Experimental Study of Hydrogen and Methane Permeation through Asymmetric PEI Membranes

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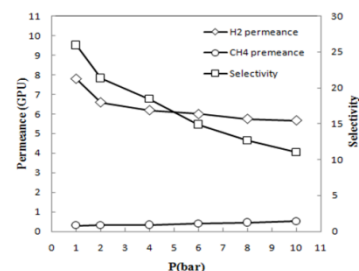
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Graphical abstract

Abstract

Reducing the amount of off-gases to flare is an important issue addressed by petrochemical plants and refineries. Therefore, separation of hydrogen from methane is crucial monetary and environmental incentives for these industries. The current research is aimed preparation of asymmetric polyetherimide(PEI) membranes for this purpose. The different mechanism of gas intake in PEI resulted in a decrease in hydrogen permeance and selectivity and adverse behavior for methane with pressure enhancement. There was a decline in both gases permeance and unexpected enhancement in selectivity. The effect of bath temperature was demonstrated. An effective coating method was applied and the selectivity increased noticeably.

Keywords: Hydrogen; methane; asymmetric; morphology

■1.0 INTRODUCTION

Hydrogen and methane are two strategic fuel sources for today and future and they are used as a feedstock in many important industries, fuel cells and power generation[1]. H_2/CH_4 separation is one of the most interesting processes in refineries and petrochemical companies because of gas recovery and decreasing flaring emissions.

Membrane separation is one of the new perspective methods for such applications. This method has more advantages than the other traditional gas separation techniques such as cryogenic distillation and pressure swing adsorption which include energy saving, easy to installation, operation and maintenance, modular and low space requirements and environmental friendly[2].

Gas separation by polymeric membrane is one of the proven technologies in many industries because of film forming capability, flexibility and low cost of polymer materials[3,4]. Commercially available polyetherimide (PEI) has several important advantages as a membrane material. This polymer has good chemical and thermal stability. The studies on gas permeation in the PEI dense film reveal that PEI exhibits impressively high selectivity for many important gas pairs. In 1987, Peinemann prepared PEI flat-sheet asymmetric membranes

for CO_2/CH_4 and reported selectivity of about 30-40[5]. Kneifel and Peinemann reported their results in preparing porous and dense PEI hollow fiber membranes for gas separation and they obtained selectivity of about 170 for He/N_2 separation. Wang and Teo reported the results of PEI hollow fiber membranes for separation of N_2 from He, H_2, CO_2, CH_4 and Argon .Kurdi and Tremblay prepared PEI/metal complex asymmetric hollow fiber membranes for O_2/N_2 separation and obtained selectivity of 2-7[5]. Ren *et al.* prepared polyetherimide membrane and investigated influence of various non-solvents on membrane morphology[5].

PDMS is the most commonly used rubbery membrane material for heavy hydrocarbons separation processes .Due to structural properties such as unique flexibility of the siloxane backbone, low intermolecular forces between the methyl groups and high bonding energy of the siloxane bond, it can be used as a coating layer for preparation of the defect free membrane by phase inversion method[6].

In this research, PEI membranes coated by PDMS were synthesized by phase inversion method and sorption and permeation of CH_4 and H_2 were studied. Effects of pressure, temperature, coagulant bath temperature were investigated. An effective coating method was applied to prepare high selective membrane.

■2.0 EXPERIMENTAL

2.1 Materials

Polyetherimide (PEI) was obtained from Sigma-Aldrich, USA, in pellet form. Isopropanol, n-Hexane and anhydrous 1-methyl-2-pyrrolidinone (EMPLURA®, 99.5%, water<0.1%) were supplied from Merck, Germany.

Deminaralized water was supplied from Marun petrochemical company. Polydimethylsiloxane (PDMS and curing catalyst) were bought from Z-mark Co., Italy.

The pure gases including CH_4 (99. 9%) and H_2 (99. 9%) was supplied from Technical gas services. These gases were used in permeation measurement experiments.

2.2 Membrane Preparation

Asymmetric membranes were prepared with 28% PEI in NMP solvent and water/Isopropanol mixture as a non-solvent by phase inversion method. The PDMS coating solution was prepared by dissolving the PDMS polymer resin and the cross-linking agent with a weight ratio of 10:1 in n-hexane to obtain a homogeneous solution.

A conventional set up was used for gas permeance measurment with high accurate transmitters and a PLC.

