exposing the membranes to pure H₂ at 450°C. Other contaminants such as Na, Mg, O, S, Hg and C were previously found on the surface of the Pd membranes tested under coal derived syngas [10].

The H₂ purity produced by these membranes began at 99.5% under H₂/N₂ and underwent a sudden increase to 99.63% when syngas was fed and up to 99.87% after being tested for 67 hours in syngas conditions. Afterwards, the purity of the module decreased steadily reaching a minimum purity of 98.84% after 670 hours under syngas conditions. Notice that at the end of the test, the H₂ purity was 98.13% under a H₂/N₂ mixture. It is important to mention that the lifetime of these Pd-Au-Pd membranes is significantly improved compared to pure Pd membranes, whose life time is estimated at 200 h under industrial settings [9,30]. Additionally, the single tube membrane tests previously reported [9] showed Pd/Au composite membranes displaying H₂ purities in the range of 99.95-99.8% with a lifetime of 535 hours for a Pd/Au/Pt membrane. Furthermore, the H₂ purity profiles achieved by this technology throughout the testing time clearly outperform the ones exhibited by conventional technologies such as cryogenic distillation [22,31]. Additionally, assuming that the purity of the permeated H₂ decreases linearly with time, as shown by Figure 11, it is expected that this module will produce H₂ with a purity of 91% after a year of continuous operation. Furthermore, once the defects of the membranes become significant, they can be regenerated by surface cleaning and palladium replating, reducing the leak of the membranes and extending their total lifetime [24].

Figure 17 shows the H₂ recovery achieved under the aforementioned conditions as a function of time. Notice that when the membrane module was under H₂/N₂ at the beginning of the test, the average recovery was estimated to be 52%. Under syngas conditions, the average H₂ recovery increased to 64%. This effect can be explained by analyzing the H₂ flow rate of the feed stream. As mentioned before, 10 lb/h of gas was fed into the module, but the different compositions between the H₂/N₂ mixture and syngas caused changes in the molar flow of H₂. For instance, 10 lb/h of gas feed is equivalent to 88 mol/h of H₂ fed for a (35/65) H₂/N₂ mixture, but it is 79 mol/h of H₂ fed for syngas enriched to 35%; there is a 10% difference in H₂ molar flow rate between the H₂/N₂ mixture and syngas. Furthermore, the space velocity

of the gases is different for H_2/N_2 and for syngas. It is estimated that $5.5 \text{ m}^3/\text{h}$ of H_2/N_2 was fed into the system at standard conditions, while syngas had a volumetric flow rate of $4.9 \text{ m}^3/\text{h}$.

Indeed, having a higher feed flow rate directly affects the recovery achieved (Figure 19) by the module since higher membrane surface area is needed to accomplish the transport of all H_2 molecules fed, even though the H_2 partial pressure is similar. Higher feed flow rate utilizes the available surface area of the membranes better, even though recovery is reduced. In other words, obtaining a low H_2 recovery directly implies that the membranes were occupied evenly and that the displayed permeance is closer to the permeance under pure H_2 . High recoveries, such as those presented in this work, do not show the maximum H_2 flux that the module can achieve, since it is hindered by H_2 depletion within the unit. Figure 19 shows the module's H_2 recovery as a function of the H_2 feed flow rate. An exponential decay is observed and a plateau can be predicted at a recovery of $\sim 40\%$.

Notice that the maximum theoretical H_2 recovery achievable by the module is $< 90\%$, which can be improved by reducing the permeate H_2 partial pressure with the presence of sweep gas in the permeate side and/or by increasing the retentate pressure. Additionally, it is expected that the presence of baffles could improve mixing and avoid mass transfer resistances, improving further the H_2 recovery of the module [18].

The successful results obtained from the 7-membrane module tests reported here demonstrate that the good performance previously found [9,10] for a single membrane tube can be scaled up. These results are promising for the future development of palladium composite membrane modules with more tubes and hence greater permeation area.

Figure 17. Hydrogen recovery and H₂ partial pressure of the multitube membrane module tested at NCCC.

Figure 19. Hydrogen recovery as a function of the feed H₂ flow rate.

4. Discussion

Through a computation fluid dynamics (CFD) model, a compelling visualization of the mass transport phenomena occurring inside the membrane module was generated. The CFD model generated data at different permeances, predicting the performance of the actual system as shown in Table 1. Key parameters (permeation rate, H₂ content at the retentate and recovery) were most accurately projected by the model, assuming a permeance of 16 Nm³h⁻¹m⁻²bar^{-0.5}; it is important to highlight that this value is close to the 16.2 obtained earlier. The results presented in this work have an error of 2%, which could be further reduced by refining further the numerical mesh, as depicted in Figure 21. Certainly, although Figure 21 does not show the results to be mesh-independent; given the purpose of this discussion and the lack of computational power, the analysis of the results with this accuracy is certainly justified.

