Utilizing a Pd82-Ag18/α-Al2O3 Membrane to Separate Hydrogen from Dry Reformer Effluent During Transient Start-Up

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Abstract: The purpose of this study is to find the optimal operating conditions for a Pd_{82}-Ag_{18}/α-Al_2O_3 membrane during transient start-up, resulting in the highest hydrogen recovery rate and the shortest time lag. Utilizing a configuration of membrane, flow meters and gas chromatography to analyze the effluent gas composition, the membrane's flow rate was adjusted, and temperature was varied from 325 to 375 ℃. The best outcome was achieved with a rate variation of the shell-side 150 mL/min and a tube-side flow rate variation of 200 mL/min at 375 ℃, resulting in a 37% average hydrogen recovery rate and time lag of 2 hours. In short, the study found that temperature and flowrate affected time lag, with a linear relationship between temperature and hydrogen recovery with also considering the presence of other DRM gas that can decrease the membrane's partial pressure which effects the permeability due to dilution and competitive inhibition.

Keywords: Pd-Ag membrane; transient start-up; DRM effluent; time lag; metallic membrane; hydrogen separation; flow rate

1. Introduction

Energy is a necessary commodity for every aspect of living and the world. These days, energy is utilized in almost every aspect of life, from domestic uses, transportation to power and industries[1)]. According to Maduko and Akuru, energy demand kept rising at 2.3% annually[2)]. Fossil fuels like natural gas and coal fulfils almost 80% of the world's energy needs.

However, these fuel sources emit greenhouse gases (GHGs), such as carbon dioxide (CO_2) and methane (CH_4). The presence of greenhouse gases displays negative effects to the environment, contributing to the greenhouse effect, global warming, and climate change[3–5)]. To mitigate, a new alternative renewable energy should be introduced as a solution to gradually replace fossil-fuels.

Hydrogen is one of the promising new alternative energies. These days, hydrogen is starting to be widely researched and developed by various countries as a new alternative energy source for the future[6,7)]. As per fact that it can be used as a transportation fuel and safely converted with higher efficiency into thermal and electrical energy, hydrogen has been termed a 21st-century energy[8–10)].

Syngas (synthesis gas) is the main source of hydrogen feed and is formed when methane (CH_4) and carbon dioxide (CO_2) are reformated to produce hydrogen and carbon monoxide (CO), as well as significant amounts of hydrocarbons[11,12)]. Several sources, such as natural gas, coal, and biomass, to virtually any hydrocarbon feedstock, can produce syngas; through hydrocarbon fuels through basic technologies: natural gas pyrolysis (NGP), methane stream reforming (SRM), methane dry reforming (DRM), methane autothermal reforming

(ATM), methane partial oxidation (POM), and other reforming processes[13].

The process of dry reforming methane is a promising reaction, as it converts two greenhouse gases CO_2 and CH_4 into syngas (CO and H_2), which could be used as a chemical feedstock for industrial processes or applications, and mixed fuel for daily usage[14]. Furthermore, other side reactions can also happen during DRM process. For example, the CO produced by the DRM, reverse water-gas shift reaction (WGSR), and steam/carbon gasification can promote the Boudouard reaction, whereas the CH_4 in the feed can decompose into carbon and H_2[15]. According to Nisa et al., the higher the conversion of CH_4, the higher the production of H_2[16]. DRM operation itself stands at the lowest temperature than other methods, which is at 973 K. Other than that, DRM's operation condition is at ambient pressure (1 bar) with an energy requirement of 24.50 kWh/kg H_2 and 62.13% in energy efficiency, making DRM one of the most prominent methods to produce hydrogen gas[13].

There are several separations and purification techniques of hydrogen, which are pressure swing adsorption (PSA), cryogenic distillation, and membrane separation. Separation by membrane methods have become more important in today's development of environmentally friendly industrial processes, due to their lower use of energy from other methods[17,18].

Utilizing membrane, particularly Pd-based membrane for separation is proven to be more than twice as more energy-saving process than other common methods. Pd-based membrane, which accounts as inorganic, metallic membrane, has stable properties and can withstand operation in high temperature and pH levels[19].

