Highly Permeable N₂/CH₄ Separation SAPO-34 Membranes Synthesized by Diluted Gels and Increased Crystallization Temperature

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Abstract

Synthesis conditions were optimized for synthesizing SAPO-34 membranes towards N₂/CH₄ separation. Compared to previous SAPO-34 membrane preparations, synthesis gels were diluted 1.3-2.7 times and an increased crystallization temperature was used. As a result, a three-four fold increase in N₂ permeance was observed in this study. The membranes separated N₂ from CH₄ with N₂ permeance as high as 1,300 GPU and selectivity of 7.4 at 23°C for a 50/50 N₂/CH₄ mixture. Furthermore, membranes were reproducible and effectively separated gas mixtures having low N₂ content which are relevant compositions of natural gas. More specifically, membranes separated N₂ from CH₄ with N₂ permeance as high as 1,160 GPU and selectivity of 7.1 at 23°C for a 18.5/81.5 N₂/CH₄ mixture. The resultant SAPO-34 membranes have potential for economic N₂ rejection in natural gas processing.

1 Introduction

The typical U.S. natural gas pipeline specification for inert gases is less than 4%. Approximately 14% of U.S. natural gas contains >4% nitrogen, and thus nitrogen rejection technologies are required [1]. Most of the N₂ rejection plants use a cryogenic distillation process, which is very costly (about \$2.40/MSCF for a plant capacity of 1 MMSCF/day and \$0.80/MSCF for a plant capacity of 20 MMSCF/day assuming \$4/MSCF gas price to the plant and 15 vol.% N₂ in feed) [2]. To compete with the cryogenic distillation, the great challenge of applying more energy-efficient membrane separation technology is to develop membranes with the necessary N₂/CH₄ separation characteristics. Two types of membranes can be used in N₂ rejection: CH₄-selective or N₂-selective membranes. For CH₄-selective membranes, CH₄ is more permeable than N₂ so that it is concentrated in the low-pressure permeate side, and needs to be recompressed before it is passed to the pipeline. Meyer and Henson [3] evaluated the economics for CH₄-selective membranes. The estimated costs were too high to be of commercial interest for the state-of-the-art CH₄-selective membranes unless the CH₄/N₂ selectivity could be increased to 7. In contrast, for a process using N₂-selective membranes, CH₄ is rejected to the retentate, and thus there is a significant saving in recompression cost as compared to CH₄-selective membranes. However, the state-of-the-art N₂-selective polymeric membranes display low N₂ permeabilities, typically less than 2 barrers (1 barrer = 10⁻¹⁰ cm³ (STP)·cm/ (cm²·s·cmHg)) corresponding to a N₂ permeance of only 20 GPU (Gas Permeation Unit, 1 GPU = 3.348 × 10⁻¹⁰ mol/(m²·s·Pa)) for a 100-nm thick membrane, at a selectivity of approximately 5, as shown in the “Robeson” plot [4].

Recently, some inorganic materials have been made into N₂-selective membranes and shown N₂/CH₄ separation performances above the so-called upper bound observed for polymers [4]. Ning and Koros [5], using a carbon molecular sieve (CMS) membrane, obtained a N₂/CH₄ selectivity of 7.7 and a N₂ permeability of 6.8 barrers at 24°C. Li et al. [6,7] prepared membranes with SAPO-34 deposited as a continuous layer on stainless steel supports. The membranes separated N₂ from CH₄ with a selectivity of 4 at 22°C. The N₂ permeance was 2.1×10⁻⁸ mol/(m²·s·Pa) (= 63 GPU). Very recently, the N₂/CH₄ separation performance through the SAPO-34 membranes has been improved by the same research group. The N₂/CH₄ selectivity was 5-7 and the N₂ permeance was ~1 ×10⁻⁷ mol/(m²·s·Pa) (= 300 GPU) as reported by Wu et al. [8], for membranes on alumina supports. They also prepared SSZ-13 zeolite membranes for

N₂/CH₄ separation and obtained selectivity of 13 and N₂ permeance of 2.2×10^{-8} mol/(m²·s·Pa) (66 GPU) at 20°C for a feed pressure of 270 kPa.

