A CFD Analysis of the Operating Conditions of a Multitube Pd Membrane for H_2 Purification

B. Castro-Dominguez[1*], R. Ma[1], A.G Dixon[1] and Y. H. Ma[1]

[1]Worcester Polytechnic Institute, Department of Chemical Engineering

*Address: 100 Institute Road, Worcester, MA 01609. Email: bcastrodominguez@wpi.edu

Abstract: The optimization of operating conditions in multitube membrane modules is a complex process. The multiple physics and irregular geometries involved on these systems create a challenge for predicting their behavior. This work analyses the performance of H_2 purification through a module containing seven membranes. Using experimental parameters, a 3-D model was devised, specifying the membrane as a reacting boundary based on Sieverts' law. Both continuity and Navier-Stokes equations were coupled and solved. The analysis of this module showed the formation of a H_2 depleted boundary layer adjacent to the surface of the membrane which is often called concentration polarization. This phenomenon is caused by radial diffusive limitations and it reduces the efficiency of the module. The axial effects of advection at higher Reynolds numbers reduced polarization, but reduced the H_2 recovery of the process. An optimum recovery-polarization point was found maximizing the efficiency of the module.

Keywords: Multitube Membrane Module, Palladium Membranes, Concentration Polarization, Mass Transfer

1. Introduction

The production of hydrogen is a major process for the chemical industry as well as for the energy sector. Currently, H_2 is mainly produced by methane steam reforming and water gas shift reactions. These processes yield syngas which is a mixture composed of H_2, N_2, CO, CO_2 and unreacted CH_4. Therefore, the economic and efficient purification of H_2 is needed. Palladium membranes provide these characteristics especially when compared to other technologies such as cryogenic distillation and pressure swing adsorption.

Palladium membranes remove H_2 by catalyzing the dissociation of the molecule at the surface and diffusing it through the lattice of the metal. Other gases do not react and cannot penetrate the solid Pd film layer; hence, ultrapure H_2 is expected.

For industrial purposes, compact modules with high membrane surface area are desired, generating the need for multitube membrane modules. The physics involved and the geometry make the behavior of multitube membrane modules difficult to predict and simulate but necessary for implementing this technology.

The simulation of single tube membrane modules has been previously reported. For instance, He et al [1] developed a mathematical model capable of predicting the presence of concentration polarization. Coroneo et al. [2] developed a one-tube membrane module in a 3-D scheme. The flux model was created using source and sink based on Sievert's law for each side of the membrane. Later, they developed a non-isothermal model to evaluate the effect of temperature on permeance [3]. It was found that the permeate flow rate increases when temperature increases. In another work, Chen et al. [4] studied the effects of the operating conditions such as flow pattern (co-current and counter-current) and flow rate. A 2-D model was used using COMSOL Multiphysics 4.0a. The counter-current flow mode was reported to improve the H_2 flux. Nevertheless, as the feed flow rate increased, the effect of the flow pattern decreased. In addition, Chen et al. [5] studied the influence of the geometry in a single tube module. It was found that a smaller module reduces concentration polarization effectively. Recently, Coroneo et al. [6] developed a model for the analysis of a 3-membrane module containing baffles. They showed that adding baffles divides the module in sections preventing the overall dilution of the retentate and increasing the driving force.

This work uses COMSOL Multiphysics 4.3b to study the operating conditions of a seven membrane module. A novel approach, a reacting boundary, was used to describe the H_2 transport across the membrane.

2. Description of the System

The multitube membrane module consists of 7 palladium membranes. Six membranes were arranged in a hexagonal shape surrounding a central one (Fig 1). An impermeable tube cap is present at the tip for each membrane tube. A nonporous tube is attached to the other side of the membranes. The feed stream is located in front of the membrane caps and its pipe diameter is smaller than the shell or module diameter as shown in Fig. 1. The permeated H_2 gas is collected from inside the membrane tubes. The gas that remained in the module, also called retentate, exits the module continuously containing H_2 depleted syngas.

