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Hydrogen separation from mixed gas (H₂, N₂) using Pd/Al₂O₃ membrane under forced unsteady state operations

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HIGHLIGHTS

- This research deals with feed modulation to improve H₂ recovery in a Pd membrane.
- The modulation is carried out by varying the switching time and amplitude.
- The dynamic operation of Pd membrane may improve H₂ recovery.

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ABSTRACT

The energy shortage and environmental pollution crises have prompted the investigation of hydrogen based cleaner energy system. Therefore, hydrogen has been considered as a promising energy carrier due to its sustainability and environmentally friendly. This research considered the separation of hydrogen from mixed gas (H₂ and N₂) by using Pd-based membrane. In order to produce extra high purity of hydrogen, the separation of hydrogen using Pd-based membrane under steady state operation suffers from long time lag and membrane deactivation. These two technical problems leading to the decrease of hydrogen permeability were intensively addressed in this work. The separation of hydrogen was conducted by using a Pd/α-Al₂O₃ membrane with aim to improve the performance of separation, indicated by time lag and hydrogen recovery. The novel method of the dynamic membrane operation was applied by performing a composition modulation of the feed gas flow rate. The steady state operation was used as a base case

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Palladium
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for comparison to dynamic operation. All experiments were carried out at 325 °C, atmospheric pressure, and H₂/N₂ ratio of 1:1, while varying the switching time and concentration amplitude for dynamic operation. The Pd based membrane was prepared, characterized, and it showed no pin hole could be found. The permeability constants for unsteady state condition resulted in higher when compared to steady state condition. The experiment results showed that the recovery of hydrogen under steady state condition was 21%. On the other hands, the recovery of hydrogen under invoked unsteady state operation was significantly improved three times higher than that of the steady state operation. The recovery of hydrogen increased 8–13% when the feed gas amplitude decreased from 1.5 mL/s to 0.5 mL/s. Operations at 300 s switching time and 0.5 mL/s flowrate amplitude reached the hydrogen recovery up to 63%.

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Introduction

Hydrogen is considered as one of main energy carriers and its production is intensively investigated by many research groups (a.o. [1–3]). Hydrogen can be produced from renewable resources by several different technologies, such as biomass gasification and electrolysis of water [4–7]. However, Steam Methane Reforming (SMR) using natural gas as feedstock is currently the most commonly applied technology for the production of hydrogen. This process requires in addition to the reformers, several downstream units, such as a Water Gas Shift Reactor (WGSR) consisting of High and Low Temperature Shift Converters (HTSC and LTSC) and also a separation unit such as Pressure Swing Adsorption (PSA) in order to purify the produced hydrogen [8]. Process intensification offers new possibilities [9–11] and benefits, especially when integrating SMR with both WGSR and PSA into a single unit, viz. the membrane reactor with perm-selective hydrogen membranes [12–14].

For the separation and purification of hydrogen from other compounds in the mixed gas Pd-based membranes have been developed showing very high permeabilities and perm-selectivities (a.o. [8,13,15–17]). Hydrogen may diffuse selectively through a Pd-membrane according to the solution-diffusion mechanism [18] and the ideal behavior of hydrogen transport rate can be predicted using Sieverts' Law. Vadrucci et al. developed a modification of Sieverts' Law by including surface kinetics resistances [19]. However, the Pd membrane has a major drawback related to the high price of the Pd material [20]. Moreover, even though the pure Pd metal has a high level of hydrogen permeation, it suffers from embrittlement at temperatures below 300 °C [21]. Therefore, the use of Pd-alloy membranes has been proposed. A Pd alloy, such as Pd–Ag exhibits an even better performance and is able to improve the chemical resistance [22–24]. The presence of Ag in the Pd-alloy membrane may result in an increase in the hydrogen permeability up to 1.17 times better than the pure Pd membrane [18]. To further improve the hydrogen permeation (and reduce the amount of Pd required), a thin Pd–Ag alloy was fabricated using an

improved electroplating technique based on a reported plating solution including PdCl₂, AgNO₃, HBr and HNO₃ [25]. According to Basile and Gallucci [8], the hydrogen flux for Pd–Ag membranes is also higher than that of Pd–Au and Pd–Cu alloys. To improve the mechanical stability of very thin-film membranes, supported Pd-membranes have been proposed [8]. Next to palladium, a number of alternative materials, which can be used for hydrogen separation using dense type of membranes cover nickel, niobium and vanadium alloys, ceramic supports for metal alloys and porous glass membranes [26], zeolite [27,28], polymeric based [29], porous ceramic [30,31], carbon-based [32], nanocomposite [33,34], microporous silica [35]. Cornaglia et al. (2015) mapped the characteristic of the palladium-based membrane with various alloys and supports such as PSS, PdAu, PdCu, PdAgAu, YSZ [36]. In addition, the upper temperature limit both oxidizing and reducing for various membrane supports was discussed in Basile et al. (2008) [37].

