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2D-NUMERICAL SIMULATION OF H_2 PERMEATION THROUGH PD- MEMBRANE

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ABSTRACT

In this study, two-dimensional CFD simulation model is developed for investigating the hydrogen separation process across the Pd-membrane type. The influences of H2 feeding flow rate and membrane thickness on the hydrogen permeation process were investigated. Also, two Pd-membrane thicknesses of 15µm and 20µm were investigated to understand the hydrogen embrittlement and diffusion through membrane. The numerical model parameters was adjusted at a reactor temperature of 150 ^{o}C and feed pressure of 100 kPa. The velocity, concentration, and diffusion mass transfer flux distribution were numerically achieved by the model. The simulation results showed that the hydrogen velocity distribution increased with the feeding gas flow rate. Furthermore, the diffusion flux was enhanced with the permeation time and the feeding flow rate increased. It can be concluded that the hydrogen concentration and diffusion mass transfer flux through thick membranes was low compared with lower membrane thickness. It can be expected that the CFD simulation model will aid in the membrane separation design, selection and development.

Keywords: Numerical simulation, Palladium membrane (Pd), Hydrogen separation, Hydrogen flux.

1. INTRODUCTION

Hydrogen production from different feed stocks is expected to enhance in the future and moves toward using hydrogen as a new energy carrier. Hydrogen can be generated by various industrial processes such as water electrolysis, steam reforming, and coal gasification, which it can be used for the hydrogen production from traditional energy sources [1, 2]. Hydrogen production from fossil fuels acts over 90% of total generated hydrogen (mainly natural gas steam reforming). Most of the produced hydrogen is utilized in a large-scale industrial application processes such as textile industries, chemical, petrochemical, metallurgical, and raw materials like ammonia, hydrogen peroxide, and methane [3]. It is considered that large-scale H2 production applications required high capital investment as well as the hydrogen separation process which controls hydrogen production cost. Therefore, the cost effective and high efficiency process is needed by means separating hydrogen from less reaction product species. Three mainly processes can be efficiently used to purify hydrogen, (1) pressure swing adsorption (PSA) [4], (2) cryogenic distillation, and (3) membrane separation [5, 6]. It has been reported that the PSA and cryogenic distillation systems are not cost effective for the hydrogen separation process. While the hydrogen separation by membrane separation system is currently considered the most promising technology because of its low investment cost, energy consumption, possibility of continuous operation, and operation is easy [7, 8]. The hydrogen separation technology is mostly based on the methane steam reforming process [9]. However, hydrogen produced in this way is mixed with other gases such as carbon dioxide that requiring ancillary separation processes increasing the cost of hydrogen production. Hydrogen separation process based on the membrane separation technique has the ability to operate under a wide range at the same efficiency. Different membrane types can be used in the hydrogen separation process such as metallic, silica, zeolite, carbon-based, and polymer membranes [7]. The hydrogen permeation across Pd-alloys often possesses greater permeation rate than pure palladium membranes. The most known binary Pd-based alloys are Pd0.75 Ag0.25 wt%, and Pd0.60 Cu0.40 wt% [10, 11]. The hydrogen permeation

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modeling becomes an important method for describing and identifying the permeation process through Pd-based membranes. Many efforts for H2 permeation modeling have been investigated to predict the hydrogen diffusion and selectivity [12, 13]. Also, the literature survey elucidated the membrane design configuration importance in enhancing the membrane performance and mass transfer process across the membrane surface. In this study, two-dimensional CFD simulation modeling is developed to investigate the hydrogen permeation process through Pd-membrane. The effects of hydrogen feeding flow rate and membrane thickness on the hydrogen permeation process through Pd-membrane are investigated. The velocity profile, concentration, and hydrogen diffusion flux are evaluated at different permeation side positions. Moreover, the hydrogen concentration is compared at the outlet of permeation side. The hydrogen separation through two different Pd-membrane thicknesses is evaluated to understand the hydrogen dissociation process.

