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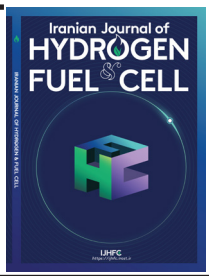

Modeling and simulation of the fluid dynamic and performance of a Pd-based membrane by CFD for hydrogen separation

Milad Khodaei[1], Zeinab Darabi[1], Mina Omidifar[1], Ali Akbar Babaluo[1*]

[1] Nanostructure Materials Research Center, Chemical Engineering Faculty, Sahand University of Technology, Tabriz, Iran

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Abstract

In this paper, the capability of the Computational Fluid Dynamics (CFD) approach to reliably predict the fluid dynamic and the separation performance of Pd membranes modules for gas mixture separation is evaluated. In this approach, the flow fields of the pressure and velocity for the gas mixture and the species concentration distribution in the selected three-dimensional domains are obtained by the simultaneous, numerical solution of continuity, momentum, and species transport (especially, the gas-through-gas diffusion term derived from the Stefan–Maxwell formulation) equations. Therefore, the calculation of the hydrogen permeation depends on the local determination of the mass transfer resistance caused by the gas phase and membrane, which is modeled as a permeable surface of known characteristics. The applicability of the model to properly predict the separation process under a wide range of pressures, feed flow rates, temperatures, and gas mixtures compositions is assessed through a strict comparison with experimental data. Moreover, in this work, the influence of the inhibitor species on the module performance, which is obtained by implementing the CFD model, is discussed. The results of the simulation showed that increasing the pressure on the feed side increases the molar fraction of hydrogen gas and the feed inlet flow on the shell side, and the hydrogen permeation through the membrane in the tube side. Comparison of simulation results with laboratory data showed good agreement. The model was obtained with an error of less than 3% at 450K and below 6% for 475K and 500K.

1. Introduction

Energy is fundamental for the development of modern nations. Fossil fuels are a major source of energy. Challenges of using this type of fuel include limited resources, high energy prices, and environmental pollution. Much efforts has been directed towards developing renewable, portable, and environmentally friendly energy technologies to address these challenges. Since the only by-product of the combustion

*Corresponding Author: a.babaluo@sut.ac.ir

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of hydrogen is water, it has been introduced as a key factor that poses no danger to the environment [1, 2].
In recent years, hydrogen has been widely used in numerous industries such as petroleum refineries, petrochemical processing (ammonia synthesis, methanol production, etc.). Nowadays, high purity hydrogen has become even more important due to new and different applications, such as fuel cells [3-5]. One of the important uses of pure hydrogen is in fuel cells. The fuel cell efficiency is 60 %, while the efficiency of the steam power plant and combustion engines is 35 % and 20 %, respectively. In other words, electric energy from fuel cells can operate at a higher efficiency than combustion engines. Hence, the use of hydrogen as a carrier of energy would extend the life of fossil fuels available today [6, 7].
Common methods of hydrogen production include electrolysis, biological methods, partial oxidation, and reforming of hydrocarbons. Among these, hydrocarbon reforming is one of the most important and main methods of hydrogen production, and about 48% of the hydrogen produced in the world comes from natural gas reforming. The hydrogen produced cannot be used directly by any of the above methods because, in addition to hydrogen, there may be impurities such as carbon dioxide, unreacted hydrocarbons, oxygen, nitrogen, and ions. Ultra-pure hydrogen is needed in numerous industries such as fuel cells. Currently, pressure swing adsorption, cryogenic recovery, and membrane separation are three methods to separate hydrogen from a gas mixture. Compared with other methods, membrane separation technologies have many significant advantages, such as low energy consumption, ease of scaling up, mild process conditions, minimizing equipment size, and low operating costs. In the field of hydrogen membrane separations, palladium and its alloys membranes have been noted due to their remarkable permeability and exclusive hydrogen perm-selectivity [8-13].
Due to the costly and time-consuming nature of laboratory studies, computational fluid dynamics can be a good predictor of fluid behavior without experimentation. In Pd-based membranes, which have a high selectivity for hydrogen, the effect of convective resistance on the mass transfer process, the concentration polarization, and ultimately the membrane separation performance can be significant. Therefore, the design and optimization of an appropriate model are aided with the use of modeling methods by simultaneous evaluation of the fluid flow and the membrane properties. Fluid dynamics calculation methods are very useful for this purpose. They also allow us to examine the membrane conditions in each part of the module, which ultimately leads to the discovery of the effect of membrane performance under different operating conditions, different membrane shapes, and sizes [14, 15]. In Pd membranes, the effect of convective resistance on the membrane is as important as the strength of the membrane and the support. Therefore, accurate evaluation of the local fluid dynamics, as well as mass transfer characteristics, is very important [16]. The purpose of this work is to provide a model for hydrogen purification using a Pd membrane. The model was implemented under different conditions, and the model's ability to predict the separation process under different operating conditions of temperature, pressure, and multi-component feed was investigated.

