POLITECNICO
MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE
E DELL'INFORMAZIONE

EXECUTIVE SUMMARY OF THE THESIS

Methanol Reforming in Pd alloy Membrane Reactor for Production of Hydrogen

TESI MAGISTRALE IN ENERGY ENGINEERING – INGEGNERIA ENERGETICA

AUTHOR: ALI HAMZA

ADVISOR: STEFANO CAMPANARI **CO-ADVISOR: MARIJA SARIC, YILIU LIU**

ACADEMIC YEAR: 2024-2025

1. Introduction

The need for clean and green energy has grown recently as a result of several developments in the energy industry. Hydrogen (H_2) is a key energy vector, and many advancements are currently being made to use hydrogen as a clean energy source. One of the most critical aspects associated with hydrogen supply chain is hydrogen storage and transportation. Being the lightest molecule with a very low energy density per volume, hydrogen is challenging to transport. H_2 carriers are seen as an attractive alternative to H_2 storage and transportation. Methanol is an attractive H_2 carriers due to various reasons: Methanol is liquid at ambient temperature. Methanol reforming to hydrogen takes place at low temperatures 240-260°C [1] and Methanol has high hydrogen content [2]. Methanol reforming through conventional reactors involves various steps as reaction and separation occur in separate steps which decrease thermal efficiency and H_2 produced is not of high purity. Therefore, membrane reactors technology is widely employed as they intensify the contact between reactants and catalyst, selectively removing the desired product from the mixtures of reactants. These reactors also overcome the problems of equilibrium conversion limits which conventional reactor faces [3]. Pd based membranes are widely used for H_2 separation owing to their thermal stability at high temperature and the ability to obtain pure hydrogen [1]. This study evaluates the energy efficiency of methanol reforming in Pd-alloy membrane reactors versus conventional systems, focusing on thermal integration and hydrogen yield. It examines how temperature and reforming by-products affect membrane performance and durability and assesses the produced hydrogen's purity for direct use in PEM fuel cells, especially for marine energy applications.

2. Materials and Methods

2.1 Membrane Selection

To ensure a representative experimental design, three different palladium-based membranes were selected to span a realistic range of performance, composition, and fabrication history relevant to hydrogen separation applications. Following are the three membranes which will be tested:

Pd-Au Alloyed Membrane (thickness: 8.039 microns). Pure Pd Membrane (thickness: 4.373 microns). Recycled Pd Membrane (thickness: 6.8 microns). The preparation of membranes falls outside the scope of this thesis; the focus herein is exclusively on the characterization of palladium-based membranes. Pd–Ag membranes provide higher hydrogen permeability, are less expensive, and easier to fabricate but are more susceptible to embrittlement and poisoning, especially by sulfur and CO. The Pd–Au alloy has slightly less permeability, is more expensive, yet it is much more stable upon cyclic and high-temperature exposures, resistant to lattice expansion, and exhibits excellent tolerance to impurities. In reality, Pd–Ag suits clean hydrogen feeds where efficiency is generally of greater importance, whereas Pd–Au performs better in reforming environments or in long-term applications where durability and chemical resistance become critical [4].

2.2 Membrane Characterization

2.2.1 SEM Analysis

The morphological characterization of the membrane was conducted using a Hitachi SU70 scanning electron microscope. SEM observations were performed under low vacuum conditions at an accelerating voltage of 15 kV.

2.2.2 Membrane Leak Testing

Membrane was characterized by a feed pressure of 3 bars and was measured inside out. This procedure served as the standard testing protocol for externally coated membranes at TNO. The resultant flow was measured thus giving us the leak rate of membrane. These experiments were performed on N_2 1 point test set up.

