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HYDROGEN GAS RECOVERY THROUGH THE PERMEATION MEMBRANE BASED BIMETALLIC PALLADIUM ALLOY

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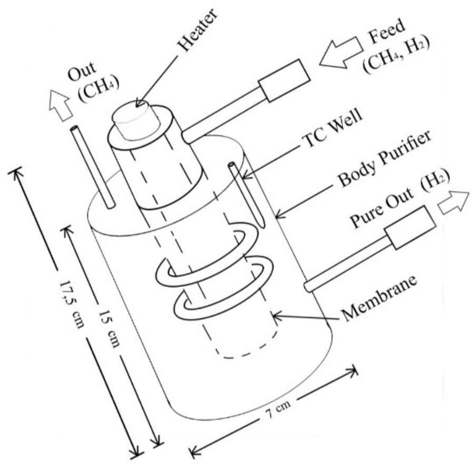

Abstract

Generally, the H_2 gas produced from the industrial processes is not in a pure state but is mixed with other compounds. For example, the off-gas produced in the oil refinery process still contains CH_4, H_2, and other gases. Thus, the process of separating as well as recovering the valuable H_2 gas from other gas compounds is of essential process. Currently, the H_2 separation process is being developed with relatively low costs with good efficiency, namely using the permeation membranes separation process, in which the compounds with high permeability tends to be more easily separated. Here we report the hydrogen recovery process from the mixed H_2/N_2 off-gas contains 61 % hydrogen and 39% balancing nitrogen, by using the bimetallic Pd-Ag membrane, where the effect of the gas feed pressure (1 and 2 bar) and operating temperature (373.15, 423.15, 473.15, and 523.15, 573.15 K) on the resulting permeate flux is comprehensively studied. We found that the flux and permeability increased with the increase in the gas feed pressure and temperature. Under the same gas temperature of 373.15 K, the permeation flux at the 2 bar gas feed pressure was found to be 2.047 mol.s-1.m-2, which was 166% greater than that of 1 bar pressure, *i.e.* 1.204 mol.s-1.m-2. Meanwhile, under the same gas feed pressure of 2 bar, the permeation flux at the operating temperature of 573.15 K was found to be 2.103 mol.s-1.m-2, which is 104,9% greater than that of 373.15 K operating temperature, *i.e.* 2.047 mol.s-1.m-2. These findings suggest the breakthrough advantages of the Pd-Ag alloy membrane for its high hydrogen permeability at low pressure.

Keywords: Hydrogen, Separation, Membrane, Palladium Alloy, Bimetallic

1.0 INTRODUCTION

The scarcity of fossil fuel sources and global warming is one of the main problems in the world. Thus, the use of environmentally friendly renewable fuels is highly recommended to replace fossil fuels, one of which is hydrogen gas. Hydrogen gas can be used as a feed in the Proton Exchange Membrane Fuel Cells process to produce electrical energy. In addition, the combustion of hydrogen gas has high efficiency and produces a by-product in the form of water (H_2O) [1]. The use of hydrogen gas is also able to reduce air pollution, minimize greenhouse gas emissions, reduce noise, and increase the supply of energy diversity [2]. This of course supports the Kyoto Protocol which aims to reduce greenhouse gas emissions such as carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, HFCs, and PFCs. On the other hand, the use of hydrogen gas in large quantities is also used in the petrochemical industry process. The petrochemical industry that requires hydrogen gas includes the process of making methanol, ammonia, and the process of breaking hydrocarbon bonds. Thus, the demand for hydrogen gas has experienced significant growth and the demand for hydrogen in the future may continue to increase [3].

Industrial processes to produce hydrogen gas are acetic acid steam reforming, bioethanol steam reforming, glycerol steam reforming, methane steam reforming, dry reforming of methane, water gas shift reaction, ethanol steam reforming, and methanol steam reforming [4]. The hydrogen gas produced from these industrial processes is not in a pure state but is in a mixed state with other compounds, for example, synthetic gas produced from the steam reforming process contains CO_2, CO, and H_2 gases. In addition, off-gas produced in the oil refinery process contains CH_4, H_2, and others [5].