This proves the bright future and the promising future of palladium-based membrane for commercialization in industries[20]. Separation by Pd-based membrane provides a similar purity rate and production scale from the PSA and cryogenic distillation, with the advantage of requiring less energy than the other methods for continuous operation[21]. Inorganic membranes and polymeric, that are further classified to dense and porous membranes, are the two types used for H_2 purification membranes. Dense palladium-based membranes are commonly used because of their high hydrogen permeability, chemical compatibility, and selectivity[22]. In order to increase hydrogen permeability, reduce embrittlement, and improve mechanical properties, rather than pure palladium, properties can be increased by adding a variety of substitute materials to palladium, such as nickel, gold, and silver[23]. Thin layers of palladium are therefore coated over porous supports made of metal or ceramic, and Pd-Ag alloys are used to prepare commercial permeator tubes with walls 150 μm thick for hydrogen purification and separation[24].

The volumetric rate of the feed gas[25–28], the pressure differential at the membrane's two ends[8,29], the operating temperature[25,30–32], and the compositions of the feed and permeate[28,33–35] all have an impact on the rate of hydrogen transport through the membrane layer. The transmembrane pressure difference, operating temperature, and feed volumetric flow rate all tend to increase hydrogen flux. The rate of permeation is significantly influenced by the partial pressure difference between the permeate and retentate sides of the membrane during membrane separation. According to Sievert's law, a greater H_2 driving force will be created by a higher transmembrane pressure difference, speeding up the rate of H_2 permeation. To raise the transmembrane pressure differential, sweep gas during operation, such as steam or nitrogen, can be used. The pressure difference produced increases with the sweep gas's flow rate.

It is essential to consider the interactions between the components when separating hydrogen from gas mixtures. Other gases present on the palladium surface can certainly act as an inhibitor during hydrogen permeation. Carbon, oxygen, and steam have all been shown to have an effect on the structure of palladium[36, 37]. They reached the conclusion to the that H_2O > CO > CO_2 is the order in which the ability of gases to adsorb on the Pd-Ag surface film corresponds to the inhibition of hydrogen permeation. Oxygen can cause palladium oxide to form, resulting in rough surfaces that increase hydrogen permeability. As a result, pore openings on the membrane surface occur, reducing the membrane's selectivity. At high temperatures, carbon can inhibit permeation and cause porosity, especially when combined with oxygen.

This study was conducted to observe the performance of the Pd_{82}-Ag_{18}/α-Al_2O_3 membrane to produce the most optimum hydrogen gas permeation from the membrane while considering several of the factors that may affect the membrane performance. Based on the explanation as aforementioned, the problem statement of this research which are the effects of the mixed gas flow rate as the effluent of DRM (consists of H_2, CO_2, CO, CH_4), the nitrogen flow rate and also the operating temperature on the hydrogen permeation by the Pd_{82}-Ag_{18}/α-Al_2O_3 membrane and time lag during transient start-up.

2. Methodology

2.1 Equipment

The experimental setup with a Pd_{82}-Ag_{18}/α-Al_2O_3 membrane and analysis using Shimadzu GC-14B capillary column Gas Chromatography (GC) was established to collect data on hydrogen permeability throughout start-up. Figure 1 displays a graphic representation of the experimental setup. The setup has three sections: feed, membrane module, and gas analysis. Additionally, the Pd_{82}-Ag_{18}/α-Al_2O_3 film's composition was determined by measuring the gas flow rate using a mass flow controller (MFC) and a bubble soap meter.

2.1.1 Feed Gas Section

The Pd_{82}-Ag_{18}/α-Al_2O_3 membrane's tube side was fed with a feed section made up of a gas mixture (50% H_2, 25% CH_4, 15% CO, and 10% CO_2). This mixed gas, in the main experiment, will be fed to the membrane's shell side, and through the membrane, the hydrogen gas will be separated as the hydrogen will be permeated to the tube side of the membrane. All gas flows will be controlled by MCF to make sure accurate flowrate. To maintain the hydrogen partial pressure difference of the tube and shell sides, ultra-pure nitrogen was used in the shell side as a sweeping gas of the permeated.

This partial pressure difference is important because it is the main driving force behind transfer of hydrogen through solution diffusion. Ultra-pure argon was used to clean and purge the Pd_{82}-Ag_{18}/α-Al_2O_3 membrane surface.