2.3 Catalyst Characterization

Two catalysts were selected for comparative characterization:

$CuO{\cdot}ZnO{\cdot}Al_2O_3$ sourced from Riogeninc

$Cu{\cdot}Zn{\cdot}Al_2O_3$ obtained from Alpha Aesar

The activation of both catalysts was performed in a controlled atmosphere using a 50:50 H_2/N_2 gas mixture. The temperature was ramped from ambient conditions to 330 °C at a rate of 2 °C·min^{-1} under an initial hydrogen concentration of 5%. Subsequently, the hydrogen concentration was increased in two incremental steps until reaching 50%. The catalysts were maintained at 330 °C for 4 hours to ensure complete reduction. Upon completion of the activation process, the system was cooled to 250 °C in the presence of steam and MeOH in the same amounts as during the activity measurements. The catalytic performance was evaluated over a temperature range from 250°C to 350°C, with increments of 20°C to systematically assess activity at various thermal conditions. Gas-phase products were quantified using calibrated Gas Chromatography (GC), while liquid-phase concentrations were estimated via Mass Spectrometry (MS). Following **Error! Reference source not found.** shows the parameters that were used during the characterization process:

Table 1 Catalyst characterization parameters

T_{min}	250°C
T_{max}	350°C
Catalyst Sieve fraction	212-425 um
Catalyst weight	250 mg
Catalyst density	0.89 g/ml
WHSV	23730, 17798, 11865 h^{-1}
Liquid to gas ratio	30:70
H_2O : MeOH	1.3:1 [5]

2.4 Gas Permeation Testing

The gas separation performance of single-channel tubular membranes was evaluated using a gas permeation rig at TNO. Tubular membrane samples were mounted within a custom-designed module as shown in Figure 1.

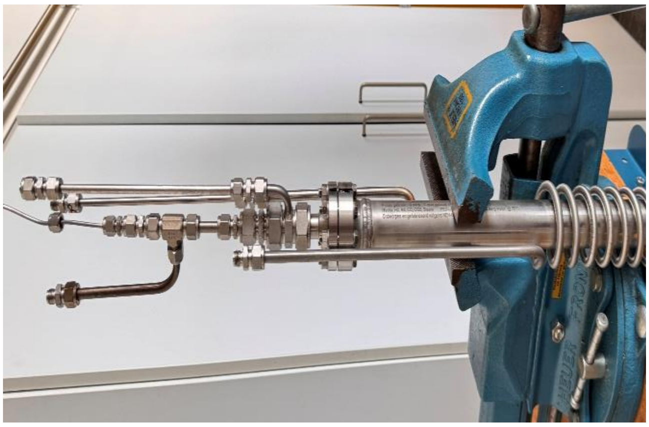

Figure 1 Membrane mounted on module

Permeation experiments were conducted in a crossflow configuration without the use of a sweep gas on the permeate side. The system operated in a dead-end mode, wherein the entire feed stream was directed towards permeate and no flow towards retentate. For measuring leak flows with N2 in the membrane a known bleed flow on the retentate is used. Gas permeation experiments were conducted to investigate and compare the H_2 and N_2 transport properties of three types of membranes: pure palladium (Pd), recycled Pd, and Pd-Au alloy membranes. Particular attention was given to the alloying behavior of the Pd-Au membranes, which was assessed by monitoring hydrogen permeance over a total duration of 150 hours. Based on prior experience at TNO, it is expected that complete alloying of the Pd and Au layers occurs after approximately 100 hours. This assumption will be validated through the current experimental data.

2.5 Equations Used

Following equations are used for the calculations of desired parameters:

$$Flux = \frac{[Gas\ flows\ in - Gas\ flows\ out]\ (\frac{mol}{s})}{Area(m^2)} \qquad (2.1)$$

$$Permeance = \frac{Flux}{\Delta P} \qquad (2.2)$$

$$Permeability = \frac{Flux \times Thickness}{\Delta P} \qquad (2.3)$$

$$H_2 Selectivity = \frac{Hydrogen\ Flux\ at\ same\ \Delta P}{Nitrogen\ Flux\ at\ same\ \Delta P} \qquad (2.4)$$

$$H_2\ Recovery = \frac{\dot{n}_{H_2,permeate}}{\dot{n}_{H_2,permeate} + \dot{n}_{H_2,retentate}} \qquad (2.5)$$

$$H_2\text{Purity} = \left(\frac{\text{moles of } H_2 \text{ in permeate}}{\text{Total moles of all other gases in permeate}}\right) \qquad (2.6)$$

$$\eta_{thermal} = \frac{\dot{n}_{H_2,out} \times LHV_{H_2}}{\dot{n}_{CH_3OH,in} \times LHV_{CH_3OH} + \dot{Q}_{in}} \qquad (2.7)$$