■3.0 RESULTS AND DISCUSSION

3.1 The Influence of Feed Pressure

The influence of feed pressure on H_2 and CH_4 permeance and selectivity in the range of 1-10 bars and 25ºC is presented in Figure 1.
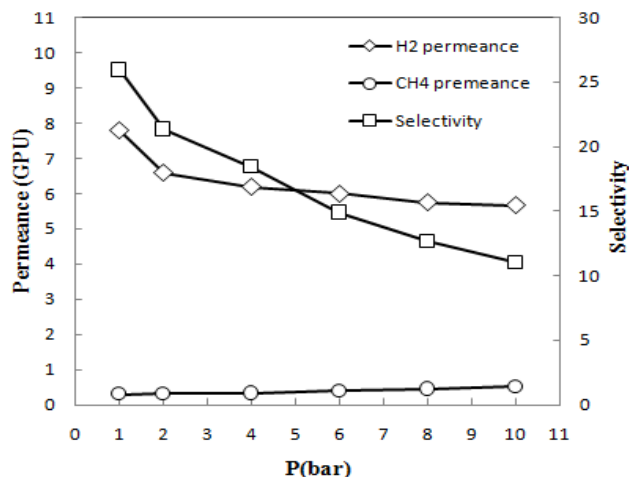

Figure 1 Influence of feed pressure on H_2 and CH_4 permeance and selectivity at 25ºC

The permeance of hydrogen declined but methane permeance increased with an increase in the gas pressure. The permeance of hydrogen declined sharply in the range of 1-2 bar and it steadily dropped especially for the pressure of 4-10 bars but the permeance of methane was enhanced steadily with the small slope in the range of 1-10 bar. The effect of pressure on the gas permeability can be explained in terms of three competing effects: membrane compaction, sorption, and plasticization. An increase in pressure will cause membrane compaction, which tends to decrease the membrane permeability. As shown in Figure 2,

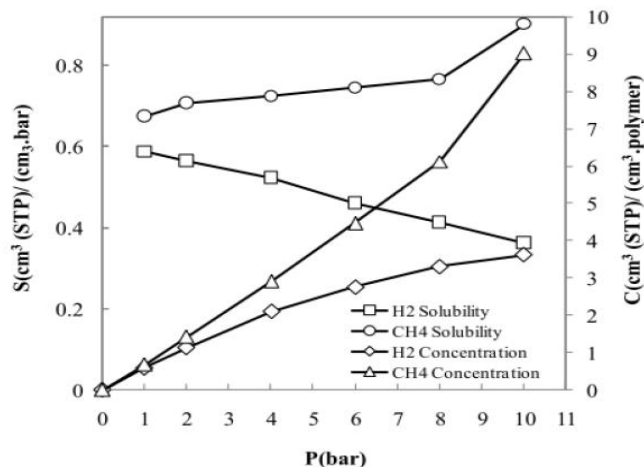mechanism of H_2 sorption in PEI membrane follows by dual mode sorption.

Figure 2 Sorption isotherms and pressure dependency of solubility for H_2 and CH_4 in the synthesized membrane at different pressures and 25ºC

In dual mode sorption mechanism, when the gas pressure increases, the gas uptake in the membrane increases, but the increase is less than proportional because of the Langmuir sorption where the active sorption "sites" are gradually saturated; thereby gas solubility and thus the permeability through the membrane reduces. As shown in Figure 2, for methane, increasing pressure leads to sorption enhancement by Flory-Huggins mechanism because of weak interaction between the polymer and methane. Increasing of methane sorption by pressure is dominant effect in pure gas permeation through the fabricated membrane and causes decrease in the membrane selectivity.

3.2 The Influence of Feed Temperature

Figure 3 shows the effect of operating temperature on the membrane permeance and selectivity as a function of inverse absolute temperature for H_2 and CH_4 at different pressures, respectively. Permeance of both H_2 and CH_4 were enhanced by an increase of temperature.

Increasing temperature results in higher mobility of the polymer chains and also higher kinetic energies of the permeating molecules can increase the gas permeation. As shown in Figure 3, the selectivity was enhanced negligibly with an increase in temperature from 25ºC to 40ºC. This is due to the higher permeation rate of hydrogen than that of methane at higher temperatures.