2. Numerical model governing equations and boundary conditions

The numerical simulation of hydrogen permeation using Pd-membrane was carried out using the commercial COMSOL Multiphysics 5.6 software to solve the hydrogen separation physical problem. Palladium and its alloys are the most attractive membranes used for hydrogen separation because of its high selectivity to the hydrogen molecules. Two Pd- membranes thicknesses were used in the simulation procedures as well as hydrogen flow rate, feeding pressure, and reactor temperature. The numerical simulation and modeling gives the ability to investigate the effect of different parameters on the membrane reactor performances. The numerical modeling governing equations include the transport species, continuity, and momentum equations. In this simulation, two-dimensional mathematical model, 2D-axisymmetric, isothermal, and laminar flow are considered as the model assumption. Figure (1) shows the designed reactor 2D geometry and the applied meshing to the membrane reactor domain.

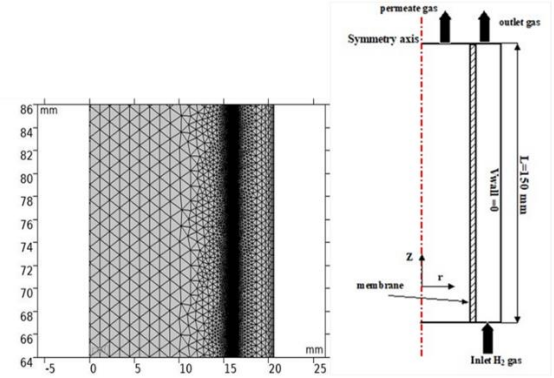

Fig 1 Schematic diagram of 2D geometry and meshing.

The numerical model governing equations will be given in this section. The continuity governing equation of hydrogen species transport in general form of the Pd-membrane separation system is given as follows [14]:

$$\frac{\partial C_i}{\partial t} = -(\nabla . C_i V) - (\nabla . J_i) + R_i \qquad (1)$$

Where V and t are velocity and time, respectively. The hydrogen separation process occurs in the cylindrical vertical z-direction coordinates and radius r. The hydrogen diffusion mass transport process can be described using Fick's first law at the steady state conditions. The hydrogen gas diffusion flux through the Pd-membrane molecules can be estimated as follows [15]:

$$J_H = -D\frac{\partial C}{\partial x} \qquad (2)$$

The hydrogen concentration gradient through the membrane lattice is $\frac{\partial C}{\partial x}$. Nevertheless, the hydrogen concentration on the membrane surface cannot practically determine. Hence, the hydrogen flux in equation (2) can be used to express about the resulting hydrogen gas concentrations. Also, the permeability can be experimentally obtained from the hydrogen permeation data by determining the slope data of the hydrogen flux versus time. Then, the activation energy Ea, and the pre-exponential factor Peo can be calculated according to the following Arrhenius equation,

$$Pe = Pe_o \exp\left(\frac{-Ea}{RT}\right) \rightarrow lnPe = lnPe_o - \frac{Ea}{RT} \qquad (3)$$

Where T is the gas temperature and R is the universal gas constant. The hydrogen flow is also investigated according to laminar fluid flow as follows:

Continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla . (\rho u) = 0 \qquad (4)$$

Navier-Stokes equation in cylindrical coordinates is used to determine fluid flow properties according to the following equation [16],

$$-\nabla.\mu(\nabla u + (\nabla u)^T) + \nabla P + \rho\frac{\partial u}{\partial t} + \rho(u.\nabla)u = F,$$
$$\nabla.u = 0 \qquad (5)$$

Where the fluid dynamic viscosity is μ (kg/m.s), u (m/s) denotes velocity, density of the fluid is ρ (kg/m3), pressure is P (atm), and the body force is F (N/m3).

The numerical model boundary conditions can be defined as follows, Initial concentration value is zero, no slip velocity, symmetry boundary, inlet velocity is V0 at z=0, and the feed side inlet and outlet pressure is atmospheric pressure.