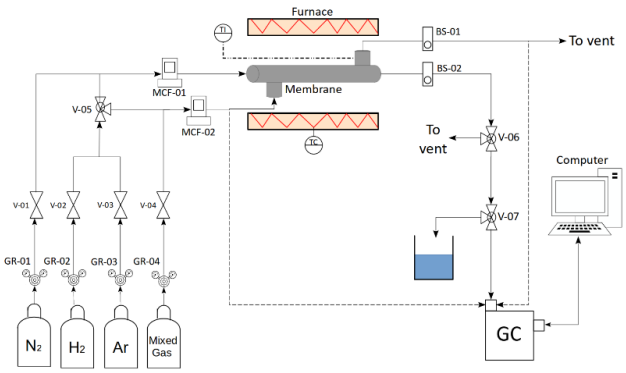

Fig. 1: Experimental set-up of H_2 separation using Pd_{82}-Ag_{18}/α-Al_2O_3.
*(GR: gas regulator, V: valve, TI: temperature indicator, TC: thermocontrol, BS: bubble flowmeter, GC: gas chromatography).

2.1.2 Membrane Section

The following technical aspects implement to the Pd_{82}-Ag_{18} membrane used in this study: weight composition of the Pd-Ag membrane (wt%): 82–18; membrane measurements: 100 mm membrane length; 20.2 m membrane thickness; 6 mm membrane outside diameter; 5 mm membrane inside diameter; and 0.1 m mean pore diameter of α-Al_2O_3[38]. The material of the shell was stainless steel, and the tube was the Pd82-Ag18/α-Al2O3 membrane. To regulate the temperature of the membrane tube, a thermocouple and an adjustable temperature were used.

2.1.3 Analysis Section

All the data from this experiment were obtained from a capillary column Shimadzu GC-14B Gas Chromatography. A molecular sieve 5 Å column at 50 ℃ and a thermal conductivity detector at 50 ℃ and 70 mA were both included in the Gas Chromatography. In this experiment, ultra-high purity (UHP) argon (99.9995) is used as carrier gas in the gas chromatography (GC).

2.2 Set-up Operation Procedure

Comparison of Pd-membrane type and the effects of flow rate and temperature on membrane's performance is conducted by literature review, experiments, and data processing. The variation of flow rate and temperature will be discussed in the latter section and comparing its performance will provide recommendations on what operating conditions should the membrane be used. The main factors to be evaluated are hydrogen recovery and time lag.

In this research, there are 6 parts of the experiment which include the leaking test, equipment set-up, preparation stage (purging and heating), preliminary experiment, the main experiment, and data analysis of hydrogen recovery. The leaking test was conducted to make sure there was no leaking at the membrane module, where shell and tube side stream goes separately and did not merge. The preparation stage consisted of purging and heating, with this stage being conducted before every trial and variation of both preliminary and main experiment.

2.2.1 Preparation Stage

The purpose of purging was to clean the membrane from any impurities. Purging occurred in 3 stages. The first stage was purging by flowing 150 mL/min of UHP argon in both shell and tube sides for 30 minutes. This served to remove the initial air inside the membrane. Then it was purged with a 1:1 mixture of UHP argon and hydrogen for 30 minutes at 150 mL/min. This served to clean and remove any impurities in the membrane. The last step of purging was to purge the membrane again with UHP argon at 150 mL/min for 30 minutes. This stage served to remove the hydrogen from the membrane from the previous purging stage and to prepare the membrane for hydrogen separation. After purging, the membrane was heated by a furnace to 325 ℃ at 50 ℃ intervals and indicated by a thermocontrol. Heating conducted to activate the membrane and prepare it for hydrogen separation. After the membrane is ready, connect the effluent of the membrane to the gas chromatography. The gas retention time of the GC was 9 minutes and data from the effluent of the membrane was collected every 15 minutes for 5 hours.

2.2.2 Preliminary Experiment

The preliminary experiment was conducted to observe hydrogen separation without other DRM gases present. In addition, this experiment was conducted to observe the separation value difference with the presence of other DRM gases at a constant temperature of 325 ℃ indicated by the thermocontrol as it was the minimum operating temperature of the membrane[39]. The inlet used for this preliminary experiment was 1:1 hydrogen-nitrogen mixed gas in the shell-side at 150 mL/min and UHP nitrogen in the tube-side at 200 mL/min. Data was collected and analyzed by the GC every 15 minutes for 5

hours. The data was saved in the data logger and the time lag was noted for further data treatment.

2.2.3 Main Experiment

The main experiment of this research was conducted to observe the hydrogen separation using DRM gas effluent. The gas composition used was a derivation of DRM process at 650 ℃ (50% H_2 25% CH_4, 15% CO, 10% CO_2)[40]. The mixed gas was flown into the shell-side and nitrogen gas, which acted as a sweep gas, was flown in the tube-side. Both the shell and tube-side flow rates are controlled by an MFC. Temperature was also varied from 325–375 ℃ using furnace and monitored by thermocouple and indicator. The hydrogen from the mixed gas that is permeated to the tube side of the membrane is the data that will be collected by analyzing the GC results. The data was collected by the GC every 15 minutes for 5 hours. The variation of the main experiment is shown in Table 1.