2. The CFD model

For proper modeling of the membrane module behavior, the fluid dynamic study was addressed, considering the influence of the permeation process on the gas velocity field and the species concentration distribution. To this aim, a CFD approach was devised that couples these two phenomena. With this method, the local fluid dynamics and mass transfer properties of the module can be calculated, and also the weight of gas resistance in the separation process efficiency can

be evaluated. A 3D-axisymmetric isothermal model was developed using the CFD method to simulate the performance of a dense Pd membrane for hydrogen production. Assumptions for this model are:

- Steady-state conditions,
- Isothermal conditions,
- Infinite hydrogen perm-selectivity of dense Pd membrane to other gases,
- Physical properties, such as gas density, are constant with temperature.

The laminar, three-dimensional, and steady-state flow of the gas mixture in the membrane module was computed through the numerical solution of Navier–Stokes equations [17]:

$$\nabla.(\rho U) = 0 \quad (1)$$

$$\nabla.(\rho UU) = -\nabla_P + \nabla.\tau + \rho g \quad (2)$$

where ρ is the gas mixture density, U is the velocity vector, p is the static pressure, τ is the viscous stress tensor, and g is the gravitational acceleration.

The transport of each component of the gas stream was obtained through the numerical solution of the local mass balance, based on the assumption that each species moves in the module by convection and molecular diffusion. The transport equation for the "i" species in the system is as follows:

$$\nabla.(\rho UY_i) = -\nabla_{j_i} + S_{H2} \quad (3)$$

where Y_i is the mass fraction of i species, J_i is its diffusive flux, and S_i is the source term, which accounts for the mass flux of the species through the membrane. The main purpose of this model is to investigate the fluid dynamics throughout the module and its transport characteristics, but it doesn't allow a detailed description of the membrane structure. Therefore, the permeability coefficients and the transport mechanisms that can take place in the membrane must be determined in advance. These characteristics are specified for any membrane and have been obtained experimentally. The hydrogen permeance through the membrane is the only unpredictable variable of the model. Thus, the membrane is described as a zero-thickness wall, and the transport through it is modeled by defining the source term (Si) introduced in Eq. (3). The source term (S_i) is zero throughout the module except in the region near the membrane [18]. So, the source and the sink terms were introduced at the two sides of the membrane using S_i; in this way, a species is allowed to pass from one side of the membrane to the other (Note: a source term equal to the sum of the source of all the permeable species that is added in the right side of the continuity Eq. (1) only to those cells). The mass flux through the Pd layer is strictly related to the molecules solution/diffusion mechanism and reads as:

$$S_{H2} = \frac{A_c}{V_c}\{Q_{\sup}\left[P_I\phi_{H2,I}P_{perm}\phi_{H2,perm}\right]\} \quad (4)$$

$$S_{H2} = \frac{A_c}{V_c}\{Q_{Pd}\left[(P_{ret}\phi_{H2,ret})^{0.5} - (P_I\phi_{H2,I})^{0.5}\right]\} \quad (5)$$

where Ac and Vc are the computational cell area and volume, respectively, ϕ is the molar fraction, and P is the total pressure [17]. The subscripts perm, I, and ret refer to the permeate side, the interface, and the retentate side, respectively. Qsup is the total permeance of the support, and Q_{Pd} is the permeance of the Pd layer. The partial pressures are also shown schematically in Figure 1([18]).

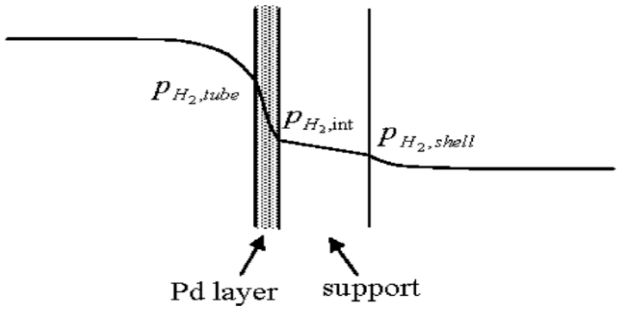

Fig.1. Schematization of H_2 partial pressure inside the Pd membrane [18].