Compared to the SSZ-13 membranes, SAPO-34 membranes are more attractive for the use in N₂ rejection because of their high N₂ permeance. SAPO-34 is a silicoaluminophosphate having the composition Si_xAl_yP_zO₂ where x = 0.01-0.98, y = 0.01-0.60, and z = 0.01-0.52 [9]. Most of the SAPO-34 membrane studies have been focused on separating CO₂ (kinetic diameter: 0.33 nm) from CH₄ (0.38 nm) [10-15]. Compared to CO₂/CH₄ separation, the separation of N₂/CH₄ mixtures using SAPO-34 membranes is much more challenging because the kinetic diameters of N₂ (0.364 nm) and CH₄ (0.38 nm) differ by less than 5% and both gases adsorb weakly on SAPO-34 [11]. Recently, we reported SAPO-34 membranes via several routes towards the N₂/CH₄ separation [16]. Membrane synthesis parameters including water content in the gel, crystallization time, support pore size, and aluminum source were investigated. The best membranes separated N₂ from CH₄ with N₂ permeance as high as 500 GPU and separation selectivity of 8 at 24°C for a 50/50 N₂/CH₄ mixture [16]. In the current study, the synthesis conditions for SAPO-34 membranes were further optimized towards N₂/CH₄ separation. The resulting membranes separated N₂ from CH₄ with N₂ permeance as high as 1,300 GPU and selectivity of 7.2 for a 50/50 N₂/CH₄ mixture. The effect of N₂ concentration (at compositions of 50 % and below) and membrane reproducibility was investigated.

2 Experimental Methods

2.1 Membrane Preparation

The membranes were synthesized by seeding (secondary growth) onto the inside surfaces of porous alumina supports with pore size of 100 nm. These tubes were typically 6-cm long with effective areas between 6.5 and 7.3 cm². About 1 cm on each end of the alumina supports was glazed to prevent feed bypass and to provide a sealing surface for O-rings. Before synthesis, the supports were boiled in deionized water for three times and each lasted for 40 minutes. They were dried at 70°C overnight.

2.1.1 Synthesis of SAPO-34 Seeds

The seeds were prepared with a gel mole composition of 1.0 Al₂O₃: 2.0 P₂O₅: 0.6 SiO₂: 4.0 TEAOH: 150 H₂O. In a typical synthesis, aluminum isopropoxide (Al(i-C₃H₇O)₃, Aldrich

99.99%) and deionized water were stirred for 1 h to form a homogeneous solution, followed by addition of phosphoric acid (H_3PO_4 , Sigma-Aldrich 85 wt.% aqueous solution) for another 2 h of stirring. This mixing order was different from previous studies reported by Wu et al. [8] and Funke et al. [15] where these three chemicals were added at the same time. Next, Ludox AS-40 colloidal silica (40% wt.% suspension in water) was added, and the resulting solution was stirred for another 3 h. Tetraethylammonium hydroxide (TEAOH, Aldrich 35 wt.% aqueous solution) was then added, and the solution was stirred overnight at room temperature ($\sim 22^\circ\text{C}$). The gel was placed in an autoclave and heated in a microwave oven (CEM Mars 5 Microwave Reaction System with XP-1500 plus control vessel) at 180°C for 7 h. After the solution was cooled to room temperature, it was centrifuged at 3,300 rpm for 10 minutes to collect the seeds, which were followed by deionized water washing. The process was repeated three times, and the resulting precipitate was dried overnight at 100°C .

2.1.2 Preparation of Gel for Growth of Membranes

Several gel compositions containing Al_2O_3 , P_2O_5 , and SiO_2 sources, templates and H_2O were mixed, stirred and aged for growth of membranes. $\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$ was used as Al_2O_3 sources, whereas H_3PO_4 and Ludox AS-40 were used as P_2O_5 and SiO_2 sources, respectively. TEAOH was used as pivotal template for the formation of SAPO-34 structure and DPA was employed as secondary structure directing agent. The gel mole composition was 1.0 Al_2O_3 : 1.0 P_2O_5 : 0.3 SiO_2 : 1.0 TEAOH: 1.6 DPA: x H_2O . To prepare the gel, $\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$ and deionized water were stirred for 1 h to form a homogeneous solution, followed by addition of H_3PO_4 into the gel for another 2 h of stirring. Then Ludox AS-40 colloidal silica was added, and the resulting solution was stirred for another 3 h. The TEAOH was then added, followed by addition of DPA (Acros 99%) after 1 h. The gel was stirred at $45\text{--}50^\circ\text{C}$ for 4 days before it was used in membrane growth.

