Journal of Industrial and Engineering Chemistry 19 (2013) 1680–1688

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

# Separation of hydrogen from methane by asymmetric PEI membranes

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ARTICLE INFO

*Article history:*
Received 6 December 2012
Accepted 15 February 2013
Available online 21 February 2013

*Keywords:*
Asymmetric PEI membrane
Permeance
Selectivity
Non-solvent
Hydrogen recovery

ABSTRACT

Hydrogen is anticipated to play an inevitable role as one of the promising sources of energy in the future. Recovery of hydrogen from flare gases is an economical and environmental policy of Marun Petrochemical Company. The asymmetric polyetherimide (PEI) membrane was synthesized and sorption and permeation of $CH_4$ and $H_2$ were studied. The influence of pressure and temperature as operating variables were investigated. Results showed that permeance was enhanced by temperature. The pressure increase caused a decline in $H_2$ permeance, whereas $CH_4$ permeance increased due to the Flory–Huggins sorption mechanism and ideal $H_2/CH_4$ selectivity reduction. The effect of different non-solvents as coagulants of the phase inversion technique in membrane morphology and behavior were explained by precipitation time. Water as a non-solvent makes membrane structures denser than others, while isopropanol leads to a porous sponge-like morphology. Lower coagulation bath temperature makes the membrane denser. Finally, a selectivity of 27.8 was achieved for the separation of $H_2$ from $CH_4$.

## 1. Introduction

Hydrogen energy technologies can play a vital role in solving problems related to the energy and environmental sectors [1]. The demand for hydrogen has continuously grown in recent years, which has motivated research in improving methods of hydrogen production, separation, and purification [2–4]. Hydrogen purification is essential to satisfy the various purity requirements for different applications.

The success of fuel cell technology is critically dependent on the supply of high-purity hydrogen (minimum 99.99%), but in the case of feedstock for hydro-cracking it requires only 70–80% purity [5].The separation of $CH_4$ from $H_2$ is relevant to refinery off-gas processing. The gas mixture being separated is approximately 50% $H_2$ at 5–10 bar [6]. In refinery and petrochemical cracking plants, $H_2/CH_4$ separation is necessary for hydrogen recovery from flare gases and methane purification is necessary for use as the balance gas in ethylene oxide (EO) plants.

Hydrogen enrichment can be achieved by various approaches including pressure swing adsorption (PSA), cryogenic distillation and membrane separation [5,7–9]. PSA is a well-established industrial process for producing high-purity hydrogen (up to 99.99%), and involves pressure (20–30 bar) adsorption in a confined space using suitable adsorbents such as activated carbon or molecular sieves [5,9]. Cryogenic distillation is an extremely energy intensive process and produces hydrogen with only moderate purity (≤95%) [5,10–12].

Alternatively, membrane technology shows great potential for hydrogen separation because of its higher energy efficiency, cost effectiveness for smaller units, simplicity in operation, compactness, portability and compatibility with the environment [5,13]. Among membrane materials, polymeric membranes, as one of the most important classes of membranes especially for gas separations, possess many desired properties including low capital investment, low energy consumption, high specific surface area per module and easy processing [14].

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 films reveal that PEI exhibits impressively high selectivity for many important gas pairs [15,16].

In 1987, Peinemann [17] prepared PEI flat-sheet asymmetric membranes for $CO_2/CH_4$ separation using a halogenated hydrocarbon as solvent and reported a selectivity of about 30–40. Kneifel and Peinemann [18] reported their results in preparing porous and dense PEI hollow fiber membranes for gas separation using *N*-methyl-2-pyrrolidone/7-butyro-lactone as a solvent and obtained a selectivity of about 170 for $He/N_2$ separation. Wang and Teo [15]

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*Abbreviations:* GPU, $10^{-6}$ $cm^3$ (STP) cm/($cm^2$ s cmHg); MFC, mass flow controller; NMP, *N*-methyl-2-pyrrolidinone; PEI, polyetherimide; PT, pressure transmitter; TT, temperature transmitter.

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http://dx.doi.org/10.1016/j.jiec.2013.02.006

## Nomenclature

| | |
|---|---|
| $A$ | Effective membrane area [$cm^2$] |
| $C$ | Concentration [$cm^3$ (STP)/$cm^3$] |
| $D$ | Gas diffusivity [$cm^2/s$] |
| $D^*$ | Pre-exponential temperature independent constant [$cm^2/s$] |
| $dC/dz$ | Gas concentration gradient [$cm^3$ (STP)/$cm^3$ cm] |
| $l$ | Membrane thickness [cm] |
| $M_p$ | Melting point [°C] |
| $M_w$ | Molecular weight [kg/kmol] |
| $N_A$ | Steady state gas flux of component A [$cm^3$ (STP)/$cm^2$ s] |
| $O$ | Volumetric flow rate of penetrant gases at standard pressure [$cm^3$ (STP)/s] |
| $P$ | Permeability [GPU] |
| $P^*$ | Pre-exponential temperature independent constant [GPU] |
| $p_f$ | Final pressure [bar] |
| $p_i$ | Initial pressure [bar] |
| $R$ | Universal gas constant [J/mol K] |
| $S$ | Solubility coefficient [$cm^3$/($cm^3$ bar)] |
| $S^*$ | Pre-exponential temperature independent constant [$cm^3$/($cm^3$ bar)] |
| $T$ | Temperature [K] |
| $T_g$ | Glass temperature transition [°C] |
| $V_m$ | Volume of the module [$cm^3$] |
| $V_p$ | Volume of the polymer sample [$cm^3$] |
| $x_A$ | Mole fraction of component A[–] |
| $z$ | Direction [cm] |
| $\Delta E_a$ | Activation energy of diffusion [J/mol K] |
| $\Delta E_p$ | Activation energy of permeation [J/mol K] |
| $\Delta H_p$ | Heat of solution [J/mol K] |
| $\Delta p$ | Membrane pressure difference [bar] |