Hydrogen enriched syngas is fed at the shell side with a pressure of 12.6 bar. Pure H_2 is recovered at the tube side exposed to atmospheric pressure. Table 1 contains a list of the parameters used in this simulation. These parameters are actual experimental values.

Table 1. Operational settings for the module

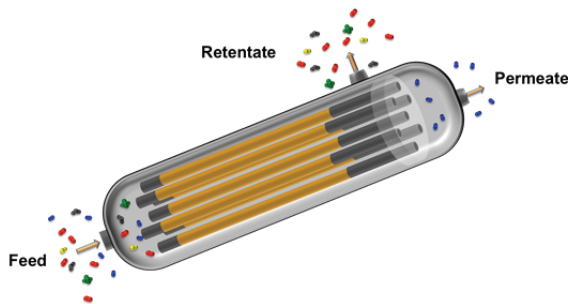| Shell Pressure / atm	12.6
Tube Pressure / atm	1
H_2 Permeance / mol m^{-2}s^{-1}Pa$^{-0.5}$	7.7×10^{-4}
Reynolds number	1-300
Initial gas composition /mole %	
H_2	43.0
N_2	50.0
CO	5.0
CO_2	1.5
CH_4	0.5

Figure 1. Representative sketch of the actual multitube membrane module

2. COMSOL Model

The geometry in Fig 1 was simplified by neglecting any physics occurring at end of the membranes as shown in Fig 2. The inlet stream diameter was specified to be smaller than the module.

The simulation used COMSOL Multiphysics 4.3b and "Reacting Flow" as the physics. This physics targets the removal of a specific species as reactants on the surface of a catalyst as specified by the species continuity equation in Eq.1:

$$\nabla \cdot j_i + \rho(u \cdot \nabla)w_i = R_i \qquad (1)$$

where $\nabla \cdot j_i$ represents the diffusion of species i, $\rho(u \cdot \nabla)w_i$ advection and R_i the rate of reaction. Diffusion of species i is assumed to be isothermal and was defined as in Eq.2:

$$j_i = - \left(\rho D_i^m \nabla w_i + \rho w_i D_i^m \frac{\nabla M_n}{M_n} \right) \qquad (2)$$

$$D_i^m = \frac{1 - w_i}{\sum_{k \neq i} \frac{x_k}{D_{ik}}} \qquad (3)$$

$$M_n = \left(\sum_i \frac{w_i}{M_i} \right)^{-1} \qquad (4)$$

The mass flux of the system was defined by Eq.5:

$$N_i = j_i + \rho u w_i \qquad (5)$$

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

$$\rho(u \cdot \nabla)u = \nabla \cdot \left(-pl + \mu(\nabla u + (\nabla u)^T) - \frac{2}{3}\mu(\nabla \cdot u)l \right) \qquad (6)$$

$$\nabla \cdot (\rho u) = 0 \qquad (7)$$

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

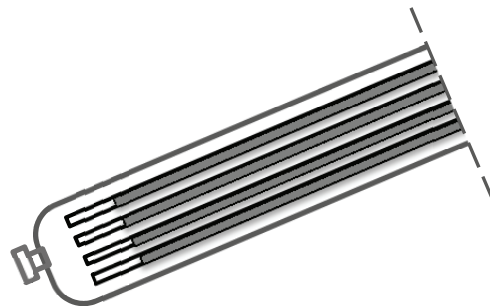$$\rho = \frac{p}{RT} \left(\sum_i \frac{w_i}{M_i} \right)^{-1} \qquad (8)$$

Figure 2. Simplified geometry of the multitube membrane module

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

$$-\text{n} \cdot N_i = \overline{P}_{H_2} \left[\sqrt{p_{H_2}^{shell}} - \sqrt{p_{H_2}^{tube}} \right] \quad (9)$$

Where $\text{n} \cdot N_i$ represents the H_2 flux across the membrane, $\overline{P}_{H_2}$ 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. Partial pressure on the tube side was set to be 1 atm.