The hydrogen transport rate through a membrane layer is affected by the volumetric rate of the feed gas [38–41], the pressure difference at both sides of the membrane [42], the operating temperature [43,44], and the feed and permeate compositions [45–48]. The hydrogen flux tends to increase with increasing volumetric feed flow rates, the transmembrane pressure difference and operating temperature. In membrane separation process, the partial pressure difference between retentate and permeate sides of the membrane plays an important role to influence the permeation rate. A higher transmembrane pressure difference will create greater a H₂ driving force, improving the permeation rate of H₂, in correspondence to Sieverts' Law. Sweep gas, i.e. steam or nitrogen, during the operation can be used to increase the transmembrane pressure difference. The higher the flow rate of the sweep gas, the larger the pressure difference created.

Moreover, the presence of CO, CO₂ and H₂O in the feed on the hydrogen permeation rate through the Pd membrane can be very important. This was evaluated by Miguel et al. [46], and Pérez et al. [47]. It was reported that the adsorption effect on the membrane flux (flux inhibition) of H₂O > CO > CO₂. Boon

et al. [49] reported an overview about the adsorption of these compounds on the Pd-based membrane surface.

When the feed gas consisted of a mixture of H_2 and N_2 , N_2 will be partially retained on the membrane surface and form a barrier layer for H_2 permeation inducing a concentration polarization phenomenon [41,50,51]. Nitrogen concentration polarization on the membrane surface decreases the H_2 flux over the operation time [44,52]. The nitrogen molecule can dissociate on the membrane surface, but it can hardly undergo the dissolution because of the activation barrier. An interaction between nitrogen and hydrogen on the membrane surface can also lead to the formation of NH_x ($x = 0, 1, 2$). This NH_x may reduce the hydrogen permeation by occupying active sites on the membrane surface, thus competing with hydrogen atoms to be adsorbed [43]. Hence the hydrogen recovery tends to decrease during the operation time.

Wang et al. [43] offered a method to regenerate the hydrogen recovery by purging the membrane using pure hydrogen at 500 °C. The square wave perturbation was also proven to improve the reactor performance by modulating the feed flow rate as a function of the switching time symmetrically or asymmetrically [53]. Hoebink et al. [54] also reported that there were three regimes of dynamic operation consisting of sliding, dynamic, and quasi-steady state. The sliding regime occurs when the switching time is slower than the response time, while the quasi-steady state is the opposite case. The dynamic regime occurs if the switching time and response time is at the same scale. Each process has its typical optimum perturbation conditions, depending on the process. In a previous study, using an unsupported $Pd_{75}Ag_{25}$ membrane of 100 μm thickness, it was revealed that dynamic operation by modulating the hydrogen flow rate while keeping the nitrogen flow rate constant can be used to improve the performance of the membrane within a certain range of switching times, either during a start-up or after a start-up period [13].

In this research, the separation of hydrogen from a feed gas containing a mixture of H_2 and N_2 using a pure and thin Pd membrane supported by $\alpha-Al_2O_3$ was investigated applying dynamic operation with the aim to improve the recovery of hydrogen. A composition modulation of the feed gas flow rate, i.e. mixed gas of H_2 and N_2 , with varying switching time was applied. The critical point to be explored here is the time scale required for different types of membrane, since every membrane type and membrane thickness requires a different specific time scale. The type of feed gas flow rate modulation instead of hydrogen flow rate only is also investigated. The membrane performance under unsteady state operation is compared with the reference case of operation under steady state conditions.

This paper is organized as follows; in next section the membrane preparation and experimental setup and procedures are described. In [Results and discussion](#) the experimental results are presented and discussed: after the characterization of the membrane the performance of the dynamic operation with feed gas flow rate modulation is investigated including the influence of the amplitude and switching time on the hydrogen recovery. Finally, the main conclusions are summarized.

Materials and methods

Materials

The chemicals used in this research and their specifications are presented in [Table 1](#). For the feed gas, it consists of the mixed H_2 – N_2 containing 50/50 (%vol/vol). In the previous study, the use of higher feed concentration of H_2 ($H_2:N_2 = 70:30$ in %-v) gave a significant effect for dynamic operation. On the other hands, equimolar feed concentration gave no significant effect when using thicker membrane (100 μm) [13]. In this study, a thinner membrane was used (10 μm) with equimolar feed concentration.