The process of purifying hydrogen gas from other compounds is an important process. Several H_2 purification technologies that have been used include cryogenics, pressure swing adsorption (PSA), and membranes. In the cryogenic process, H_2 gas is separated by adjusting the temperature and pressure in such a way that compounds other than H_2 gas melt so that only H_2 gas remains in the gas phase. The second technology is pressure swing adsorption (PSA) where the purification of H_2 gas by adsorption at varying pressures (Pressure Swing). This process works based on the physical bonding of gas molecules with the adsorber material. The next technology is purification using permeation membranes [6]. Purification of H_2 gas by membrane permeation method which is based on differences in the permeability of the compounds. Compounds with high permeability will be more easily separated [7]. The last method mentioned is a modern method which is very profitable. Membrane methods of separation could reduce capital investment, operating cost, and process safety [8].

Several membranes commonly used in the H_2 gas purification process include polymer membranes, metal membranes, and carbon membranes (Table 1). From the data mentioned above, hydrogen gas purification with several types of membranes will have different operating conditions, hydrogen gas purity, and recovery percentages [9]. From these types of membranes, metal membranes have advantages, namely low operating pressure, with a high percentage of recovery and hydrogen gas purity compared to other membrane types. Types of metal membranes that can be used in the purification of hydrogen gas are Niobium (Nb), Vanadium (V), Tantalum (Ta), and Palladium (Pd). However, Niobium (Nb), Vanadium (V), and Tantalum (Ta) have a stronger surface tension for hydrogen transport phenomena than Palladium (Pd). Therefore, palladium membranes are more recommended with Palladium-Argentum (Pd-Ag) type membranes [10].

2.0 METHODOLOGY

2.1 Material

The materials used in this study were obtained from PT. Industrial Gas Samator, namely: UHP pure hydrogen gas (H_2) and mixed gas H_2 61% with 39% balancing N_2. The Pd-Ag membrane used in this study obtained from REB Research & Consulting. A series of gas membrane separator devices include a gas regulator, rotameter, and pressure gauge, as well as a Pd-Ag membrane with specifications shown in Table 2. Figure 1 presented the Pd-Ag Membrane Gas Separator unit.

Table 2 Specification of Pd-Ag Membrane

Name	Unit
Metal Composition	78,65% Pd : 21,35% Ag
Membrane Modul	Tubular Membrane
Membrane Surface Area ($m^{2)}$	0,006
Housing Diameter (cm)	6
Housing Length (cm)	15,5
Membrane Diameter (inch)	1/8
Membrane Length (cm)	61
Membrane Thickness (mm)	0,1

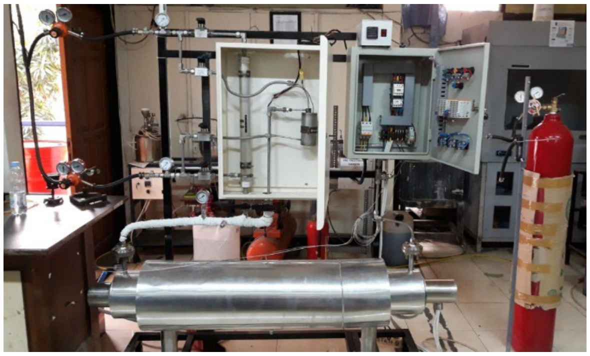

Figure 1 Pd-Ag Membrane Gas Separator Unit

Table 1 Comparison of Several Type of Membrane for Hydrogen Separation

Feature	Membrane			
	Polymer	Metallic	Carbon	Ceramic
Temperature Range (K)	<373	573 – 873	298 - 423	873 - 1173
Operating pressure (MPa)	2 - 20 MPa	<2 MPa	2 – 15 Mpa	<2 Mpa
Transport mechanism	Solution Diffusion	Solution Diffusion	Solution Diffusion, Molecular sieving, Surface diffusion	Solution Diffusion
Typical Hydrogen Permeability	Low	High	Moderate	Moderate
Typical Hydrogen Selectivity	Low	Very High	Moderate	High
Chemical stability	Degraded by H_2S, HCL, CO_2, SO_x	Poisoned by H_2S, HCL, CO_2, SO_x	Oxidizing and susceptible to organic solvent	Poisoned by H_2S
Operating cost	High	Very Low	Low	Low

2.2 Procedure

The experiment was carried out by flowing hydrogen gas and/or gas mixture into the Pd-Ag membrane. Then the permeate obtained was tested by gas chromatography to determine flux, permeability, and % recovery with any pressure (1 and 2 atm) and temperature (373,15; 423,15; 473,15; 523,15; 573,15 K) [11].