The flow was assumed to be laminar in all cases. The inlet was specified to be a normal inlet flow. The outlet had a pressure of 12.6 bar with no viscous stress. The species transport had the initial mole fractions shown in Table 1. A Fine mesh was defined as shown in Fig 3 containing 3,181,368 degrees of freedom. 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.
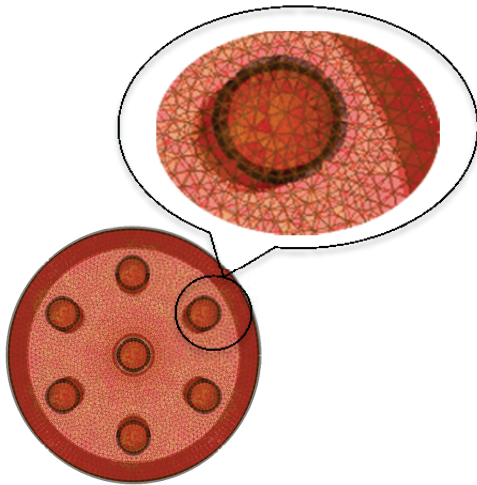

Figure 3. Cross-sectional view of developed mesh

Additionally, the H_2 recovery was analyzed and defined as the percentage extracted from the module through the tubes:

$$R_{H_2}(\%) = \frac{F_{H_2}^{in} - F_{H_2}^{out}}{F_{H_2}^{in}} \cdot 100 \quad (10)$$

Where $F_{H_2}^{out}$ and $F_{H_2}^{in}$ are the amount of H_2 at the outlet and the feed of the module, respectively. The usage of the membrane $\varphi(\%)$ was studied as well and defined as:

$$\varphi(\%) = \frac{\gamma}{\gamma_{max}} \cdot 100 \quad (11)$$

where γ is the amount of H_2 removed at any given Re, and γ_{max} the maximum theoretical H_2 flux across the membrane.

3. Results and Discussion

The behavior of the module was tested under different Reynolds numbers since advection forces affect the mass transport properties of the system. Different inlet velocities were used to modify the Re of the fluid flow. The velocity profiles, shown in Fig 4, depict that the velocity of the gas decreases after the expansion between the inlet and the membrane module. Velocity increases when the gases encounter the membranes; this is due to the reduction of available cross-sectional area.
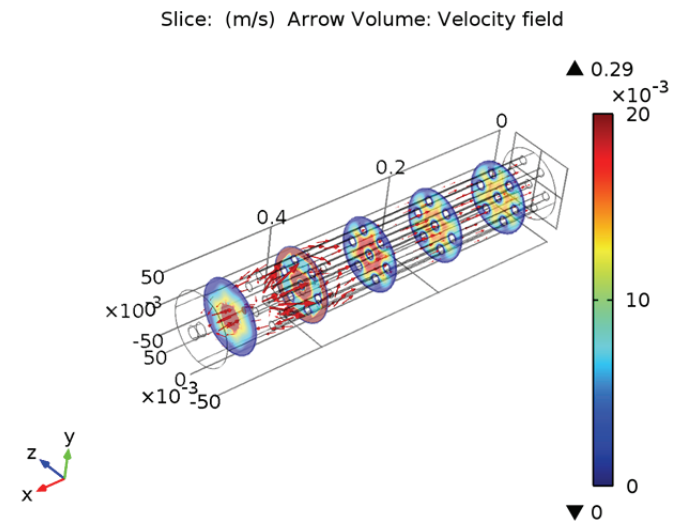

Figure 4. Velocity profile of syngas inside the membrane module at moderate Re numbers

As shown in Fig 5 and Fig 6, different Re numbers displayed different H_2 mole fraction profiles within the membrane module. For instance, at low Re numbers, H_2 is totally removed from the module (Fig 6a). Hydrogen has enough time to diffuse radially towards the surface of the membranes, before it is ejected out of the module. The H_2 recovery at this point is at its maximum point, but the membrane usage capacity is not exploited.