In general, four constants were introduced for the source semester, and their values were obtained by experimentation. Based on the experimental data, pure hydrogen permeation tests were performed by different measurement methods. Then, the same set of constants was used for all simulations under different operating conditions. Forasmuch as the molecular transport in bulk may significantly affect the results of the overall model, the dilution approximation was eliminated, and the interaction between gas species was considered. The diffusive mass flux of the i species, Ji, in Eq. (3) was modeled as [17]:

$$J_i = -\sum_{j=1}^{N} \rho D_{ij} \nabla Y_i \qquad (6)$$

Where Y_i is the mass fraction of i species, N is the number of gas species in the mixture, and D_{ij} is the mass diffusion coefficient of the i–j components in a multi-component mixture.

Two mass transfer modules and a fluid flow module have been used to solve the equations mentioned in the previous sections. The simulated membrane had a diameter of 9 mm and a length of 10 cm. It was also used to simulate a 3D model (Figure 2).

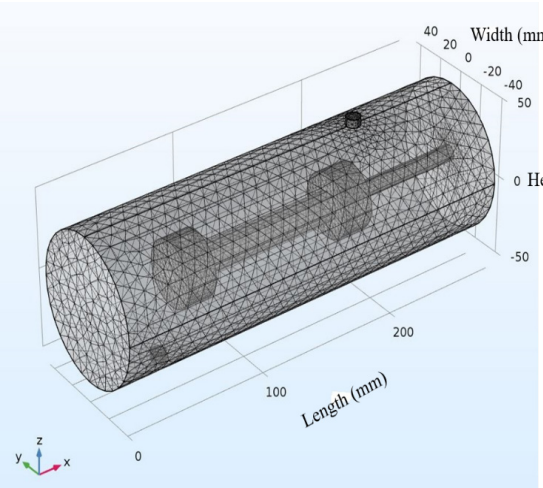

Fig. 2. Computational domain of the membrane module.

3. Results and Discussion

For characterizing the hydrogen purification performance by the membrane under variable operating conditions, the hydrogen permeation data provided the gas flow rates and the composition information required to strictly evaluate the CFD model accuracy. As mentioned above, all of the experimental data are relevant to pure hydrogen gas permeation conditions already adopted to determine the model constants.

The simulation results in different operating conditions, such as temperature and pressure, are very important for assessing the model capability in predicting the effect of temperature and pressure on gas separation. For this purpose, the simulation was performed in two modes for pressures of 1 and 2 bar in the temperature range of 450-500K. The results are shown in Figures 3 and 4, and as expected, the hydrogen permeation flow increases with the increase of temperature and pressure.

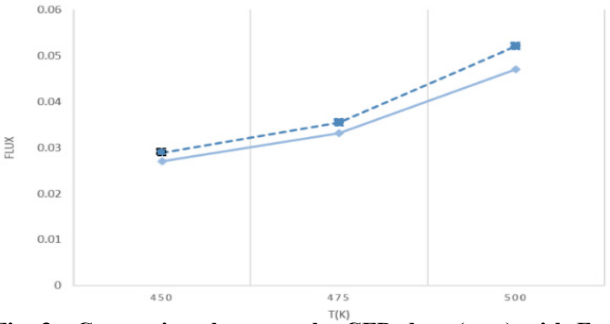

Fig. 3. Comparison between the CFD data (- - -) with Exp. data (—)[19] at P_{ret} =2 bar and Pure H_2

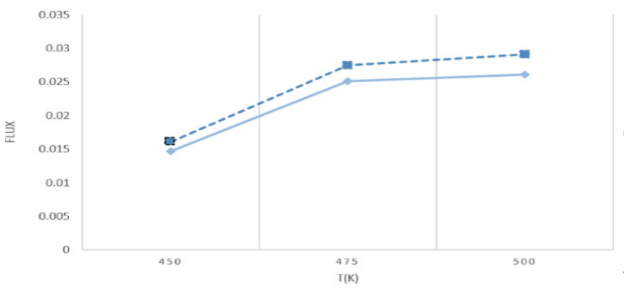

Fig. 4. Comparison between the CFD data (- - -) with Exp. data (—) [19] at P_{ret} =1 bar and Pure H_2

The model was obtained with an error of less than 3% at 450K and below 6% for 475K and 500K. This model provides a reliable prediction compared to existing experimental data. Thus, the local information obtained by the simulation can be used to evaluate the module behavior and the effect of operating conditions on Hydrogen permeation.