2.6 Gas Separation Testing

A palladium-gold (Pd-Au) alloy membrane was tested for hydrogen production in a methanol steam reforming process using the gas separation setup available at TNO. Palladium-gold (Pd-Au) alloy membrane was selected due to their enhanced durability and reliability under prolonged testing conditions. Water-methanol mixture (molar ratio 1.3:1) was introduced to simulate reforming conditions. The feed composition was calculated using Aspen Plus simulations to determine the equilibrium product gas composition under the designated operating conditions. The reforming process was conducted at elevated temperatures of 325°C and 350°C, with a feed pressure of 35 bars and a permeate side pressure of 1.5 bars. Methanol, being in the liquid phase at ambient temperature, was fed into the reactor, while the generated H_2 was selectively extracted through the membrane, collected, and compressed. To optimize the membrane system, a series of separation tests with dry gases (N_2, H_2) under varying operating conditions were conducted. This included changing feed flows (6, 4, 3 liters/min) and sweeping conditions (with or without). With the best optimized conditions, the influence of individual feed components on membrane performance is investigated through the introduction of water (H_2O), carbon monoxide (CO), carbon dioxide (CO_2), and methanol (CH_3OH). The concentrations of feed components are given in Table 2.

Table 2 Concentrations of components

Tests	1	2	3	4	5
H2	65	65	65	65	65
CO	0	0	0	8	8
CO2	0	0	17	17	17
MeOH	0	0	0	0	1
H2O	0	4	4	4	4
N2	35	31	14	6	5

Subsequently, the membrane will be integrated into a fixed-bed reactor containing a catalyst bed to simulate realistic reforming conditions. Under this configuration, the same experimental protocol will be applied, maintaining identical pressures and feed flows. Tests involving the gas compositions listed in Table 2 will be performed at both 325°C and 350°C in the presence of the catalyst.

3. Results and Discussion

3.1 Membrane Leak Testing Results

Table 3 shows all three membranes demonstrated very low leak rates, indicating strong integrity and performance. The module leak rates for each membrane are within the system's acceptable limits, confirming compliance with operational standards.

Table 3 Membrane leak rates

Membrane type	Effective Length(mm)	Thickness (µm)	N2-1-Point test (ml/min)	Module leak rate (ml/min)	Membrane leak test (ml/min)
Pd-Au	99	8.039	> 0.1	2.567	0.01
Pure Pd	95	4.373	1	4.998	0.001
Recycled Pd	96	6.8	0	2.5	0.05

3.2 Gas Permeation Results

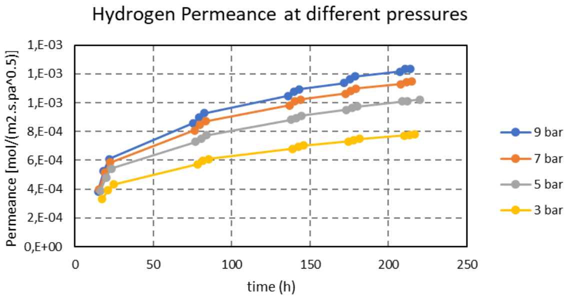

Figure 2 H_2 permeance [mol/(m^2.s.pa$^{0.5}$)] at different pressures for Pd-Au membrane

Hydrogen permeance was evaluated at various feed pressures for Pd-Au membrane. The results indicate that while hydrogen permeance [mol/(m^2.s.pa$^{0.5}$)] is stable over time due to alloying as shown in Figure 2. Notably, the system exhibits signs of alloy stabilization beyond 200 hours, suggesting that the alloying process reaches equilibrium, thereby contributing to the sustained permeance.