2.1.3 Preparation of SAPO-34 Membranes

The inside of the supports was seeded by rubbing with SAPO-34 seeds (prepared under 2.1.1). The outside of the supports was wrapped with Teflon tape to avoid growth of membranes on the outside surface. After seeding, the supports were placed in an autoclave filled with the synthesis gel (prepared under 2.1.2). Usually two seeded supports were placed in an autoclave, which was then filled with the synthesis gel to about 0.5 cm above the top of the supports. Hydrothermal treatment was carried out in a conventional oven at 230°C for 6 h. After this step,

the membranes were washed for 15 minutes with flowing tap water and dried at 100°C for ~2 h. The membranes were calcined at 400°C for 4 h with heating and cooling rates of 0.8°C/min under a vacuum (pressure of 10 Pa).

2.2 Characterization

Crystals collected from the bottom of the support tubes during membrane synthesis were used in various analyses including powder X-ray diffraction (PXRD) using a Siemens Kristalloflex 810 diffractometer operating at 30kV and 25 mA with Cu K α 1 radiation ($\lambda=1.54059\text{\AA}$). Some SAPO-34 membranes were broken and analyzed by scanning electron microscope (SEM, JEOL JSM-7000F).

Gas adsorption isotherms were measured by a volumetric method using a home-built adsorption system. In these measurements, ultra-high purity N₂ (99.999%, Airgas) and CH₄ (99.999%, Airgas) were used. SAPO-34 crystals (~0.20 g) were first outgassed at 200°C for 2 h. Helium was then introduced to calibrate the volume of adsorption cell containing SAPO-34 crystals. After volume calibration, the system was evacuated, and then N₂ or CH₄ was introduced to the sample cell. The pressure change was measured using an ASHCROFT K17MO242C13000 model transducer. Based on the pressure change and volume calibrated, the amount of gas adsorbed at that equilibrium pressure was calculated.

2.3 Gas Permeation Measurement

Single-gas and mixture permeations were measured in a flow system. The membrane was mounted in a stainless steel module and sealed at each end with silicone O-rings. The pressure on each side of the membrane was independently controlled. Fluxes were measured using a bubble flow meter. For mixture separation, a pre-mixed 50/50 N₂/CH₄ mixture was used as feed. The total feed flow rate was 100 mL/min. The compositions of the feed, retentate and permeate streams were measured, after attaining the steady state, using a gas chromatograph (SRI instruments, 8610C) equipped with a thermal conductivity detector and HAYESEP-D packed column. The oven, injector and detector temperatures in the GC were kept at 40°C, 50°C and 150°C, respectively.

All selectivities are permselectivities (ratios of permeances). The permeances were calculated as the fluxes divided by the partial pressure driving forces. Because the module has a cross-flow design, a logarithm of the mean partial pressure drop was used to calculate the driving force.

3 Results and Discussion

2.1 Membrane Synthesis and Characterization

As compared to the SAPO-34 membranes reported by Wu et al. [8] for N_2/CH_4 separation, *five major improvements* have been employed in the current study for SAPO-34 membrane synthesis. Firstly, the membrane synthesis gel was diluted 1.3-2.7 times by adding more water to the gel. Note that the previous gel compositions for fabricating SAPO-34 membranes were evolved from SAPO-34 catalyst synthesis where the gel was concentrated in order to get a high yield of the power. In contrast, membrane synthesis is in an opposite direction. The more the gel is diluted, the more the saving is in the chemical cost for membrane fabrication. In addition, diluted gels have potential to grow thinner membranes and thus higher permeances. Secondly, in both studies by Li et al. [6,7] and Wu et al. [8], the SAPO-34 membranes were prepared by single template of TEOH. In the current study, SAPO-34 membranes were prepared by dual-template TEOH and DPA. Carreon et al. [12] found that DPA acts as secondary structure directing agent promoting the formation of smaller SAPO-34 crystals. Mertens and Engels reported that the addition of small amine molecules, such as DPA, can help to improve crystallization SAPO-34 [17]. Thirdly, $Al(i-C_3H_7O)_3$ was used as Al source rather than $Al(OH)_3$ reported by Wu et al. [8]; we found $Al(i-C_3H_7O)_3$ is more soluble in aqueous solution than $Al(OH)_3$, which leads to a more homogenous gel solution for membrane synthesis. Fourthly, the order of mixing chemicals was optimized for better dispersion of monomers into a colloidal solution. Fifthly, pervious SAPO-34 membranes were prepared with crystallization temperatures between 180 and 220°C. In the currently study, crystallization temperature was increased to 230°C.

The crystals used as seeds for the membrane preparation were slice-shaped crystals as described in our previous report [16]. The lengths and widths were between 200 and 800 nm, and thicknesses were between 50 and 220 nm. XRD confirms the CHA topology typical of SAPO-34.