Table 1: Comparison of CFD data with experimental data.

	Experimental	Simulation Permeance=14 Nm ³ h ⁻¹ m ⁻² bar ^{-0.5}	Simulation Permeance=16 Nm ³ h ⁻¹ m ⁻² bar ^{-0.5}	Simulation Permeance=18 Nm ³ h ⁻¹ m ⁻² bar ^{-0.5}
Permeate flow rate (L/min)	17.47	17.77	18.99	20.04
Retentate H ₂ Percentage (%)	22.35	23.30	22.34	21.50
Recovery (%)	37	35.37	38.06	40.39

Figure 21. Mass balance error at different mesh refinements.

The CFD model generated representative H_2 concentration profiles inside the multitube membrane model as shown in Figure 23. Syngas is fed on the right side of the picture and exits the multitube module on the left side of the picture. The axial H_2 concentration profile (Figure 23a) shows syngas with a high H_2 concentration on at the entrance (red) , which gradually reduces when approaching the exit of the module. The radial H_2 concentration profile (Figure 23b) changed axially. For instance, close to the syngas feed side, an even radial H_2 distribution is depicted (red); nonetheless, downstream, radial distribution gradients become more apparent. In particular, a H_2 depleted region (blue) adjacent to the membrane surfaces is clearly observed, while an increased H_2 concentration appears between the membrane tubes. These radial concentration differences cause the aforementioned concentration polarization effect.

Figure 23. a) Axial and b) radial H_2 concentration profile inside the retentate of the multitube membrane module.

Based on the visualization presented in Figure 23, it is possible to infer that multitube membrane systems differ with single tube systems in two main aspects: i) multitube modules have higher membrane surface area to volume ratio and ii) not all membranes operate evenly. High surface area to volume ratio is beneficial in terms of productivity, as these architectures can generate higher amounts of H_2 than single tube modules, notably shown in hollow fiber membrane units [32]. Nonetheless, increasing the membrane surface area in a constraint volume raises issues of cleaning, design and operation.

The uneven operation of the membranes is analyzed by comparing the productivity of each membrane within the module. The membranes are numbered from 1 to 7, as shown in Figure 25, and their productivity normalized by the total system output or total H_2 flux. The bar chart in Figure 25 shows

variations in the productivity of all tubes; nevertheless, the variation among tubes 2 to 7 can be explained by the numeral error of the simulation. Tube number 1, on the other hand, shows a slightly reduced productivity, compared to the surrounding membranes. In order to explain this phenomenon, three regions are defined in the cross sectional view of the module (Figure 25): α region represents the area between the wall of the module and the surface of membranes 2 to 7, β is the area surrounding membrane 1, and γ is the zone entangled by the outer tubes and the wall of the module.

Membrane tube 1 has a reduced productivity due to the competition for H_2 among adjacent membrane tubes. In other words, the local H_2 concentration at zone β is shared among membrane 1 and its surrounding counterparts. In contrast, the surrounding tubes have an “exclusive” region denoted by the α zone. This area has little to no competition for H_2 with other membranes, and therefore, it appears to be preferentially depleted compared to other regions. It is important to mention that the area comprising α is lower than β , and therefore, β is less prone to depletion. Zone γ is shared by two neighboring membranes positioned externally, making competition less intense than β and also less exclusive than α . Therefore, this γ zone contains the highest H_2 content radially. As the flow moves downstream, H_2 in the γ region will preferentially diffuse towards the depleted α zone, due to a higher concentration gradient, and then towards membranes. This effect allows membranes 2-7 to have higher H_2 productivity than membrane 1.

Figure 25. Radial H_2 distribution and single membrane performance of the multitube membrane module.

To support this hypothesis, the H_2 permeation rate of the central membrane and that of a surrounding one is comparatively analyzed axially, as shown in Figure 27. The origin of the x-axis is defined as the tip of the membranes and it is the closest point to the feed stream. The flux across a single point on the surface of the membrane was computed along the membrane length (x-axis). It is important to mention that the outer membrane was analyzed in four different sections, designated by the “zone” normal to its surface. The central membrane was analyzed at the points where its surface faces other surrounding membranes directly, as shown in the schematic in Figure 27. In other words, the “central”, “ β ” and “ α ” permeation points always lined up in a straight line, while “ γ ” points remained at 90° from the “ β ” point.

To begin the analysis of Figure 27, it is important to recognize that at distances smaller than the origin, no H_2 flux occurs as it belongs to the non-permeable stainless steel caps of the membranes; therefore, a sudden increase in flux can be appreciated afterwards. Further downstream, all points show the largest permeation rates, as syngas contains the largest amount of H_2 at this location. Subsequently, the permeation rate is reduced consistently until syngas exits the module.