3. Results& discussion

3.1 Influence of hydrogen feeding flow rate on hydrogen separation

The velocity field inside the feeding side was determined using Navier-Stokes equation. Figure (2) represents the velocity profile inside feeding side in z-direction versus separation time. The velocity profile inside the feeding side is decreased reaching to zero at the membrane surface and reactor wall. Moreover, the velocity at different feeding flow rates was estimated, the velocity magnitude of all flow rates does not changed after 30 s. The hydrogen diffusive flux evolution was determined at the center of permeation side as a function of the membrane thickness and the diffusion coefficient. The simulation analysis was carried out for pure Pd-membrane with a diffusion coefficient of 2×10-7 (cm2/s). The diffusive mass transfer flux for hydrogen molecules transfer from feed to permeate side at the center of the permeate side is shown in Figure (3). The diffusion mass transfer flux increased with the reaction time and H2 feeding flow rate increased. This figure refers to the evolution of H2 flux at the center of permeate side in z-direction for the Pd-membrane with thickness of 20μm and temperature of 150 ºC. It was noticed that the hydrogen diffusion flux increased with the hydrogen feeding flow rate increased. Moreover, the diffusive flux is greater than convective flux at the same permeation side positions.

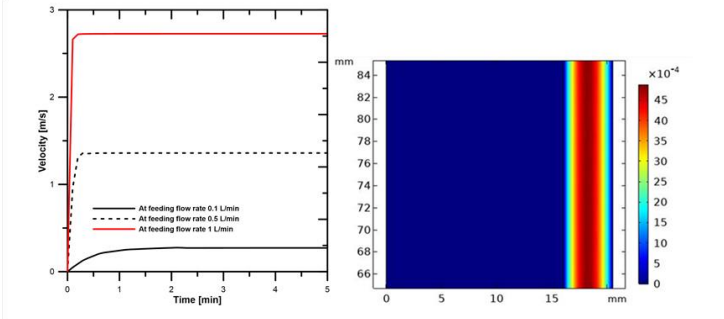

Fig 2 Velocity profile and distribution inside center of feeding side.

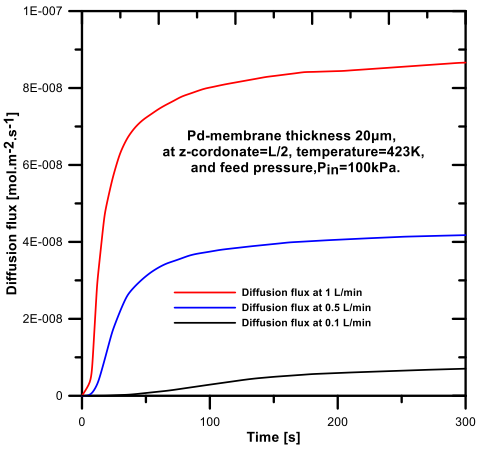

Fig 3 The diffusion mass transfer flux distribution at different H2 feeding flow rates.

The hydrogen concentration was evaluated at different permeation side positions. Figure (4) represents the hydrogen concentration results of H2 flow rates of 0.5, 1 L/min at different z-direction positions. It was observed that the hydrogen concentration at zero position is greater than that obtained at the center and outlet of permeation side. Also, the numerical simulation results of H2 concentration at the permeation side outlet are compared in Figure (5). The hydrogen concentration increases with the reaction time because of more hydrogen molecules is dissociated across the Pd-membrane lattice. It was observed that the highest permeated H2 concentration was obtained from H2 feeding flow rate of 1 L/min. the hydrogen concentration gradient is expected to increase with the permeation time as well as the feeding flow rate increased.