2.2.4 Hydrogen in Permeate

The retention time of the GC was 9 minutes and all data from the variations were taken at 15-minute intervals for 5 hours or longer. The gas chromatograph reading results was the composition of the permeate output gas and fresh feed represented by $X_{H_2,\,GC}$. Bubble soap meter is utilized to quantify the gas flow rates. The feed composition was measured beforehand and was expressed as $X_{H_2,\,\text{fresh feed}}$ and its feed flow rate was expressed as $F_{\text{fresh feed}}$. The value of the permeate flow rate was also measured by a bubble soap meter and was expressed as F_{permeate}. To obtain the concentration of H_2 in the permeate, a mass balance was carried out. The hydrogen density in the permeate, fresh feed and detector streams were the same because the pressure and temperature were not significantly different in the three streams. The formula to obtain these is stated in Equation (1).

$$\dot{m}_{H_2,GC} = \dot{m}_{H_2,\text{permeate}} + \dot{m}_{H_2,\text{fresh feed}} \quad (1)$$

$$x_{H_2,GC} \times F_{GC} = \left(F_{GC} \times F_{GC} \times x_{H_2,GC}\right) - \left(F_{fresh\ feed} \times x_{H_2,fresh\ feed}\right)$$

Table 1. Main experiment variations.

Run	Variable		
	Mixed Gas Flow Rate (mL/min)	**Nitrogen Flow Rate (mL/min)**	**Temperature (℃)**
2.1	150	150	325
2.2	150	200	325
2.3	200	200	325
2.4	250	200	325
2.5	150	200	350
2.6	50	200	375
2.7	100	200	375
2.8	150	200	375
2.9	200	200	375
2.10	250	200	375

2.2.5 Hydrogen Recovery

The permeate side of the membrane which is the hydrogen flow rate was compared to the total hydrogen flow rate in the feed to determine the percentage of hydrogen recovery on the Pd_{82}-Ag_{18}/α-Al_2O_3 membrane for each variation of operating conditions. The amount of hydrogen flow rate at the shell outlet and tube inlet sides as measured by installing a flow meter was compared for hydrogen recovery in an expression known as the recovery of hydrogen, stated in Equation (2). In this research, the hydrogen recovery in one variation was presented into one representative value, which was the average hydrogen recovery. Average hydrogen recovery is the average hydrogen recovery of every hydrogen recovery data gained after the membrane performance passed the transient stage (which was indicated by time lag in one variation).

$$\text{H}_2\text{Recovery} = \frac{\text{mol permeated hydrogen in the tube side}}{\text{mol hydrogen in feed gas}} \text{ x } 100\% = \frac{F_{\text{permeate}} \times x_{H_2,\text{permeate}}}{F_{\text{membranefeed}} \times x_{H_2,\text{ membrane feed}}} \text{ x } 100\% \quad (2)$$

2.2.6 Time Lag during Start-up

Time lag is defined as the time required for membrane performance to pass its transient stage, in order to reach a stable membrane performance level. In addition, time lag indicates the start of stable and steady hydrogen recovery rate, where the oscillation deviation response is below 5%.

3. Results and Discussion

3.1 Preliminary Experiment Results

This preliminary experiment was conducted to observe hydrogen separation without other DRM gasses present. In addition, this experiment was conducted to observe the separation value difference with the presence of other DRM gases. The inlet gas used for this preliminary experiment is hydrogen-nitrogen mixed gas.

The membrane was kept at constant operation conditions, at 598 K (325 ℃) and constant pressure. At a steady-state operation mode, 150 mL/min of H_2-N_2 gas feed was inserted into the Pd_{82}-Ag_{18}/α-Al_2O_3 membrane's shell side. While 200 mL/min of ultra-high purity (UHP) nitrogen gas was inserted in the tube side. Then, the membrane separation was initiated for data collection every 15 minutes for 5 hours. To collect and obtain the data, install the gas detector for the hydrogen permeation effluent in every time interval. The obtained data was saved in the data logger and the time lag that occurs in

the process is noted for further data treatment. The result of the preliminary experiment is shown in Fig. 2.