Pd/ $\alpha-Al_2O_3$ membrane preparation

A Pd membrane was prepared on the outer surface of a porous $\alpha-Al_2O_3$ tube (OD: 10 mm, ID: 6 mm, mean pore diameter: 0.1 μm , length: 0.1 m) by electroless plating with the procedure described as follows [15,55]. The calcined porous $\alpha-Al_2O_3$ tube was ultrasonically washed by water and ethanol. Palladium nuclei were then supported on the outer surface of the tube by sensitization and activation treatments with stannous chloride and palladium chloride solutions, respectively, and this process repeated several times. Palladium was autocatalytically deposited on the outer surface of the tube from an electroless plating bath containing a tetraamine complex of palladium, ethylenediamine tetra-acetic acid, ammonium hydroxide and hydrazine. During the electroless plating, both ends of the porous alumina tube were sealed to avoid generation of Pd on the inner surface of the support.

The activation and sensitization procedures are crucial in the preparation of the $\alpha-Al_2O_3$ support prior to the electroless plating. A washed $\alpha-Al_2O_3$ support was immersed in a stannous chloride solution for 1 min. The support was washed in deionized water for 30 s. Then, it was immersed with $PdCl_2$ solution for 1 min. The support was subsequently rewashed by deionized water for 30 s. These steps were continuously repeated for three times to ensure the activation quality. In the end of the procedure, the support was immersed in a hydrazine solution for 30 s. Finally, the support was required to be washed again by deionized water for 10 s. During the process, all solutions used were kept at 25 °C.

Both ends of the palladium nuclei supported $\alpha-Al_2O_3$ tube were sealed using silicon rubber plugs to avoid the solution entering the inner part of the $\alpha-Al_2O_3$ tube. The $\alpha-Al_2O_3$ tube was immersed in a palladium electroplating bath for 90 min with the temperature maintained at 50 °C. During the electroless plating, the $\alpha-Al_2O_3$ tube was swung in the plating bath. The $\alpha-Al_2O_3$ tube was then washed with deionized water to remove unnecessary particles on the $\alpha-Al_2O_3$ tube surface. The whole procedure as mentioned above was repeated up to 10 times to ensure the plating quality for the complete coverage of the $\alpha-Al_2O_3$ tube.

Research procedure

The switching time is a time period used to change the concentration of the feed gas from low to high values and vice

Table 1 – Materials used in the experiment.

Material	Specification	Function
H ₂	High purity, 99.995% of H ₂	Membrane activation
Ar	High Purity, 99.995% of Ar	Purge gas
N ₂	High purity, 99.995% of N ₂	Sweep gas
Mixed gas of H ₂ /N ₂	50/50 (%vol/vol)	Feed gas
Silica wool	–	Heat insulator in electric heater (tube furnace)
Silica gel	–	Moisture adsorber to trap possible water in the stream

versa, repeated periodically. In ideal condition, this flow rate change will create a square wave perturbation, leading to a partial pressure change, which might influence the permeation of hydrogen through the membrane wall. Based on our previous study, the order of the time scale for palladium-based membrane spans from seconds to minutes [13,17]. In this work, the influence of the flow rate amplitude indicating the level of high or low concentration and also the concentration in the feed on the hydrogen recovery and time lag of the hydrogen permeation through Pd/ α -Al₂O₃ membrane are investigated. The experimental procedure basically consists of a preparation stage, main experiment stage of hydrogen separation, and data interpretation. The details for each procedure are described as follows.

Preparation stage

The preparation stage consisted of setting up the equipment, purging the membrane both shell and tube sides using argon (Ar), and gently heating the membrane up to 325 °C. The experimental setup configuration is depicted in Fig. 1. Purging was aimed to remove initial air inside the membrane by flowing Ultra High Purity (UHP, 99.995%) argon into the membrane for 30 min. The next period for 30 min, UHP

hydrogen and UHP argon, each with a flow rate of 1 mL/min, were fed together into the membrane unit to remove all impurities on the Pd/ α -Al₂O₃ membrane surfaces. The next period of 30 min, argon was fed again to ensure no hydrogen was left inside the membrane unit. The composition modulation of the feed gas was created by blending the feed gas mixture of H₂/N₂ (50/50 %-v/v) with a modulated N₂ stream.

The use of Ar as inert for purging was to assist interpretation of the experiment data with the gas detector in the early minutes of each experiment. The gas detector used in this experiment was a TCD (Thermal Conductivity Detector). Since He gas has a thermal conductivity approaching that of H₂ gas, difficulties in the analysis of the data could occur in the early minutes of the main experiment, if purging would be carried out with He gas. The thermal conductivity of Ar largely deviates from H₂, and is thus suitable for this study.