$$\text{Flux permeate} = \frac{Q_{p,H_2} \times \rho}{A \times BM\ H_2}$$

$$\text{Permeability} = \frac{jH_2}{\left(P_{f,H_2}^{0.5} - P_{p,H_2}^{0.5}\right)}$$

$$\%\ \text{Recovery} = \frac{Q_{p,H_2}}{Q_{f,H_2}} \times 100$$

3.0 RESULTS AND DISCUSSION

3.1 Flux Permeate

The separation process on the Pd-Ag membrane uses the principle of atomic diffusion, where diatomic gases will dissolve on the membrane surface and diffuse atomically [12]. Table 3 shows that the flux permeate gas mixture of H_2/N_2 is lower than the flux of pure H_2 gas. The process of separating H_2 with mixed gas feed H_2/N_2 at a pressure of 1 bar and a temperature of 573.15 K has a permeate flux value that is 40% lower than the permeate flux value with pure H_2 gas feed [3]. The same thing happened to all operating temperature variables and 2 bar feed pressure at the same operating temperature variable. The decrease in permeate flux in the H_2 mixed gas feed is caused by a decrease in the H_2 feed partial pressure[13]. A decrease in the partial pressure of the H_2 feed causes a decrease in the driving force [14].

Table 3 also shows that the permeate flux values of pure H_2 gas and H_2/N_2 mixture gas increase with increasing feed pressure. At a feed pressure of 2 bar, the flux permeate gas mixture H_2/N_2 at 573.15 K was 2.103 mol.s-1.m-2 which was 166.5% greater than the permeate flux at a pressure of 1 bar at the same temperature. The phenomenon of increasing flux value with increasing feed pressure also occurs in other operating temperature variables and pure hydrogen gas feed at the same operating temperature variable. This is because an increase in pressure will increase the solubility of H_2 on the membrane surface so the flux value will also increase[15].

Table 3 Flux Permeat Mixed Gas H_2/N_2 and Pure H_2

T (K)	H_2/N_2		Pure H_2	
	Flux (mol.s^{-1}.m^{-2})			
	Feed Pressure (Bar)			
	1	2	3	4
373.15	1.204	2.047	2.230	3.167
423.15	1.227	2.061	2.292	3.667
473.15	1.237	2.066	2.354	3.728
523.15	1.243	2.071	2.676	4.212
573.15	1.263	2.103	2.804	4.608

If observed further, Table 3 also shows that the increase in flux value is directly proportional to the increase in operating temperature. This can be seen at a pressure of 1 bar, the flux permeates value of the gas mixture H_2/N_2 at a temperature of 573.15; 104% greater than the value of flux permeates at a temperature of 373.15 K. The phenomenon of increasing permeate flux with increasing temperature also occurs in mixed gas H_2/N_2 with a feed pressure of 2 bar and pure H_2 gas at varying feed pressures [12]. The cause of the increase in permeate flux to temperature is that an increase in temperature will increase the diffusivity of H_2 so that the flux value will increase [16].

3.2 Permeability

Permeability is the rate of permeation, which is defined as the volume that goes through a membrane per unit area in a given unit of time, driven by pressure.

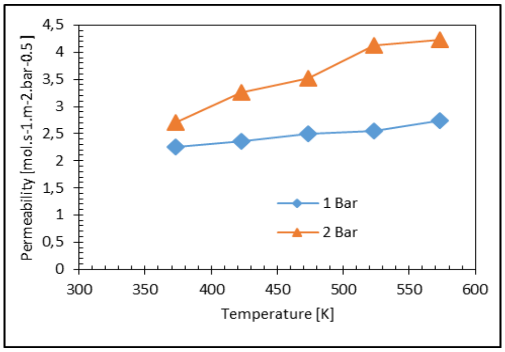

Figure 2 Permeability at Variation of Feed of Feed Pressure and Operating Temperature of Mixed Gas H_2 61%

Figure 2. shows that the increase in temperature will increase the permeability value. At feed pressures of 1 bar and 2 bar, the permeability values at a temperature of 573.15 K, respectively, of 2.4 and 4.2 mol.s^{-1}.m^{-2}.bar$^{-0.5}$ increased by 120% and 155% compared to the permeability at a temperature of 373.15 K of 2.2 and 2.7 mol.s^{-1}.m^{-2}.bar$^{-0.5}$, respectively. Meanwhile, at a temperature of 573.15 K the permeability value at a feed pressure of 2 bar of 4.2 mol.s^{-1}.m^{-2}.bar$^{-0.5}$ increased 154% compared to the permeability at a feed pressure of 1 bar of 2.4 mol.s^{-1}.m^{-2}.bar$^{-0.5}$.