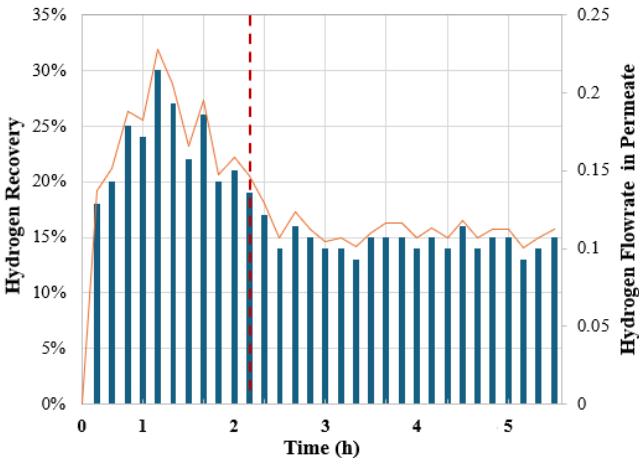

Fig. 2: Preliminary experiment result at 150 mL/min of H_2-N_2 (shell) and 200 mL/min of UHP N_2 (tube) at 325 ℃.

Hydrogen permeates from the shell to the tube side as there was a lower partial pressure of hydrogen gas in the tube side compared to the shell side $P_{H_{2,shell}} > P_{H_{2,tube}}$. From Fig. 2, it was observed that the initial trend of hydrogen recovery was increasing up to around 25% from 0–0.75 hours then showed continuous fluctuation but at a decreasing trend, being stable from around 2 hours onwards. The reason for the sudden increase in hydrogen recovery was due to the sudden presence of hydrogen gas which was initially not present due to purging. The driving force was the high partial pressure difference, leading to quick hydrogen permeation. The hydrogen recovery fluctuates as it was still trying to reach a steady state and adsorption-desorption equilibrium[41]. The time taken for the membrane to exhibit stable hydrogen recovery is known as the time lag where the oscillation deviation response is below 5%. In this experiment, it was more important to examine the membrane performance during the stable oscillation period as it was a more accurate representation of the membrane's performance. By using Fick's and Sievert's Law shown in Equation (3) and taking note of the inlet and outlet flow rates of the shell and tube section, Equations (1) and (2) were used to determine the hydrogen recovery. From data processing, the average membrane performance is around 15% hydrogen recovery from the preliminary experiment. The result of this preliminary experiment was compared to similar research done by Budhi et al.[42], where a 19% hydrogen recovery was obtained from a 50:50 H_2/N_2 gas mixture with flowrate of 1.5 mL/s and UHP nitrogen gas at 2.0 mL/s conducted at 325 ℃ with a time lag of 1.94 hours using a Pd/Al_2O_3 membrane.

$$J_{H_2} = Pe^{\circ}_{H_2} \times e^{\frac{-Ea}{R.T}} \times \left[\frac{P^n_{H_2,retentate} - P^n_{H_2,permeate}}{\delta}\right] \quad (3)$$

3.2 Main Experimental Results

Effect of Temperature on Hydrogen Separation

The temperature effect was observed by heating the membrane module inside furnace in three different temperature variations (325 ℃, 350 ℃, and 375 ℃) while keeping the shell-side and tube-side flowrate constant between the variations (150 mL/min and 200 mL/min, respectively). The temperature was controlled by furnace and indicated by a thermocontrol, while the hydrogen recovery was determined by using bubble soap flow meter and GC is used to analyze the gas composition of the effluent of the membrane. Time lag is measured when the hydrogen recovery is stable, and the oscillation deviation of hydrogen recovery is approximately 5%. The effect of temperature on hydrogen recovery is shown in Fig. 3.