As the Re numbers increase, H_2 molecules do not reach the surface of the membranes as fast as before. This allows for the membranes to be used further down axially (Fig 6b). This continues up to the point where H_2 is unable to diffuse totally towards the adjacent membrane. At this point recovery starts to decrease. High Re numbers supply enough syngas, allowing the membrane

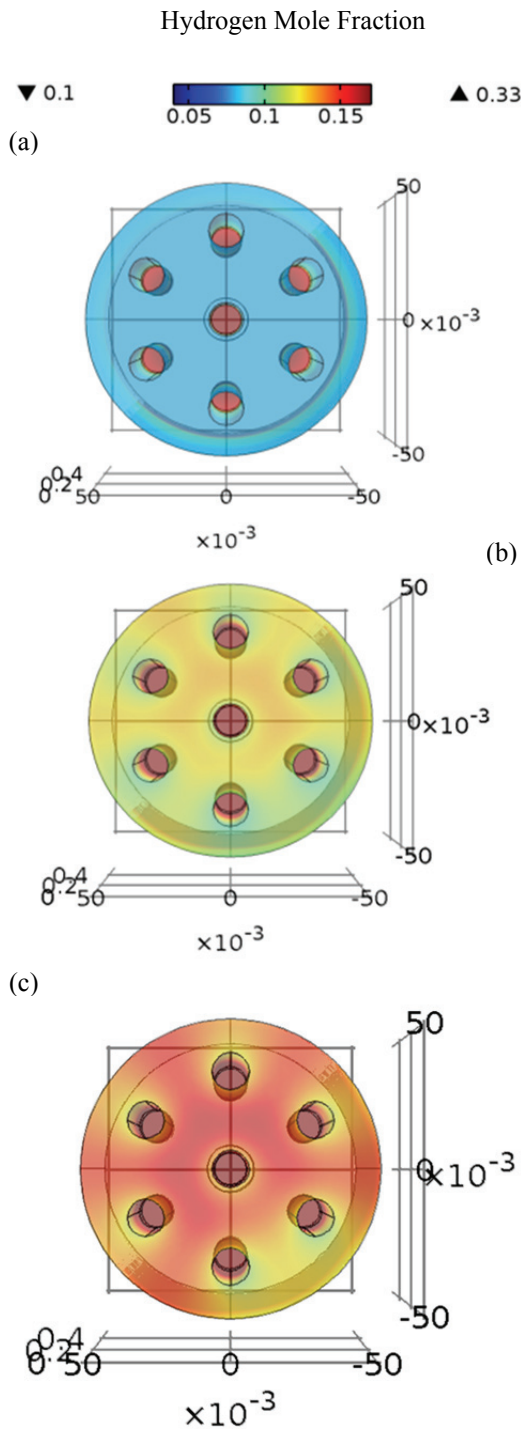to be more uniformly used axially (Fig 6c). However, recovery is significantly reduced.

Hydrogen Mole Fraction

Figure 5. Cross-sectional view of the H_2 mole fraction distribution at different Re numbers: a) Low Re number, b) Medium Re, c) High Re
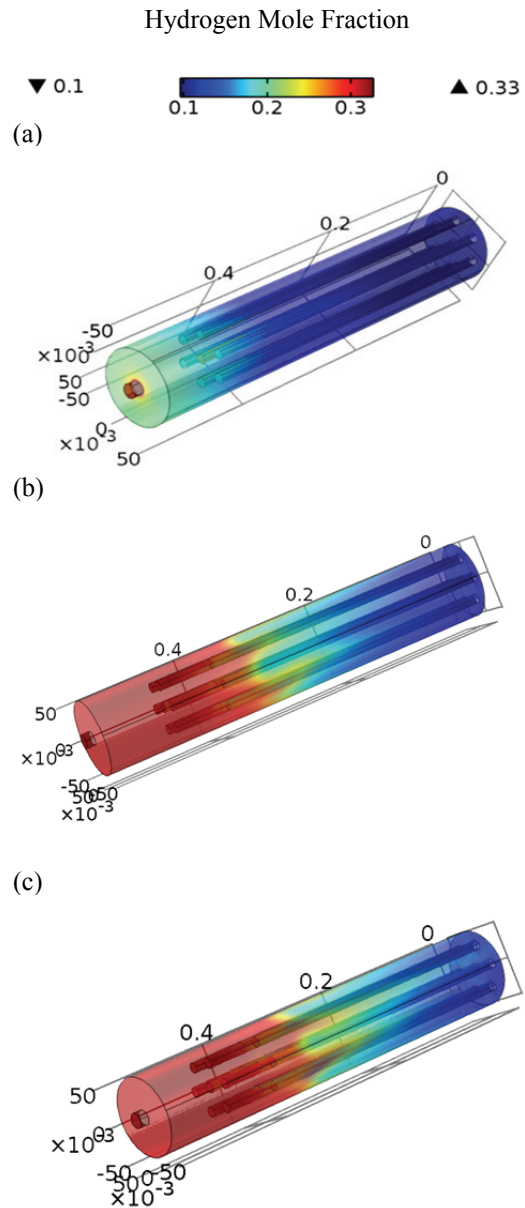
Hydrogen Mole Fraction