3.3 Comparison of Hydrogen Permeability of Membranes

The comparison of Pd-Au, pure Pd and Recycled Pd membrane is made in terms of hydrogen permeability at 9 bars as shown in Figure 3. Recycled Pd membrane has the highest hydrogen permeability among all while Pd-Au membrane has the lowest hydrogen permeability among the three membranes. It should be noted that all the membranes are not of the same thickness. While comparing recycled Pd and pure Pd membrane, it should be noted that recycled one is thicker than pure Pd. So, if only hydrogen permeance is compared then recycled one has lower permeance than pure Pd because of surface contamination with particles. Pd-Au membrane is tested for long hours compared to the other two membranes. Addition of Au to Pd reduces the active surface for H_2 to permeate through it but it increases mechanical strength, durability and resistance to poisoning that is why Pd-Au is used in gas separation experiments.

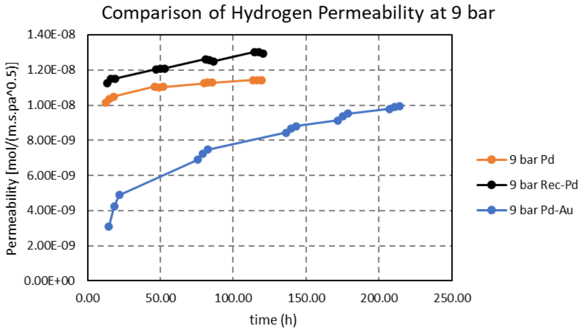

Figure 3 Comparing Hydrogen Permeability

3.4 Gas Separation Results

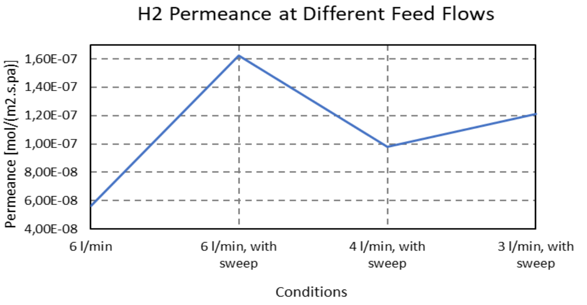

Figure 4 H_2 Permeance at different feed flows

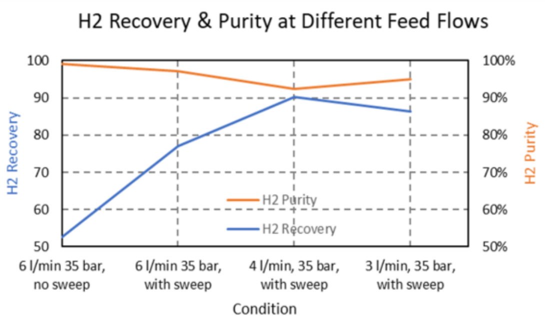

Figure 5 H_2 Recovery and Purity at different feed flows

From Figure 4, it can be seen that at feed flow of 6 l/min, the maximum value of Permeance for hydrogen is obtained. The higher feed flow helps in avoiding concentration potential which helps in obtaining higher permeance value and high purity but H_2 recovery obtained is low because of low residence time. The optimized conditions are 6 l/min and with sweep as sweeping with N_2 gas reduces the permeate pressure of H_2 and increases permeance.

3.4.1 Comparison of Permeance at Different Temperatures

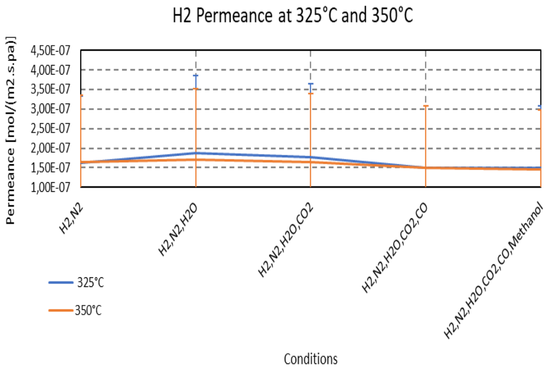

Figure 6 H_2 permeance at different temperatures

Initial tests with dry gases (H_2 and N_2) showed that hydrogen permeance remained comparable upon the introduction of water vapor. The introduction of CO_2 and CO reduces H_2 permeance indicating that there are hindrance and poisoning of the membrane. The values of H_2 permeance at two temperatures are comparable to each other as shown in Figure 6.