The increase in temperature and pressure will increase the value of the permeate flux. This causes the permeability value to increase with the increase in operating temperature and feed pressure [17]. It can be seen that the permeability value is directly proportional to the flux and inversely proportional to the driving force (ΔP) [18]. On the other hand, physically, the kinetic energy of hydrogen is higher at high temperatures. This facilitates the chemical dissociation of hydrogen on the membrane surface so that the increase in temperature will increase the permeability value [12]

3.3 Percent Recovery

Percent recovery is the ratio of the intended material to the total amount of feed, represented as a percentage. This parameter will indicate the equipment's effectiveness.

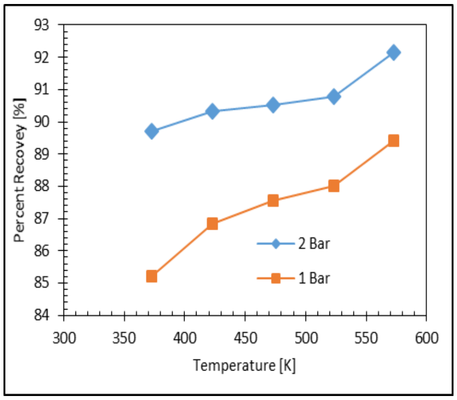

Figure 3 Percent Recovery at Variations in Feed Pressure and Operating Temperature (Gas Mixture H_2 61%)

Figure 3. shows the smallest and largest percent recovery values with a feed pressure of 1 bar of 85.2% at a temperature of 373.15 K and 89.42% at a temperature of 573.15 K. While the smallest and largest percent recovery values are with a feed pressure of 2 bar respectively 89.7% at a temperature of 373.15 K and 92.15% at a temperature of 573.15 K. Thus, it can be concluded that the higher the feed temperature and pressure, the higher the percent recovery value will be. This is because the increase in temperature and pressure will result in an increase in the diffusivity and solubility of H_2 and will result in an increase in flux. Meanwhile, the flux value is directly proportional to the percent recovery [19]. The value of percent recovery at a feed pressure of 2 bar is higher than the value of percent recovery at a feed pressure of 1 bar. Therefore, it is necessary to review the relationship between the increase in the percent recovery and the hydrogen purity in the permeate as shown in Figure 4.

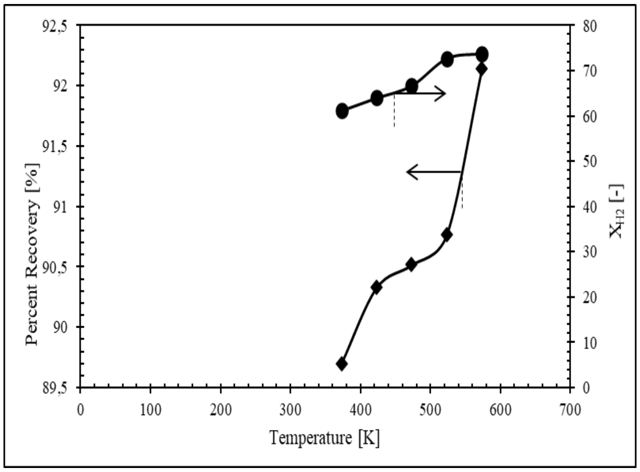

Figure 4 Effect of Operating Temperature on Percent Recovery and Purity Hydrogen in permeate (H_2 mixed gas 61%, P_{feed} = 2 bar)

The results of observations that see the relationship between percent recovery and the purity of H_2 gas obtained results that the purity of H_2 gas in permeate is directly proportional to the percent recovery [20]. Fig 4. shows that the largest percent recovery was obtained at a temperature of 573.15 K at 89.419% with a hydrogen purity of 73.8%.

4.0 CONCLUSION

The separation of hydrogen with Pd-Ag membranes is better under conditions of high pressure and temperature. With increasing operating temperature and feed pressure, the value of gas permeates flux, permeability, and % recovery also increases. The flux value of the mixed H_2/N_2 gas permeate is lower than the pure H_2 gas flux.

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