*Greek letters*

| | |
|---|---|
| $\alpha$ | Selectivity [–] |
| $\rho$ | Density of polymer [$kg\ m^{-3}$] |

reported the results of PEI hollow fiber membranes prepared from the NMP/ethanol solvent system for separation of $N_2$ from He, $H_2$, $CO_2$, $CH_4$ and Argon. Kurdi and Tremblay [19] prepared PEI/metal complex asymmetric hollow fiber membranes for $O_2/N_2$ separation using NMP as solvent and obtained a selectivity of 2–7. Ren et al. [20] prepared polyetherimide membranes with *N*-methyl-2-pyrrolidone (NMP)/non-solvent system and investigated the influence of various non-solvents on membrane morphology. Peng et al. [21] fabricated a hollow fiber PEI membrane in NMP with an ultra-thin dense-selective layer for $O_2/N_2$ separation and reported a selectivity of about 2–7.5. Simons et al. [22] investigated the $CO_2$ sorption and transport behavior of PEI membranes and obtained a selectivity of about 40–60 for $CO_2/CH_4$ separation. These researches show the importance of PEI as a proper polymer material in preparation of gas separation membranes.

In this research, asymmetric PEI membranes were synthesized. The optimum conditions for membrane preparation such as concentration of the polymer in NMP and suitable non-solvents were determined. Moreover, the prepared membranes were characterized and evaluated for $H_2/CH_4$ separation. The effects of operating conditions, polymer concentration, and coagulant bath temperature on pure gas permeance and selectivity were investigated. Operating conditions were selected similar to the real tail gas streams in Marun Petrochemical Company and refineries of Iran. The influences of different non-solvents on the membranes structure and behavior were demonstrated by precipitation time and difference of solubility parameters between the solvent and non-solvents.

## 2. Theory

The transport of gases through nonporous polymeric membranes is usually described by a solution–diffusion mechanism.

The permeability of a pure gas A across a membrane is defined by [23]:

$$P_A = \frac{N_A}{(p_F - p_P)/l} \tag{1}$$

where, $p_F$, $p_P$, $N_A$ and $l$ are feed side pressure, permeate side pressure, the steady state gas flux and membrane thickness, respectively.

The steady state one-dimensional flux of gas A through the membrane in the $z$ direction ($N_A$) is given by [23]:

$$N_A = -\frac{D}{1 - x_A}\frac{dC}{dz} \tag{2}$$

in which $C$ is concentration of component A, $D$ is gas diffusivity, $dC/dz$ is gas concentration gradient in the polymer in $z$ direction, and $x_A$ is mole fraction of component A.

Combining Eqs. (1) and (2) and integrating $z = 0$ ($C = C_0$) to $z = l$ ($C = C_1$) results in

$$P = -\frac{1}{p_0 - p_1}\int_{C_1}^{C_0}\frac{D}{1 - x_A}dC = [D]\frac{C_0 - C_1}{P_0 - P_1} \tag{3}$$

in which $[D]$ is a concentration averaged diffusivity defined as follows [24]:

$$[D] = \frac{1}{C_0 - C_1}\int_{C_1}^{C_0}\frac{D}{1 - x_A}dC \tag{4}$$

When the permeate side pressure is low, the permeability can be expressed by

$$P = [D]\,S \tag{5}$$

where $[D]$ is the effective diffusion coefficient and $S$ is the solubility coefficient. Therefore, the gas permeability can be expressed as a product of a kinetic parameter $[D]$ and a thermodynamic parameter ($S$).

## 3. Experimental

### 3.1. Materials

Polyetherimide (PEI) was obtained from Sigma–Aldrich (USA) in pellet form. Table 1 shows physical properties of the PEI. Fig. 1 represents the molecular structure of the polyetherimide.

Ethanol, methanol isopropanol, and anhydrous 1-methyl-2-pyrrolidinone (EMPLURA®, 99.5%, water <0.1%) were supplied from Merck (Germany).

Demineralized water (maximum conductivity of 0.2 μS/cm) was used throughout the experiments.

The pure gases including $CH_4$ (99.9%) and $H_2$ (99.9%) were supplied from Technical Gas Services. These gases were used in the permeation and sorption measurement experiments.