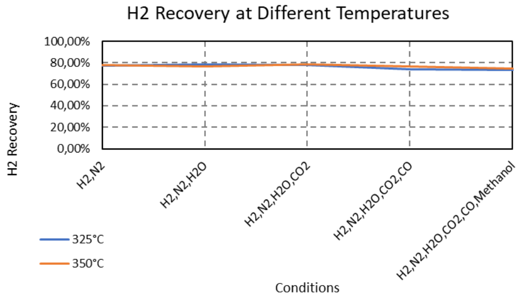

Figure 7 H_2 Recovery at different temperatures

The comparison of hydrogen recovery and purity at two temperatures has been plotted in Figure 7 and Figure 8. Hydrogen recovery and purity are comparable at temperatures 350°C and 325°C. High-purity hydrogen was obtained, with a maximum purity level of approximately 99.5%. Hydrogen recovery is around 80%.

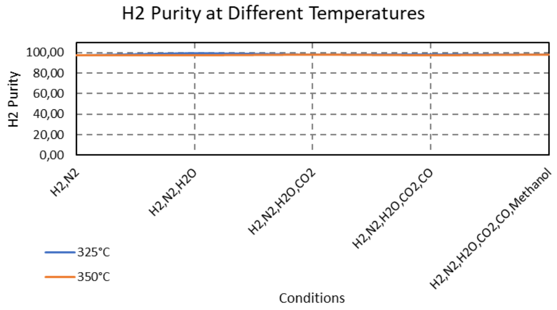

Figure 8 H_2 purity at different temperatures

3.5 Catalytic Activity Results

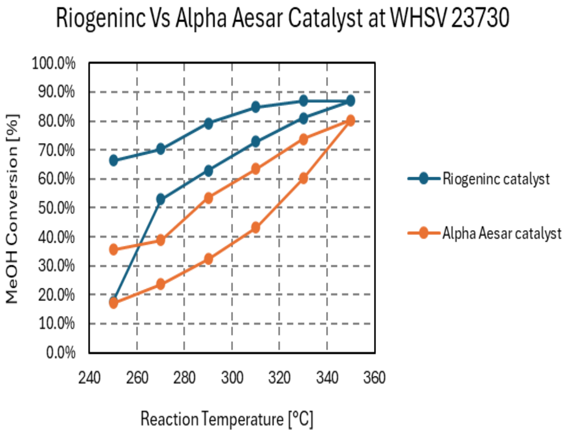

Figure 9 Catalytic activity results

Figure 9 showed that the catalytic activity of both catalysts decreased when temperature is reduced. This means that both catalysts are still reducing.

Also, none of the catalysts reached 100 % methanol conversion. It concluded that these catalysts are not fit for methanol reforming and attention should be given to nickel based catalysts.

3.6 SEM Results

SEM analysis was carried out because Pd-Au membrane characterized with mixed gases in the presence of catalyst bed ($CuO.ZnO.Al_2O_3$) was not permeating hydrogen gas. EDS mapping revealed zinc as the dominant surface element, with detectable diffusion into the Pd–Au layer, confirming migration from the catalyst. This likely altered the alloy composition, potentially forming Pd–Zn or Au–Zn intermetallic phases. Table 4 shows the % of elements in different spectrums of membrane.