Hydrogen separation

Hydrogen separation from a mixture of H₂/N₂ was conducted in two operating conditions: the steady state operation as a base case for comparison and the Forced Unsteady State Operation (FUSO). In the steady state operation, 1.5 mL/s mixed gas consisting of H₂/N₂ 50%/50%-v/v was fed into the

Fig. 1 – Experimental setup of H₂ separation from H₂–N₂ using Pd/ α -Al₂O₃.

membrane shell side and 2 mL/s UHP nitrogen was fed into the membrane tube side as the sweeping gas to enable maximum pressure difference between the shell and tube sides. This pressure difference created the driving force for hydrogen permeation through the Pd layer. The gas detector for hydrogen measurement logged the data every certain time for 5 h operation. This data was saved in the data logger for further data treatment. Subsequently, the hydrogen separation from a H₂/N₂ gas mixture was carried out under forced unsteady state operation by modulation of the feed gas flow rate or composition with a modulator system before it was fed to the shell side of the membrane. The modulator system basically consists of needle valves, solenoid valves, and check valves, which enables either the flow rate or gas composition to be adjusted. Three variations of the feed gas flow rate amplitude as described in Table 2 were applied to investigate the hydrogen recovery. High flow rate (HFR) and low flow rate (LFR) were regulated to adjust the value of the total flow rate while keeping the composition constant, so that its average was similar to the steady state value (1.5 mL/s). The purpose was to enable a fair comparison of the results of the FUSO experiments to the steady state reference case. The amplitude was defined as the maximum deviation from the average value. A schematic diagram showing the gas flow rate amplitude and the switching time is presented in Fig. 2. The effect of the gas flow rate amplitude can be seen from the value of the hydrogen recovery on the same switching time value. Moreover, variations in the switching time were also investigated with aim to explore the regimes of operation for FUSO, either sliding, dynamic, or quasi-steady state.

Data interpretation

The hydrogen recovery was determined from the hydrogen composition detected using gas detector and the gas flow rate, which was measured either in the feed gas or permeated gas. The feed gas concentrations of hydrogen as well as its products in the permeate stream and retentate stream were analyzed using the H₂ gas detector (Cosmos XP-3140, thermal conductivity), which could measure in real time to follow the dynamic changes during the process. Based on the balance of hydrogen component and the volumetric flow rate data obtained from the experiment, the recovery of hydrogen could be calculated using Equation (1):

$$R_{H_2} = \frac{\text{mol permeated hydrogen in tube side}}{\text{mol hydrogen in feed gas}} \times 100\% \quad (1)$$

The determination of permeability constant was calculated using Equation (2):

$$J_{H_2} = P_{H_2}^0 e^{\left(\frac{-E_a}{RT}\right)} \left[\frac{P_{H_2, \text{retentate}}^n - P_{H_2, \text{permeate}}^n}{\delta} \right] \quad (2)$$

where $P_{H_2}^0$ is the permeability constant of H₂ [mol·m/(m²·s·Pa^{0.5})], E_a is the activation energy [J·mol⁻¹], R is the ideal gas constant [J·mol⁻¹·K⁻¹], T is the absolute temperature of system [K], and δ is the membrane thickness [m]. This equation holds for Sieverts-Fick's law, which is generally known as Richardson's equation [18]. The n -values, either 0.5 or 1, depends on the rate-limiting step. Nevertheless, an experimental approach has found that n -values typically range from 0.5 to 0.8 for thin palladium membranes.

Results and discussion

Characterization of Pd membrane

The Pd membrane layer was initially characterized to check the cross over surface using SEM (Scanning Electron Microscope) as shown in Fig. 3(a). Based on this measurement, pin holes could hardly be found in this point of view, indicating that the Pd/ α -Al₂O₃ membrane should be working properly for the experiments without any leakage over the membrane surface. This condition should result in (virtually) pure hydrogen production at the permeate side. SEM analysis on the Pd layer membrane surface was conducted and is shown in Fig. 3(b).

Determination of permeability constants

In this work, the permeability constant of hydrogen transport through the Pd/ α -Al₂O₃ membrane was determined by varying the mixture of feed gas, such as H₂-Ar and H₂-N₂-Ar in steady state conditions, and also comparing H₂-N₂-Ar between steady state and unsteady state conditions. The experimental results for the determination of the permeability constants are shown in Fig. 4. For pure hydrogen in the feed gas without N₂, the permeability indicated the highest value when compared to feed gas containing N₂. It could be induced by the possibility of N₂ to interact with Pd and covered the membrane surface [56–58]. As consequence, the possibility of H₂ to be adsorbed on the membrane surface became smaller since some surfaces were occupied by N₂, and therefore the

Table 2 – Flow rate amplitude, High Flow Rate (HFR), Low Flow Rate (LFR), and switching time. The sweep gas flow rate was set at 4 mL/s.