Moreover, for a gas mixture, the analysis of the CFD results allows us to evaluate the effect of the temperature on the gas species distribution inside the separation module. The H_2 molar fraction maps are shown in Figure 5 when a mixture of H_2 –Ar (90% H_2) is fed to the module at 450K.

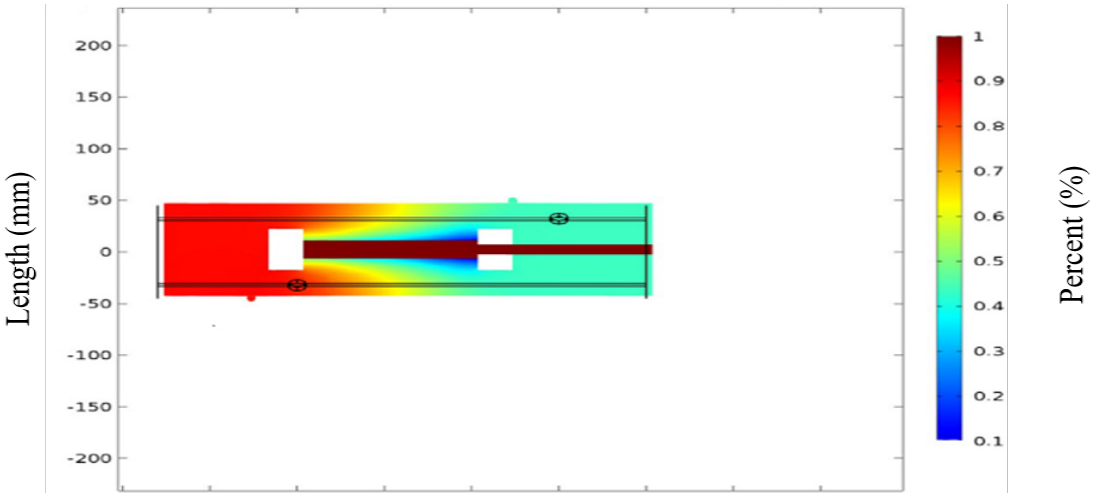

Fig. 5. Map of H_2 molar fraction at T=450K and P_{ret} =1bar.

As a result, the influence of the convective resistances, in this case, is expected to be more important due to the high value of the mass transfer resistance. In this case, a local and accurate evaluation of the convective resistance is crucial, and significant improvements of the permeate flow rates predictions are expected with the CFD approach to lumped parameters models. In other words, if the temperature increases, the membrane permeance increases, and as a result, the membrane resistance becomes less important to the convective mass transfer resistance. When the feed is composed of hydrogen and various other components, a boundary layer is formed upon the palladium film. The presence of this boundary layer causes the concentration of hydrogen near the surface to be less than its concentration in the bulk, which eventually reduces the partial pressure difference of hydrogen on the membrane surface. Also, at a constant pressure, the hydrogen flux passing through the membrane decreases compared to that of the pure hydrogen feed. This effect is called external mass resistance and occurs on the transfer of hydrogen.

4. Conclusions

The simulation results at different operating conditions showed that the hydrogen permeation flow increases with increasing temperature and pressure. Moreover, for a gas mixture, the analysis of the CFD results showed when the feed is a mixture of H_2/Ar, a boundary layer is formed upon the palladium film. The presence of this boundary layer causes the concentration of hydrogen near the surface to be less than its concentration in the bulk, which eventually reduces the partial pressure difference of hydrogen on the membrane surface resulting in the reduction of hydrogen flux passing through the membrane in comparison with the pure hydrogen feed. Good agreement between the ex-

perimental and the predicted data shows that CFD can be considered a useful and reliable tool for designing new modules or optimizing existing methods.

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Nomenclature

Ac	computational cell area (m^2)	T	temperature (K)
D	The diffusion coefficient in multi-component mixtures (m^2 s^{-1})	U	velocity vector (m s^{-1})
J	diffusive flux (kg m^{-2} s^{-1})	Vc	computational cell volume (m^3)
N	number of chemical species	ρ	density (kg m^{-3})
P	pressure (bar)	**τ**	viscous stress tensor (Pa)
Q_{Pd}	The permeance of the Pd layer (kg m^{-2} $Pa^{-0.5}$ s^{-1})	ϕ	molar fraction
Q_{sup}	The permeance of the support (kg m^{-2} Pa^{-1} s^{-1})	i	generic species
R	ideal gas constant (kJ $kmol^{-1}$ K^{-1})	j	generic species
S	source term (kg m^{-3} s^{-1})	ret	retentate

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