Previous SAPO-34 membranes have been prepared with water mole contents of 55-150. Even with a water content of 150, phase separation of gel occurred during the synthesis of the membranes on tubular supports, and settling of crystals to the bottom of the autoclave was observed. This decreases the quality of the membrane [13]. To avoid gel phase separation and settling of crystals to the bottom of the autoclave, water contents of 150, 200, 250, 300 and 400

were investigated, and two membranes were prepared at each water content. The XRD patterns (Figure 1) of crystals collected from membrane synthesis were essentially identical as water mole content increased from 150 to 400, and the peaks match those for simulated SAPO-34. Moreover, the crystallinity did not show any decrease due to a 2.7 fold increase of water content.

Figure 1. XRD patterns of powders collected from the bottom of the membranes with gel composition of 1.0 Al_2O_3 : 1.0 P_2O_5 : 0.3 SiO_2 : 1.0 TEAOH: 1.6 DPA: x H_2O , and simulated XRD pattern for pure SAPO-34 crystals is shown at the bottom for comparison.

Some membranes were broken and analyzed by EDX and SEM. The Si/Al and Si/P ratios of the surfaces of the membranes prepared by different water contents were essentially identical (Figure 2). These ratios ($\text{Si/Al} = 0.18\text{-}0.19$; $\text{Si/P} = 0.23\text{-}0.25$) were higher in the membranes than in the gel ($\text{Si/Al} = 0.15$; $\text{Si/P} = 0.15$), indicating under the current synthesis conditions, Si in the gels was preferentially incorporated into the SAPO framework. In contrast, when using single template of TEAOH and a crystallization temperature of 200°C for SAPO-34 membrane synthesis, the Si/Al ratio was lower in the crystal ($\text{Si/Al} = 0.13$) than in the gel ($\text{Si/Al} = 0.15$) [18]. The differences in Si/Al and S/P ratios would affect specific retention volumes and adsorption enthalpies of N_2 and CH_4 in SAPO-34 crystals as reported by Maple and Williams [19], which would further affect the N_2/CH_4 separation performance of the SAPO-34 membranes.

Figure 2. Si/Al and Si/P ratios for the membranes prepared with difference water mole contents.

SEM images of the membrane surfaces (Figure 3 left column) show well-intergrown micron range zeolite crystals for SAPO-34 membranes prepared with different water contents. Cross-sectional SEM images of the membranes (Figure 3 right column) show zeolite layers. The thickness of the layer decreases from ~ 6.8 to ~ 2.7 μm as water content increases from 150 to 400; indicating that diluted gel forms a thinner membrane layer.

Figure 3. Surface (left column) and cross-sectional SEM (right column) micrographs of SAPO-34 membranes prepared with gel compositions of 1.0 Al_2O_3 : 1.0 P_2O_5 : 0.3 SiO_2 : 1.0 TEAOH: 1.6 DPA: x H_2O : (a) $x = 150$, (b) $x = 200$, (c) $x = 250$, (d) $x = 300$, and (e) $x = 400$.

3.2 Gas Permeation and Adsorption Properties

Membranes prepared with different water contents were used to separate a premixed 50/50 N₂/CH₄ mixture. The feed pressure was 223 kPa, and the pressure in the permeate side was 85 kPa. The separation results at 23°C for these membranes are shown in Table 1. N₂/CH₄ separation selectivities were greater than 5.4 for membranes with water molar contents of 150, 200, 250, and 300. The maximum average N₂/CH₄ selectivity was 7.2 obtained for the water content of 300. The maximum average N₂ permeance was 1,200 GPU obtained for the water content of 250. When the water content was increased to 400, the resulting membranes could not hold pressure for a trans-membrane drop permeation measurement, indicating the membranes had high concentration of defects. Although the SEM surface image of the membrane prepared with water content of 400 (Figure 3e left column) shows intergrown zeolite crystals, some crystals were as large as 2.7 μm, which was about the SEM thickness of the membrane (Figure 3e right column). Intercrystalline boundaries around these large crystals might have resulted in the high concentration of defects.

Table 1. Membrane thickness and N₂/CH₄ separation performance

Water content	Membrane SEM thickness (μm)	N ₂ /CH ₄ separation*	
		N ₂ permeance (GPU)	Selectivity
x = 150	6.8	670 ± 31	5.4 ± 0.92
x = 200	6.3	670 ± 40	6.2 ± 0.71
x = 250	4.2	1,200 ± 240	6.5 ± 0.28
x = 300	3.0	880 ± 47	7.2 ± 0.070
x = 400	2.7	-	1

*: Two membranes were prepared at each water content. Average permeances and selectivities are presented. All the +/- values are standard deviations.