Flowrate amplitude (mL/s)	High Flow Rate/HFR (mL/s)	Low Flow Rate/LFR (mL/s)	Average Flow Rate of HFR and LFR (mL/s)	Switching Time (s)
0.5	2.0	1.0	1.5	30, 34, 300
1.0	2.5	0.5	1.5	30, 34, 300
1.5	3.0	0.0 ^a	1.5	30, 34, 300
Steady ^b			1.5	–

^a There is no flow of H₂/N₂ 50/50 (%v/v) and is replaced by inert gas (argon) flow at 3 mL/s.

^b Base case for comparison to unsteady state.

Fig. 2 – Schematic diagram of the gas flow rate amplitude and the switching time (ST) applied in dynamic operation.

Fig. 3 – (a) SEM image of Pd membrane cross sectional area; (b) SEM image of Pd membrane surface area.

Fig. 4 – Permeability constants of hydrogen through Pd/ α -Al₂O₃ membrane: (a) steady state condition, (b) unsteady state condition.

dissociation process of H₂ to H atom was also smaller. In the case of H₂-N₂-Ar, the permeability constant of hydrogen through Pd/ α -Al₂O₃ membrane under unsteady state conditions increased when compared to steady state conditions. As indicated in Fig. 4, the dynamic operation would be able to create a molecular vibration of the fluid flow leading to turbulence, so that the adsorbed compounds such as N₂ were removed from the membrane surface. It would open for hydrogen to adsorb more efficiently over the clean membrane surface and carry out the solution diffusion.

When the feed gas contained a mixture of H₂ and N₂, part of the N₂ would retain over the membrane surface and create the barrier layer for H₂ permeation, which is known as concentration polarization [41]. It could cause a larger resistance for H₂ permeation and decrease the H₂ flux through the membrane. The nitrogen molecules in the bulk phase could encounter the dissociation and adsorbed on the membrane surface, but they could not undergo the dissolution due to activation barrier. N and H atom on the membrane surface could drive the formation of NH_x. The NH_x molecule would

cover the membrane surface, hence decreasing the permeability of hydrogen [43].

Start-up behavior with constant feed gas flowrate

The evolution of the hydrogen recovery in time during a permeation experiment with the Pd/ α -Al₂O₃ membrane with a constant feed gas composition is shown in Fig. 5. Based on this experiment, there were two periods during the operation, consisting of a start-up period and a period where the hydrogen recovery has become stable. The time period required from the initial start-up to reach stable recovery is referred to as time lag. The time lag for this experiment with a constant feed gas composition is approximately 7000 s and the average hydrogen recovery after reaching steady state conditions reached 19%. In the start-up period, the feed gas containing hydrogen commenced permeating from the retentate (shell) side into the permeate (tube) side by following the solution-diffusion mechanism [55,59]. At the beginning of the process, the driving force induced by the concentration difference between both sides was very high, leading to quick hydrogen permeation through the membrane wall. It was observed that the hydrogen recovery was varying during the start-up period, which might be induced by the reversible adsorption-desorption mechanism before it reached the steady state condition. The fluctuation occurred when the hydrogen adsorption-desorption mechanism was still moving toward its equilibrium [13]. Each step encountered the movement of either forward or forward-backward steps [43]. When starting with initial concentration of hydrogen over the membrane surface equals to zero, then just after introducing the feed gas, there was high gradient concentration of hydrogen between bulk phase and membrane surface. High hydrogen concentration in the bulk phase moved to the membrane surface against the external layer. The reversible

Fig. 5 – Dynamic behavior of hydrogen permeation through Pd/ α -Al₂O₃ membrane during start-up period. The feed flowrate of the mixed gas was 1.5 mL/s. Open circles represent the hydrogen recovery over time for 5.5 h, red solid line represents the membrane behavior trend, and vertical dashed black line represents the time lag. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

adsorption-desorption with dissociation/association of H₂(g) to H(ads) took place as follows [43]:

Similar case might happen for nitrogen as can be written in the following reaction:

Either N₂(ads) or N(ads) was able to react with H(ads) to form NH(ads) over the membrane surface. Therefore, only part of H(ads) would diffuse through the membrane wall, while the rest would react with N₂(ads) and N(ads) to form NH(ads) and NH(ads), respectively. This reaction occurred on the membrane surface as follows:

The solution-diffusion of H(ads) through the membrane layer could be written as follows:

In the permeate side, H(ads) would be associated to form H₂(g), which was subsequently desorbed in the gas phase as the main product.