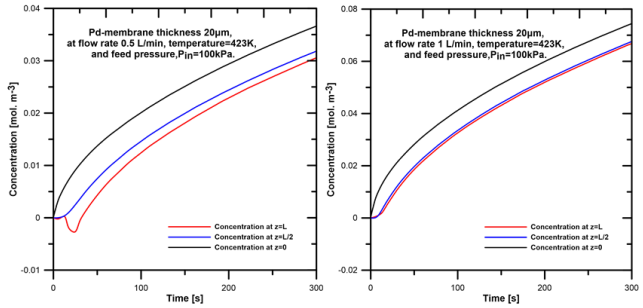

Fig 4 Comparisons of H2 concentrations at different positions.

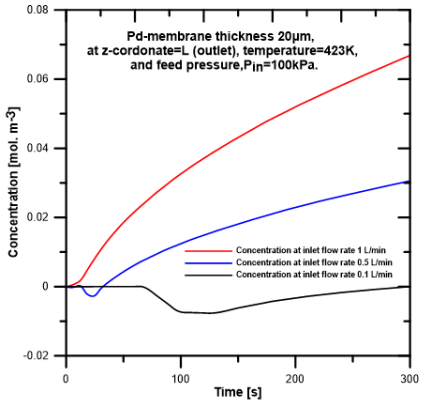

Fig 5 Concentration results at the permeation side.

3.2 Influence of Membrane thickness on hydrogen separation

The membrane separation technology is considered the best solution for all hydrogen separation problems because of its great characteristics and low cost. Hydrogen can be used as clean energy carrier to overcome all environmental issues. Hydrogen separation using Pd-based membranes and its alloys are registered great hydrogen permeability. Different parameters are influenced the permeation process such as the feeding flow rate, membrane thickness, reactor temperature, feeding and permeate pressures. The membrane thickness effect on the hydrogen permeation rate is also investigated. Two membrane thicknesses of 15µm and 20µm were simulated at hydrogen feeding flow rate of 0.1 L/min, feeding pressure of 100 kPa and reactor temperature of 150 ^{o}C. Figure (6) shows the diffusion mass transfer flux with the permeation time at different Pd-membrane thicknesses. The hydrogen diffusion across lower membrane thickness was higher than thick membrane thickness due to the total dissociation time increased with larger membrane thickness. Furthermore, the hydrogen diffusion flux is enhanced with the reaction time increased. The hydrogen concentration gradient of both membrane thicknesses at the center of permeation side is presented in Figure (7). It was clear from the concentration results that hydrogen permeation rate increased with the membrane thickness decreased. Also, the concentration of permeated hydrogen is revealed with the increase of permeation time. The computational fluid dynamics (CFD) model was developed to help in the membrane separation reactor designing process. It can be concluded that the membrane thickness has an important effect on the permeated hydrogen.

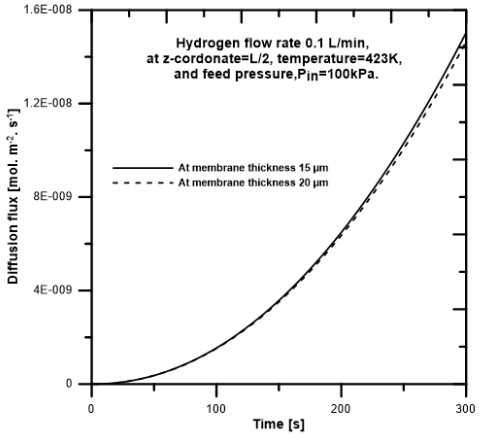

Fig 6 The diffusion flux distribution at different membrane thicknesses

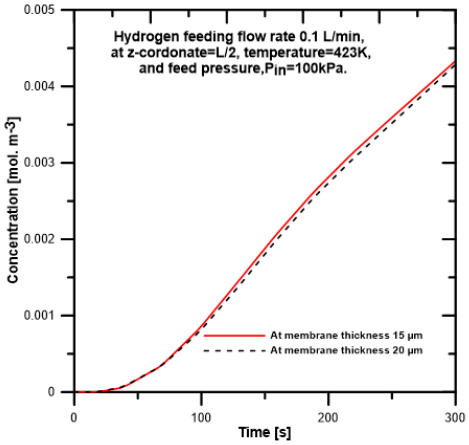

Fig 7 H2 concentration of both membrane thicknesses at center of permeate side.