Figure 6. Axial view of the H_2 mole fraction distribution at different Re numbers: a) Low Re number, b) Medium Re, c) High Re

The module shows the formation of a H_2 depleted boundary layer adjacent to the surface of the membrane which is often called concentration polarization (Fig. 5). This phenomenon is caused by the slow diffusion of H_2 molecules in the radial direction.

Concentration polarization decreases the efficiency of the membrane since the driving force is dictated by the H_2 partial pressure difference between the H_2 molecules located next to the membranes surfaces at the retentate and the tube sides. At the tube side, it was assumed to be uniform since pure H_2 is present. However, at the retentate it changes according to the flow, gas composition and rate of removal.

The behavior of concentration polarization can be clearly seen in Fig 5, where the bulk syngas located far from the surface of the membrane is not disturbed. The boundary layer of depleted H_2 becomes thicker as the flow moves along the axial direction. At high Re numbers, the boundary layer becomes thinner. This caused by the constant H_2 supply by the advective flow. Therefore, high Re numbers increase the efficiency of the membranes; nonetheless, the H_2 recovery of the process reduces.

For the effective utilization of membrane technology, an optimization between recovery and membrane utilization needs to be performed. Fig 7 shows the Re number where the recovery and membrane utilization intersect, suggesting an optimal point for operating the module.
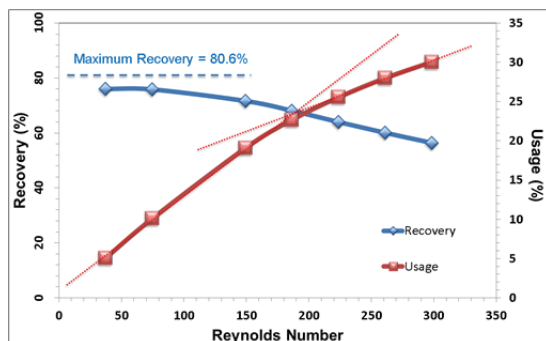

Figure 7. Recovery of H_2 and membrane utilization as a function of different Re numbers

The maximum theoretical recovery based on the operating conditions was estimated to be 80.6%, which corresponds to a membrane usage of <5%. At the optimum point, the recovery reaches ~65%, but the usage of the membranes dramatically increased to 25%. After the optimum point, the effect of higher Re numbers keeps improving the usage of the membranes, but to a lower extent. The recovery of H_2 keeps deteriorating after reaching the optimized condition.

4. Conclusion

The behavior of a seven-membrane module was simulated at different Reynolds numbers for the separation of H_2 from syngas. Low Re numbers showed that the membrane was utilized ineffectively but the recovery was high. At high Re numbers, the membrane was more evenly used but the H_2 recovery decreased significantly.

A boundary layer appeared adjacent to the membrane surface, caused by the depletion of H_2 and low diffusion rate in the radial direction. This boundary layer, also known as concentration polarization, decreased the efficiency of the membrane by reducing the H_2 partial pressure at the vicinity of the membranes' surface.

High flow rates reduced concentration polarization but at the same time lowered the recovery of the membrane. Therefore, the optimal Re number of operation was found to be at the point where the recovery and the membrane usage intersect.

5. References

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6. Acknowledgements