The NH_x(ads) would cover the membrane surface, hence it could inhibit or reduce the number of sites for H(ads) since some H(ads) would be consumed by NH_x(ads). Providing larger amount of H(ads) from H₂(g) at the surface, it could drive the formation of NH₃(ads) and subsequently NH₃(g), which desorbed to the gas phase at the retentate side.

Fig. 6 – Recovery of hydrogen during start up under dynamic operation: switching time of 34 s and amplitude of 0.5 mL/s, time averaged value was 51%.

During start-up period, this reaction mechanism occurred and might take several minutes to hours before it reached the steady state reaction rates. When the steady state adsorption-desorption reactions were obtained, the permeation of hydrogen through the Pd/ α -Al₂O₃ indicated more stable oscillation. However, it showed a slow decrease of hydrogen recovery as function of time with gradient of 0.04% in the time period of 7200 to 21,600 s. In the stable oscillation period, the hydrogen recovery tends to decrease that might be induced by NH_x coverage on the membrane surface according to Wang et al. [43], leading to decreased membrane performance. In the current study, the start-up behavior with constant feed gas composition was used as a base case for comparison to dynamic operation.

Start-up behavior with dynamic feed gas flowrate

The start-up behavior with constant feed gas composition showed a relative long period of time lag, low hydrogen recovery, and tendency of hydrogen recovery decrease. The proposed solution to overcome long time lag and deactivation of membrane by suspending the process and purging with pure hydrogen for a dozen minutes was not appropriate. It might become impractical, expensive, and reduce productivity. A forced feed gas flow rate of H₂ and N₂ was applied during start-up period with the aim to investigate the influence of the feed gas flow rate on hydrogen recovery, time lag to reach the steady state operation, and the stability of Pd/ α -Al₂O₃ membrane. The experiment results are shown in Fig. 6. As before in the experiment with a constant feed gas flow rate, the variation in the hydrogen recovery during the start-up period was also observed in this case. However, the time lag occurred in the dynamic feed gas flow rate was only about 2400 s after feeding the gas, which was much shorter when compared to a constant feed gas flow rate, which was around 7000 s. After reaching the stable oscillation, the recovery of hydrogen was significantly improved up to 51%, calculated in time average value. The shorter time lag in the dynamic feed gas composition might be induced by the appropriateness of time scale to influence the adsorption, dissociation, solution diffusion, re-association, and desorption rates to reach the equilibrium conditions. In addition, higher recovery of hydrogen of Pd/ α -Al₂O₃ membrane operated under dynamic feed gas flow rate might be induced by faster rate of mass transfer of hydrogen from bulk gas phase to membrane surface, followed by the rate of solution diffusion. This condition was provided by changing hydrogen flow rate from higher and lower values, which might drive to clean the membrane surface from impurities (N₂(ads), N(ads), NH_x(-ads), and NH₃(ads)). Some possible coverages of nitrogen over membrane surface might be cleaned under this perturbation, since during dynamic feed gas flow rate, the momentum of total flow rate would remove nitrogen containing compound

including NH₃(ads). As other positive trend, the recovery of hydrogen showed incremental as a function of time, approximately 3% during 16,000 s.

At 1 mL/s amplitude, the lower flow rate used was 0.5 mL/s. This lower flow rate might cause the polarization of N₂ concentrations on the membrane surface as the contact time between N₂ and the membrane surface became long enough, following the reaction as written in Equation (4). Higher concentration of nitrogen shifted the reaction to the right, so that the potential for the formation of N from dissociation of N₂ became high. From the reaction in Equation (4), when N₂(ads) formed on Pd surface, it would dissociate to form N(ads) and it was not reversible reaction. Therefore, N(ads) would undergo the hydrogenation reaction with H(ads) to form NH(ads), NH₂(ads), and NH₃(ads), which covered the membrane surface. This condition caused the flux of hydrogen passing through the membrane wall and its association to form H₂ became lower, leading to low hydrogen recovery. The mechanism of N(ads) effect on H₂ permeation had also been studied previously by Chantaramolee et al. [21]. In addition, at low flow rates the formation of film coating on the membrane surface would be greater [39,52]. As consequence, this film layer inhibited any transports mechanisms H₂.

Regimes of operation

The switching time is a key parameter to influence of the regimes of operation, which leads to overall process performances [10,54,60]. The effect of the switching time may differ for each process and operating condition due to different time scale either microprocessing or macroprocessing. Therefore, it should be explored for every case to determine the proper switching time to be applied. In this study, the response of each switching time as function of time is shown in Fig. 7. As can be seen, the switching times of 10 s (Fig. 7(a)) could hardly influence the dynamic response, which was indicated by the steady state values. It means that up to switching time of 10 s, the operation regimes could be categorized as sliding or relaxed-steady state regime [54]. It occurred due to the faster switching time when compared to the time scale of modulator system to respond the disturbance. As a result, the system could hardly follow the feed gas perturbation, which leads to so called relaxed-steady state. At larger switching time (34 s), the output response showed the dynamic feed gas composition as can be seen in Fig. 7(b). This switching time created the sinusoidal wave as indicated by the dynamic regime. The quasi-steady state regime occurred at the switching times larger than 60 s as shown in Fig. 7(c). In this case, the output response could easily follow the feed gas flow rate modulation repeated from high to low concentration. After reaching high or low value of the flow rate, the system achieved the steady state condition.