Conclusions

The current study presented the two-dimensional CFD simulation model for two parameters influencing the hydrogen separation process across the Pd-membrane type. The effect of H2 feeding flow rate and membrane thickness on the hydrogen permeation process was investigated. The simulation analysis was carried out at a reactor temperature of 150 ^{o}C and feed pressure of 100 kPa. Pure hydrogen with a concentration of 100% was considered in this simulation analysis. The velocity, concentration, and diffusion mass transfer flux distribution were numerically reported by the model. The simulation results showed that the hydrogen velocity distribution increased with the feeding gas, while the velocity decreased and reach zero at the membrane wall. Furthermore, the diffusion flux increased with permeation time and the feeding flow rate increased. Also, the hydrogen concentration was influenced by the feeding hydrogen flow rate. It was clear that the

hydrogen concentration gradient of feeding flow rate 1 L/min was greater than 0.1 and 0.5 L/min because of larger H2 flow rate will lead to more H-atoms adsorbed by the Pd-membrane surface. Two Pd-membrane thicknesses were investigated by the current model. It can be concluded that the hydrogen concentration and diffusion mass transfer flux through thick membranes was low compared with small membrane thickness values. It can be expected that the CFD simulation model will be helpful in the membrane separation design and development.

References

[1] El-Shafie M, Kambara S, Hayakawa Y. Hydrogen production technologies overview. J Power Energy Eng 2019; 7:107-54.

[2] Holladay JD, Hu J, King DL, Wang Y. An overview of hydrogen production technologies. Catal Today, 2009; 139:244-60.

[3] Ogden, J. Lecture (Oct 2004); available electronically at http:// www.its.ucdavis.edu/education/classes/pathwaysclass/ 7-StationaryH2- (Ogden).pdf.

[4] Sircar, S.; Golden, T. C. Sep. Sci. Technol. 2000, 35, 667.

[5] Bredesen, R.; Jordal, K.; Bollard, O. Chem. Eng Process. 2004, 43, 1129.

[6] Adhikari, S.; Fernando, S. Ind. Eng. Chem. Res. 2006, 45, 875.

[7] Nathan W. Ockwig and Tina M. Nenoff, Membranes for Hydrogen Separation, Chem. Rev. 2007, 107, 4078−4110.

[8] Spillman, R. W.; Grace, W. R. Chem. Eng. Prog. 1989, 85, 41.

[9] Gunardson, H. Industrial Gases in Petrochemical Processing; Marcel Dekker, Inc.: 1998.

[10] J. Piper. Diffusion of Hydrogen in Copper-Palladium Alloys. J. Appl. Phys. 1966, 37 (2), 715.

[11] D.L. McKinley. Metal alloy for hydrogen separation and purification, US Patent 3,350, 845 (1967).

[12] Kamakoti, P.; Morreale, B. D.; Ciocco, M. V.; Howard, B. H.; Killmeyer, R. P.; Cugini, A. V.; Sholl, D. S. Science 2005, 307, 569.

[13] Kamakoti, P.; Sholl, D. S. J. Membr. Sci. 2006, 279, 94.

[14] Farjami M, Moghadassi A, Vatanpour V. Modeling and simulation of CO2 removal in a polyvinylidene fluoride hollow fiber membrane contactor with computational fluid dynamics. Chem Eng Process Process Intensif. 2015;98:41-51.

[15] Livshits AI. The hydrogen transport through the metal alloy membranes with a spatial variation of the alloy composition: potential diffusion and enhanced permeation. Int J Hydrogen Energy 2017;42:13111-9.

[16] Oxarango L, Schmitz P, Quintard M. Laminar flow in channels with wall suction or injection: a new model to study multi- channel filtration systems. Chem Eng Sci. 2004;59(5):1039-1051.