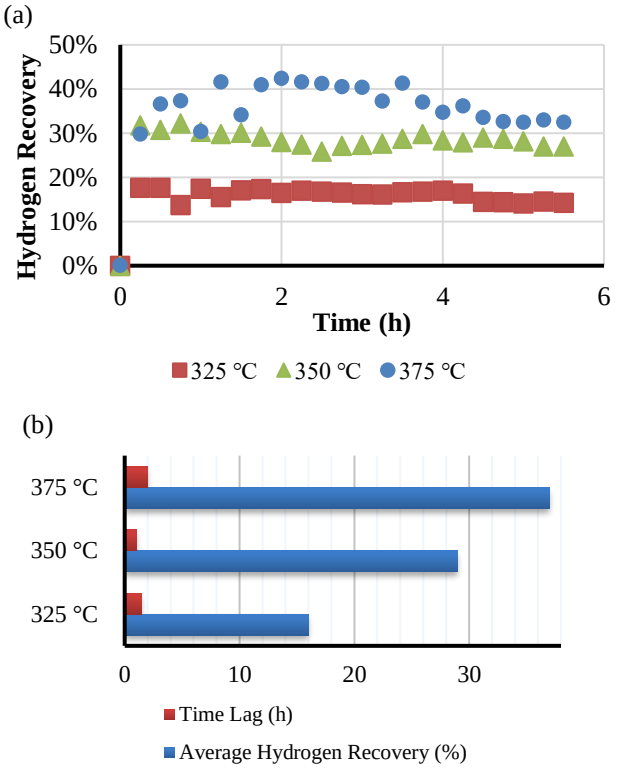

Fig. 3: Comparison of membrane performance at: (a) Different operating temperatures; and (b) Effect of temperature on time lag and hydrogen recovery with flow rate of shell-side and tube-side, 150 mL/min and 200 mL/min, respectively.

The results of the operating temperature impact were consistent with the Sievert's Law and Arrhenius Law, where increase in temperature was proportional to reaction rate which in this case increasing the rate for the hydrogen molecule to be adsorbed to the membrane surface, which also occur to the hydrogen flux. The permeability of hydrogen increased as temperature increased because the average kinetic energy of molecules is increased, which causes the hydrogen atoms to diffuse through the membrane faster[9]. Therefore, at higher temperatures, the diffusion rate of hydrogen is favored. The hydrogen permeability increased linearly with an increase in pressure difference regardless of the operating temperature, because the pressure difference

($P_{feed} - P_{permeate}$) was the driving force for the diffusion process, Similar results were reported by other researchers[38].The hydrogen recovery at 375 ℃ was 37% compared to 16% at 325 ℃. Due to an increase in the average kinetic energy of molecules, hydrogen became more permeable as temperature was raised[43].

3.2.1 Effect of Nitrogen Flow Rate on Hydrogen Separation

Nitrogen was used as a sweeping gas in the membrane's tube side. A sweeping gas was used to maintain the hydrogen partial pressure difference between the shell and tube and to sweep permeated hydrogen[26]. This pressure differential provides the drive for hydrogen to migrate through the Pd-Ag layer was created by this pressure difference[42]. The flowrate of the nitrogen gas was adjusted from 150 to 200 mL/min while the temperature and mixed gas flowrate were maintained at 325 ℃ and 150 mL/min, respectively. In Figure 4, the hydrogen recovery and time lag for both variations are displayed. The hydrogen recovery is calculated using Fick's and Sieverts' Law, which is represented in Equation (3), as well as Equations (1) and (2) regarding hydrogen recovery calculation. Time lag is measured when the hydrogen recovery is stable, and the oscillation deviation of hydrogen recovery is approximately 5%.

Less time lag was experienced due to a faster flowrate of hydrogen gas which provided a higher partial pressure difference between the shell and tube section which promoted hydrogen permeation following Ficks's and Sievert's Law. Nordio et al. stated that the driving force of permeation can be affected by the existence thru of stagnant sweep gas in pores of membrane support, which will raise hydrogen partial pressure at the interface between the Pd-layer and support and reduce hydrogen diffusion support[44]. The low nitrogen flow rate had been linked to N_2 concentration polarization on the membrane surface as the concentration of N_2 gas increased over time, the dissociation of N_2 to N became favorable and this was an irreversible reaction. There would be a higher probability of N atoms binding with H atoms forming NHx molecules which cover the surface of the membrane and lowering hydrogen permeability[41]. With a higher nitrogen flow rate, the higher the hydrogen permeate flux, the higher the hydrogen recovery. This increased the partial pressure difference which also increased the amount of hydrogen gas permeated. Moreover, a higher nitrogen flowrate could sweep the surface of the membrane causing NHx to be hydrogenated[45]. Therefore, a nitrogen flow rate of 200 mL/min was kept constant for the experiment varying the mixed gas flow rate. The reaction mechanism of nitrogen on the Pd-membrane is shown in Table 2.

Table 2. Reaction mechanism of nitrogen on Pd membrane[27].