The flux across the different points shows a similar trend, but with different magnitude. Let us compare those points that share the β zone, which include the “central” and “ β ” points. These permeation-points show a similar flux magnitude and both comprise the lowest flux among the points analyzed. Indeed, as mentioned previously, the H_2 contained in the β zone is removed and shared by two adjacent membranes, causing a reduced driving force for permeation. The “ γ ” points show a higher flux than those points sharing the β zone. Although, the γ zone is shared by two membranes like β , competition is less prominent since this “ γ ” point does not have a parallel membrane surface that competes for the H_2 available. Furthermore, the “ γ ” point is constantly supplied with H_2 that diffuses from local H_2 enriched spots depicted in red-orange in Figure 25 and Figure 27. Point “ α ” appears to be the most effective spot surrounding an externally placed membrane. The lack of competition for H_2 allows these zones to be effectively depleted at first, generating a “black hole” which attracts H_2 from the γ zones. The significant concentration gradient between the α and γ zones, induces diffusion to the noncompetitive region, thus allowing higher permeation rates.

Through these simulation results, it is possible to conclude that these multitube membrane units differ from single tube modules and that special consideration needs to be addressed while designing them. The model presented in this work showed symmetry which significantly simplified the analysis; nonetheless, a change in flow pattern due to the presence of baffles and/or the location of the feed and retentate, still represents a significant challenge. Furthermore, this work shows that through a detailed CFD analysis, it is possible to improve the design of the modules and further optimize their operation.

Finally, through a “localized membrane analysis”, such as the one presented in this work, it is possible to predict deteriorations on specific membranes and/or sections of the membranes within multitube membrane units. Defects on these membranes, which are usually generated by usage, can be replaced or mechanically fixed [24].

Figure 27. Hydrogen flux along the membranes at different points around the membranes.

5. Concluding Remarks

A multitube membrane module using seven membranes was tested in actual coal derived syngas at NCCC, demonstrating the high robustness and excellent physical integrity of composite membranes. The membranes were synthesized over pretreated porous stainless steel supports to form composite asymmetric Pd/Au/Pd layers. The replicability of this technology was demonstrated by the synthesis of membranes with similar thickness and deviating by only 1%. Furthermore, the multitube membrane module was tested for 842.25 hours at 450°C producing a 6 lb/day of high H₂ purity in the range of 99.87-98% throughout the test. The H₂ permeance of the membrane was very stable showing values of 8.8 and 8.2 Nm³m⁻²h⁻¹bar^{-0.5} under H₂/N₂ mixture and syngas, respectively. Furthermore, by neglecting mass transfer resistances, but taking into consideration the nonlinearity of the Sieverts' law, a more realistic average permeance of 16.2 Nm³m⁻²h⁻¹bar^{-0.5} was obtained. The H₂ recovery of the module was between 52

- 64% and was a function of the volumetric feed flow rate of the gases. Furthermore, it is clear that the membranes developed displayed a reliable performance under adverse industrial conditions such as those presented in this work including medium-high temperatures, high contaminant concentrations and fluctuations in operating parameters. It can be therefore concluded that this technology could be scaled up and seriously considered as a viable option in industrial applications. Furthermore, the developed computational fluid dynamic model (CFD) revealed differences in membrane usage for this seven-tube configuration. The membrane located at the center displayed a reduced efficiency, possibly caused by the presence of the surrounding membranes which increased competition for the H_2 available. The surrounding membranes displayed variations in flux for each quadrant of the membrane surface, mainly caused mass transfer phenomena. Finally, it is possible to conclude that multitube membrane systems require specific considerations in scale-up that differ from single tube membrane units.

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Nomenclature

ρ	Density of the gas mixture	kg/m^3
P_i	Partial pressure of component i in the reaction zone	bar
Da	Damkohler number	–
$GHSV$	Gas hourly space velocity	h^{-1}
	Mass flux of component i	mol/s
R_g	Ideal gas constant	$J/K/mol$
	Hydrogen permeance of the membrane	$Nm^{-2}\cdot m^{-2}\cdot h^{-1}\cdot bar^{-0.5}$
T	Temperature	K
Δ	Delta index	–
t	Membrane's thickness	μm
u	Velocity field	m/s
F	External body forces (gravity, electric, etc.)	N
I	Identity matrix	–
	Binary diffusion coefficient between components A and B	cm^2/s
	Molecular weight of component A	g/mol
	Collision integral for diffusion	$\text{\AA}$
σ_{AB}	Lennard–Jones potential between molecules A and B	–
	Mass fraction of species	–
	Molar fraction of species	–
	Viscosity of the fluid	$Pa\cdot s$

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