Forced unsteady state operation

Forced Unsteady state operation (FUSO) was carried out by modulating the feed gas flow rate of H₂–N₂ in the form of

Fig. 7 – The output response of dynamic operation at three different switching times: (a) 10 s; (b) 34 s; (c) 60 s. This output response of the modulator system entered to the membrane.

square wave before entering the Pd/ α -Al₂O₃ membrane. The actual feed gas behavior entering the membrane strongly depends on the applied switching time as previously discussed. This kind of operation was aimed to improve the membrane performance in term of time lag, hydrogen recovery, and membrane deactivation.

Effect of gas flow rate amplitude on hydrogen recovery

The moderate switching times at 34 s determined from preliminary experiment represented the dynamic regime of operation. The experiment results for this switching time at various feed gas amplitudes are presented in Fig. 8. From these results, it can be seen that the dynamic permeation of hydrogen through Pd/ α -Al₂O₃ membrane proceeded well without decreasing the recovery of hydrogen over time on stream. All flow rate amplitudes resulted in positive trends without membrane deactivation, which kept the recovery of hydrogen high. The periodic operation with proper switching time could affect the rate of adsorption-desorption in the membrane layer, either internal or external one. It was correlated with the external resistance when hydrogen started diffusing from bulk phase into membrane surface, while the concentration wave would give a momentum for molecule to diffuse. The external layer became thinner when high flow rate of feed gas was fed into the membrane [52]. However, when this condition was applied, the recovery of hydrogen would decrease due loss of hydrogen through the retentate. The modulation of the feed gas might affect the mechanism of permeation, leading to hydrogen recovery changes. The stable oscillations occurred at small (0.5 mL/s) and large (1.5 mL/s) amplitude values, while it indicated increased hydrogen recovery at moderate amplitude value (1 mL/s) during 300 min of time on stream. In term of hydrogen recovery, all applied flow rate amplitudes in the dynamic operation mode resulted in better performance when compared to steady state condition.

Effect of switching time on hydrogen recovery

The influence of other switching times (30 s, 34 s, 300 s, and 900 s) on hydrogen recovery were also investigated and the results are shown in Fig. 9. At all switching times, the recovery of hydrogen decreased when the flow rate amplitude increased. At high flow rate amplitude (0 mL/s – 3 mL/s), there was time where no hydrogen introduced to the membrane system. This condition probably stimulated the formation of nitrogen-adsorbed containing species, which blocked the membrane surface and inhibited the permeation of hydrogen. Fast switching time induced the system of membrane could hardly respond to the feed perturbation, which resulted in small effect of dynamic changes. It showed the consistency towards the steady state hydrogen recovery, which was only 21% recovery hydrogen. On the other hands, slow switching time showed higher hydrogen recovery. As previously mentioned that up to 300 s switching time, the system of membrane still behaved in the dynamic condition and it

resulted in better performance for hydrogen recovery, which may relate to the increase in mass transfer coefficient towards the membrane. This condition still applied up to switching time of 900 s, even when compared to the switching time of 300 s, the recovery of hydrogen slightly decreased. In accordance with research in dynamic operation that slow perturbation to the system will give rise to quasi-steady state [13,17,53,54]. It means that the performance of the system would also get closer and even similar to the steady state condition.

It was observed that the increase of the gas flow rate amplitude from 0.5 mL/s to 1.5 mL/s caused the decrease in hydrogen recovery. At higher gas flow rate amplitude, the residence time of the gas inside the membrane got shorter. As a result, there was a significant contribution of the gas to flow out of the membrane before permeating through the Pd membrane. However, higher gas flow rate could reduce the external mass transfer barrier [52]. Therefore, further criteria design and optimization in operation procedure of membrane system are required.