Reaction	Phenomenon
$H_{2(g)} \rightleftharpoons 2H_{(ads)}$	Dissociative/combination adsorption and desorption
H	Diffusion (surface/bulk)
$N_{2(g)} \rightleftharpoons N_{2(ads)} \rightarrow 2N_{(ads)}$	Dissociative adsorption and desorption
$N_{2(ads)} + 2H \rightarrow 2NH_{(ads)}$	Hydrogenation
$N_{(ads)} + H_{(ads)} \rightleftharpoons NH_{(ads)}$	Hydrogenation/Dehydrogenation
$NH_{(ads)} + H_{(ads)} \rightleftharpoons NH_{2(ads)}$	Hydrogenation/Dehydrogenation
$NH_{2(ads)} + H_{(ads)} \rightleftharpoons NH_{3(ads)}$	Hydrogenation/Dehydrogenation
$NH_{3(ads)} \rightarrow NH_{3(g)}$	Desorption

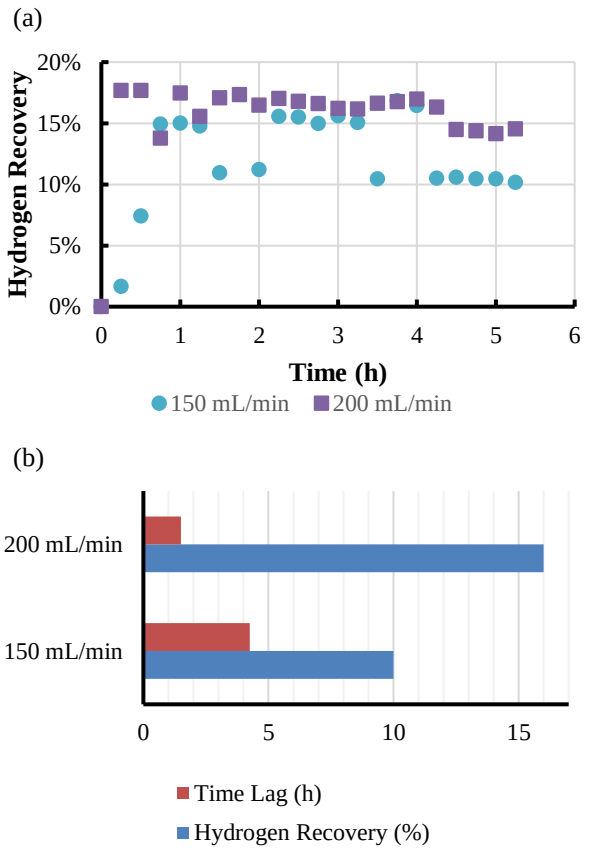

Fig. 4: Comparison of membrane performance at: (a) Different nitrogen flow rate, and (b) Effect of nitrogen flowrate as sweep gas to hydrogen recovery on hydrogen recovery and time lag (T = 325 ℃).

3.2.2 Effect of Mixed Gas Flow Rate on Hydrogen Separation

The mixed gas effect to the permeation was observed by flowing a steady state flow rate to the shell-side of the membrane in different flow rates, from 50 mL/min to 250 mL/min. The inlet flowrate was adjusted and controlled by MFC, while the hydrogen recovery was determined by utilizing bubble soap flow meter and gas chromatography result of the tube side of the membrane. From previous runs, higher temperatures resulted in higher hydrogen recovery, thus an operating temperature of 375 ℃ was used. The result of mixed gas flow rate variation on hydrogen recovery is shown in Table 3.

Table 3. Effect of mixed gas flow rate variation at 375 ℃.

	2.6	2.7	2.8	2.9	2.10
$F_{shell-side}$ (mL/min)	50	100	150	200	250
$F_{tube-side}$ (mL/min)	200	200	200	200	200
Average Hydrogen Recovery (%)	12	15	37	35	31

A higher flower did not always bring a higher hydrogen recovery rate. In accordance to Sievert's law shown in Equation (3), higher flow rate should bring higher flux up to a certain level. When the flow rate of the feed is too high, the hydrogen permeation does not depend on the feed gas flow rate. In addition, as the flow rate was too high, there was some hydrogen that left the membrane before being adsorbed[28]. The presence of other gases could reduce the flux of the permeating gas and present more fluctuating hydrogen recovery than without other gases present. Presence of gas could affect in two ways, either dilution or competitive adsorption[43]. In mixed gas, there are three other gases present besides hydrogen, which are CH_4, CO_2 and CO. Hence, the optimum flow rate for the shell and tube were 150 mL/min and 200 mL/min respectively which resulted in 37% hydrogen recovery.