3.3 Influence of Bath Temperature

Coagulation bath condition has a great influence on membrane structure. Temperature of coagulation bath is one of the most important factors that should be considered in membrane preparation. Figure 4 presents the influence of coagulation bath temperature on selectivity and permeance of the membranes with 28wt% polymer in an isopropyl alcohol-water (1:4) bath.
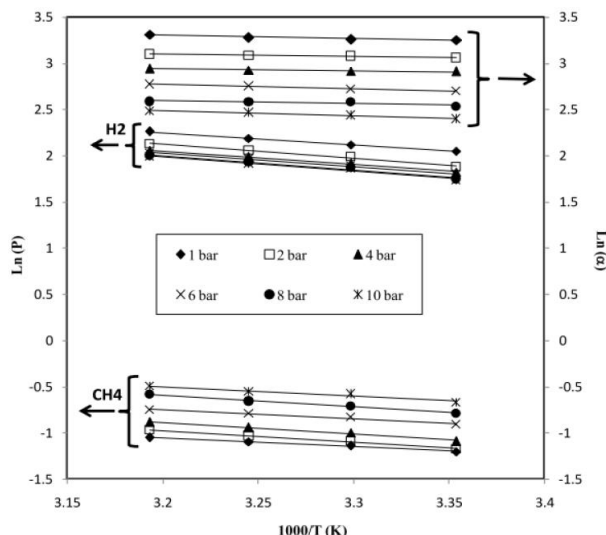
Figure 3 Effect of operating temperature on the permeances of H_2 and CH_4 and on H_2/CH_4 selectivity through PEI membrane at different pressures
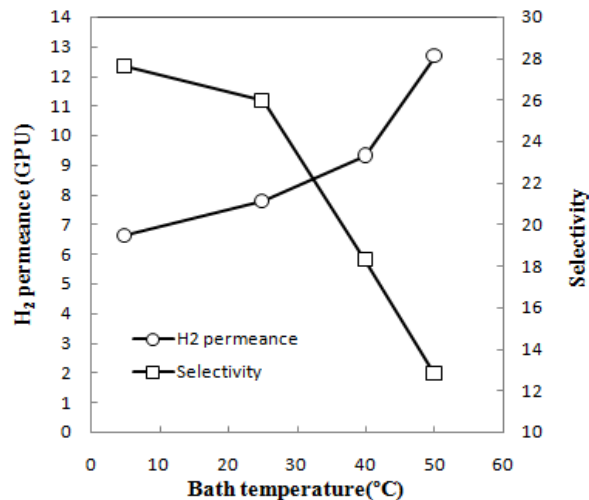

Figure 4 Effect of coagulation bath on ideal selectivity and permeability of pure H_2 at 1 bar and 25ºC

The results show that decrease in the coagulation bath temperature resulted in denser membranes with higher selectivity and lower permeability. This can be attributed to molecular movement, which becomes more rapid at higher temperatures. Therefore the rate of solvent diffusion in solvent increases and causes more chances for the forming of macro-voids and porosity enhancement. One thing need to be pointed out is that as temperature increases, it's much easier to form defect pores, which deteriorates the separation performance.

3.4 The Influence of Effective Coating

Four sequential dip-coating with different concentration of PDMS was applied for the fabricated membranes. Four pot of PDMS solution with different concentration were prepared (3, 5, 10, and 15%), fabricated membrane was submerged in the lowest concentration of coating solution to the higher concentrations. Three minutes residence time was applied for each coating.

Figure 5 indicates H_2 permeance and selectivity for fabricated membrane with this coating method for three coupons of membranes and the average results was reported.
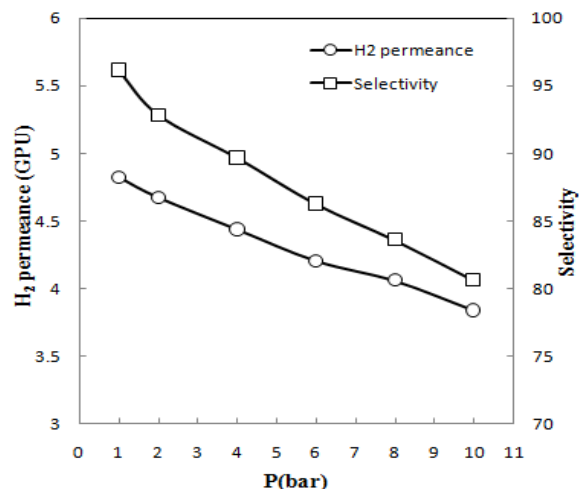

Figure 5 Influence of pressure on H_2 permeance and selectivity of fabricated membrane by sequential coating with different concentration of coating solution at 25ºC

The results show a decline in gases permeance but the selectivities were enhanced in comparison with the membranes coated with 15 wt.% PDMS concentration .Selectivity increased from 25.94 to 96.12 at 1 bar and 25ºC. It was due to better penetration of PDMS solutions with different viscosities into the surface pinholes with different sizes.

■4.0 CONCLUSION

In this study, PDMS/PEI membranes were prepared and permeation and sorption of pure hydrogen and methane was measured at different conditions. The results showed that

- Pressure tests indicated that by increasing the trans-membrane pressure the H_2 permeance descended but CH_4 permeance was enhanced. This led to selectivity reduction by increasing the pressure.
- Temperature tests showed gases permeance increased with increasing temperature. Selectivity enhancement is higher increasing rate of hydrogen than methane.
- Lower coagulation bath temperature makes dense membrane and increased selectivity.
- An effective coating was applied and selectivity enhanced from 25to 96 at 1 bar and 25ºC.

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