When lower flow rate was applied, the residence time of H₂ and N₂ inside the membrane system was long enough to dissociate and adsorbed on the membrane surface. Next to larger mass transfer limitation, this condition also induced severe competitive adsorption on the membrane surface. Due to irreversibility of nitrogen dissociation reaction, the adsorbed nitrogen might react with adsorbed hydrogen to form NH_x(ads). In addition, lower flow rate might cause the concentration polarization and increased the thickness of the interphase layer [52]. On the other hands, high flow rate of gas feed could provide better permeation because it induced the formation of a thin layer in the interphase. Moreover, the periodic use of high and low flow rates at certain switching time might sweep the adsorbed nitrogen on the membrane surface and made it clean. In overall operation, the time average value of hydrogen recovery for amplitude of 0.5 mL/s showed higher than that of 1.0 mL/s. It could be caused by the formation of concentration polarization during LFR applied, which then delivered major effect on overall hydrogen recovery. On the other hands, there were some circumstances in which the flow rate of the feed gas was zero when the amplitude of 1.5 mL/s was applied. As a result, this flow rate amplitude gave the lowest overall hydrogen recovery among other amplitudes at the same switching time.

Effect of switching time on time lag

Next to hydrogen recovery, time lag during start-up period is another important parameter of membrane performance. The comparison of time lag at various switching times and feed flow rate amplitudes is shown in Fig. 10. At equal flow rate amplitude, the lower switching time produced the lower time lag. Similar phenomenon was also observed by Budhi et al. [13] with different Pd–Ag membrane operation. In FUSO, continuous perturbation increased the rate of adsorption-desorption. At constant switching time, higher flow rate

Fig. 8 – Stability of hydrogen permeation under forced unsteady state operation of switching time 34 s and flow rate amplitude (a) 0.5 mL/s, time average value = 56%, max = 59%; (b) 1.0 mL/s, time average value = 52%, max = 63%; (c) 1.5 mL/s, time average value = 48%, max = 57%.

Fig. 9 – Influence of the switching time and flow rate amplitude on hydrogen recovery, compared to steady state condition.

Fig. 10 – Time lag at various switching times for two different flow rate amplitude, compared to steady state operation.

amplitude produced smaller time lag since higher flow rate amplitude would produce better sweeping effect over the membrane surface.

The time lag for unsteady state operation was observed much shorter than the time lag obtained in the steady state operation. The time lag in the steady state operation with feed flow rate of 1.5 mL/s was about 6900 s (or 115 min). Meanwhile, the time lag in the unsteady state operation with flow rate of 1 and 2 mL/s at switching time of 34 s was 2400 s (or 40 min). Detailed experimental results are presented in Fig. 10.

Based on Fig. 10, it can be observed that at the same amplitude, the smaller the switching time, the smaller the time lag. Similar results also occurred in the operation of the Pd–Ag membrane, as has been studied by Budhi et al. [13]. Meanwhile, at the same switching time, the greater the amplitude of the flow rate, the smaller the time lag. This showed that the high and low frequencies of the flow rate resulted in the adsorption rate, solution diffusion, and desorption reaching equilibrium.

In the steady state conditions, the hydrogen permeation took place naturally, i.e. without any deliberate interference

factor, so the time required to achieve stable oscillation conditions was prolonged. In the unsteady state operation, the system was fed by flow rate that varied following a certain switching time, so that the hydrogen permeation became accelerated. At a small switching time, the frequency of disruption was increasing frequently, hence the adsorption-desorption process on the membrane surface progressed faster toward equilibrium. On the membrane, there was a thin film layer, in which the part was located on the inter-phase segment that separates the bulk phase and membrane surface. In the operation of the forced unsteady state membranes, high flow rates could narrow the film layer, decreasing the resistance of mass transfer. The effect of the flow rate that disrupted the film layer on the membrane surface had been studied previously by Chen et al. [52].

Conclusions

The Pd/ α -Al₂O₃ membrane for separating H₂ from the mixed gas of H₂–N₂ has been developed and operated under steady

state and forced unsteady state operation by modulating the feed gas flow rate. In the steady state operation, the recovery of hydrogen showed low value, and it was observed the tendency of downward trend as function of time. The phenomenon of long-time lag during this separation was also indicated in this steady state condition. The forced unsteady state operations have proven to achieve higher hydrogen recovery when compared to steady state operations. The membrane stability during 5 h test showed no deactivation, and even accelerated to increase a little bit. In the forced unsteady state operations, the switching time of 30 s was able to produce the shortest operating time lag; while the switching time of 34 s was able to reach higher hydrogen recovery compared to 30 s, even the flow rate amplitude for 34 s switching time did not change so much in recovery of hydrogen. Increasing the switching time at 300 s increased the recovery of hydrogen, but it was not the case at switching time of 900 s. Too long switching time would shift the time scale of the membrane system approach the steady state operation. In the forced unsteady state operation, the amplitude of 0.5 mL/s gave a higher hydrogen recovery than other amplitude values. Forced feed gas flow rate in the form of square wave perturbation was proven to improve the membrane performance in term of hydrogen recovery and time lag.

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