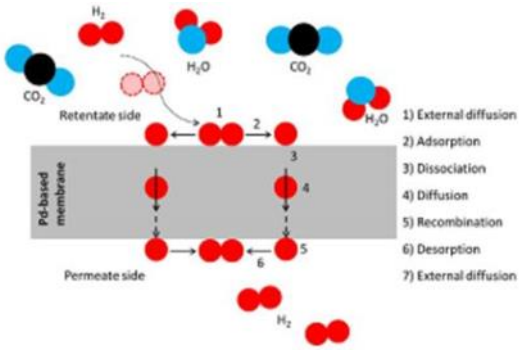

Fig. 5: Schematic diagram of hydrogen permeation through Pd_{82}-Ag_{18}/-Al_2O_3 membrane[42].

3.3 Determination of Optimum Operating Conditions for Hydrogen Separation

In this study, Variation 2.8, which used 150 mL/min mixed gas (shell) and 200 mL/min nitrogen gas (tube) at 375 ℃, produced the best results for hydrogen recovery and time lag. This flow rate variation provided sufficient partial pressure difference. A higher temperature brought significantly higher hydrogen recovery. This was because higher temperature provided more energy and pressure, increasing the average kinetic energy of molecules. As a result, the hydrogen atoms diffused through the membrane more rapidly, leading to the best hydrogen recovery and the shortest time lag. The optimum value of operating temperature for membrane performance in this experiment was 375 ℃. The result of the main experiment is shown in Fig. 5 and Table 4.

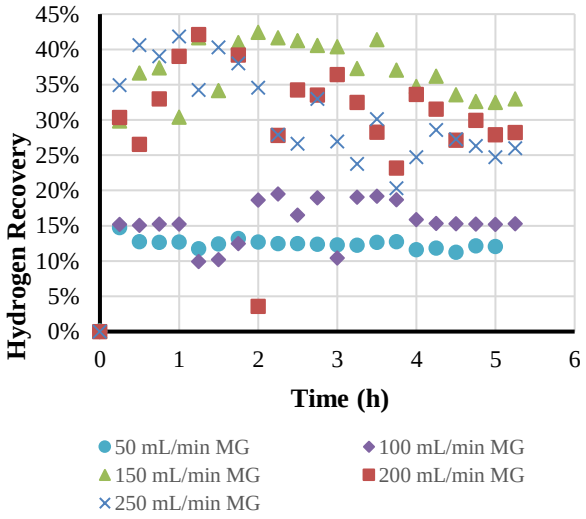

Fig. 6: Comparison of membrane performance with various mixed gas (MG) flow rate at 375 ℃ and 200 mL/min nitrogen flow rate.

Table 4. Result of main experiment.

Run	Variable			Average Hydrogen Recovery (%)	Time Lag (h)
	$F_{Mixed\ Gas}$ (mL/min)	$F_{Nitogen}$ (mL/min)	Temperature (℃)		
2.1	150	150	325	10	4.25
2.2	150	200	325	16	1.50
2.3	200	200	325	14	2.00
2.4	250	200	325	12	2.50
2.5	150	200	350	29	1.00
2.6	50	200	375	12	1.75
2.7	100	200	375	15	3.25
2.8	150	200	375	37	2.00
2.9	200	200	375	35	4.50
2.10	250	200	375	31	3.00

4. Conclusion

In the preliminary experiment, the average hydrogen recovery was 15%, with time lag of 2 hours. A decrease in hydrogen recovery after time lag was not observed. The presence of other DRM gas in the inlet; CH_4, CO_2 and CO affected the hydrogen permeation as it decreased the hydrogen flux due to dilution or competitive inhibition. Flow rate and temperature of operation also affected the time lag of the membrane. It was observed that membranes with high partial pressure and at higher temperatures had a tendency of a shorter time lag and higher hydrogen recovery due to increased kinetic energy of the gas molecules. For shell-side variation, the optimum inlet flow rate of the mixed gas was 150 mL/min, and the tube-side inlet flow rate of the nitrogen gas was 200 mL/min, as it brought the highest hydrogen recovery (37%) amongst other flow rate variation due to

greater partial pressure difference. With an hydrogen recovery average rate of 37% and time lag of 2 hours, Variation 2.8, which had flow rates of 150 mL/min on the shell side and 200 mL/min on the tube side, produced the best results. The Pd_{82}-Ag_{18}/-Al_2O_3 membrane performed best at a temperature of 375 ℃ in this study, but it has not been established whether that temperature is optimal for that membrane. In the future, some direction that could improve this research are conducting this experiment in a membrane reactor instead of only membrane, as part of process intensification towards blue energy, and examine the permeation behavior of hydrogen at a longer time interval (eg: 24 hours) to observe stability, and if possible to conduct the operation at forced unsteady state, as it was found to produce better and higher permeation rate.

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