Table 4 Percentage of elements in spectrums

Elements	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5
Pd %	19,9	39	65.6	59.5	73.8
Zn %	16.71	20.7	2.5	1.7	1.7
Au %	32.0	14.0	6.4	13.9	0.5
C %	17.4	9.0	7.2	7.3	6.7
O %	6.4	7.2	9.6	9.3	9.9
Al %	4.2	4.9	4.9	4.7	4.9
Cu %	2.1	2.5	2.5	2.2	2.6

4. Conceptual Membrane Reactor Design

In order to mitigate the problem of catalyst diffusion into the Pd-Au membrane, a new conceptual membrane reactor design is proposed as shown in . The proposed reactor configuration consists of a shell-and-tube membrane reactor incorporating palladium-alloyed membrane tubes. Catalyst is housed in shell and when feed comes in the shell reforming reaction occurs and mixture of gases produced are transported through stainless steel tubing to membrane and H_2 is permeated through the membrane. This design is further scaled up to produce $10Nm^3/hr$ of H_2. In order to reach target production of H_2, 6 membranes of 1 m length and 0.014 m diameter are needed. The tube and shell diameter needed are 0.05 m and 0.185 m respectively.

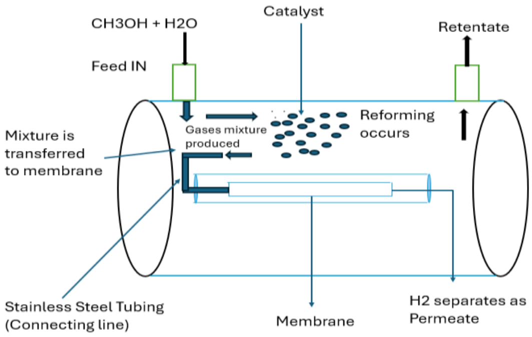

Figure 10 Conceptual membrane reactor design

5. Conclusions

A comparative study of pure Pd, Pd–Au alloy, and recycled Pd membranes showed that recycled Pd had the highest H_2 permeability, followed by pure Pd, with Pd–Au performing lowest due to its greater thickness. Despite this, Pd–Au membranes were chosen for gas separation due to enhanced strength and resistance to hydrogen embrittlement. Experiments revealed CO and CO_2 inhibit hydrogen permeation, with CO having a stronger effect via competitive adsorption. Higher feed flow rates improved hydrogen permeance and purity (up to 99.5%), though recovery slightly declined within acceptable limits. While further purification is needed for low-temperature PEMFCs, the hydrogen is suitable for high-temperature PEMFCs. The Pd–Au membrane reactor achieved 76% thermal efficiency (calculated from equation 2.7), far surpassing the 28% reported for conventional reforming systems[6]. Catalytic activity showed that both catalysts are not fit for methanol reforming and attention should be given to nickel-based catalysts. New conceptual membrane reactor design can mitigate the problem of catalyst diffusion into the membrane.

References

[1] O. Jazani, J. Bennett, and S. Liguori, “Carbon-low, renewable hydrogen production from methanol steam reforming in membrane reactors – a review,” *Chemical Engineering and*

Processing - Process Intensification, vol. 189, p. 109382, Jul. 2023, doi: 10.1016/j.cep.2023.109382.

[2] C. Wang *et al.*, "Configuration of coupling methanol steam reforming over Cu-based catalyst in a synthetic palladium membrane for one-step high purity hydrogen production," *Journal of the Energy Institute*, vol. 108, p. 101245, Jun. 2023, doi: 10.1016/j.joei.2023.101245.

[3] I. M. Atadashi, M. K. Aroua, A. R. Abdul Aziz, and N. M. N. Sulaiman, "Membrane biodiesel production and refining technology: A critical review," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 9, pp. 5051–5062, Dec. 2011, doi: 10.1016/j.rser.2011.07.051.

[4] 'Correlations in palladium membranes for hydrogen separation: A review, Journal of Membrane Science', [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0376738811002353)

[5] D.-W. Lee, S.-E. Nam, B. Sea, S.-K. Ihm, and K.-H. Lee, "Preparation of Pt-loaded hydrogen selective membranes for methanol reforming," *Catalysis Today*, vol. 118, no. 1–2, pp. 198–204, Oct. 2006, doi: 10.1016/j.cattod.2005.12.005.

[6] G. Wang, F. Wang, and B. Chen, "Performance Study on Methanol Steam Reforming Rib Micro-Reactor with Waste Heat Recovery," *Energies*, vol. 13, no. 7, p. 1564, Mar. 2020, doi: 10.3390/en13071564.