Adsorption isotherms and single-gas permeation were measured for N₂ and CH₄ to help explain the N₂/CH₄ separation mechanism for the selective membranes. Adsorption isotherms showed that CH₄ adsorbs more strongly than N₂ on SAPO-34 crystals (Figure 4). The calculated ideal N₂/CH₄ adsorption selectivities are 0.25-0.55 in the pressure range measured. Thus, the preferential adsorption of CH₄ would favor separating CH₄ over N₂ in the mixture. On the other hand, the smaller molecule N₂ (0.364 nm) diffuses faster than the larger molecule CH₄ (0.38 nm). For example, Li et al. [6] reported that the diffusivity of the N₂ is 24 times of that of the

CH₄ through a SAPO-34 membrane prepared by single-template. The differences in diffusivity would favor separating N₂ over CH₄ in the mixture. Table 2 shows the measured N₂/CH₄ ideal selectivity through the membrane was 8.7 at a feed pressure of 223 kPa. At the same feed pressure, the mixture separation selectivity (7.2) was only slightly lower than the ideal selectivity (Table 2), indicating that differences in diffusivity played a more critical role than the competitive adsorption in the mixture.

Figure 4. Adsorption isotherms of N₂ and CH₄ on SAPO-34 powder at 23°C.

Table 2 . Adsorption, ideal and mixture selectivities through a SAPO-34 membrane.

N ₂ /CH ₄	Value	Pressure (kPa)
Adsorption selectivity	0.25-0.55	58-1,100
Ideal selectivity through membrane	8.7	223
Mixture separation selectivity through membrane	7.2	223

3.3 Effect of N₂/CH₄ composition

In addition to 50/50 premixed N₂/CH₄ gas, we tested N₂/CH₄ separation performance for 18.5/81.5 N₂/CH₄ and 33.8/61.2 N₂/CH₄ mixtures for the best membrane. For these mixtures 200

sccm flow rate was employed. The N_2/CH_4 selectivity almost kept constant in the N_2 concentration range tested (Figure 5). For the N_2 permance, it increased from ~1160 GPU to ~1300 GPU with the increasing N_2 concentration. Figure 5 shows the separation performance of the SAPO-34 membranes as a function of N_2/CH_4 composition. These results demonstrate that even at low N_2 % (typical of natural gas composition), membranes display high N_2 permance and moderate N_2/CH_4 separation selectivities.

Figure 5. Effect of N_2/CH_4 compositions on N_2/CH_4 separation performance

Table 3 compares N_2/CH_4 selectivities and N_2 permances for our membranes vs other N_2 -selective inorganic membranes reported in the literature. Among these materials, the SAPO-34 membranes prepared in the current study showed *the highest N_2 permance, which is the critical factor to reduce the nitrogen separation costs in natural gas processing as discussed below.*

Table 3. Comparison of N₂/CH₄ separations through inorganic membranes.

Material	α	N ₂ permeance (GPU)	Thickness (μm)	Ref.
Carbon molecular sieve	7.7	~0.1	70 $\pm$ 15	⁵
SSZ-13	13	66	7.8	⁸
SAPO-34	5-7	300	2.0-3.0	⁸
SAPO-34	8	500	6.2	¹⁶
SAPO-34 prepared in the current study	6.5-7.4	880-1,300	3.0-4.2	This study

3.4 Membrane Reproducibility

Reproducibility is an important pre-requisite for any membrane to be considered for potential industrial applications. As a representative example, Table 4 shows the separation performance for a premixed 50/50 N₂/CH₄ mixture of 3 membranes prepared independently. Membranes were highly reproducible, with almost identical separation selectivity and only slight variations on N₂ permeance. Membrane synthesis conditions were 6 hr, 230° C, with gel composition: 1.0 Al₂O₃: 1.0 P₂O₅: 0.3 SiO₂: 1.0 TEAOH: 1.6 DPA: 300 H₂O. All membranes calcined at 400 °C for 4 h in vacuum. Heating rate: 0.8 °C/min ; Cooling rate: 0.8 °C /min

Table 4. Separation data illustrating SAPO-34 membrane reproducibility .

Membrane	N ₂ /CH ₄ selectivity	N ₂ Permenance (GPU)
1	7.1	830
2	7.2	900
3	7.1	850

3.5 Potential for N₂ Rejection in Natural Gas Processing

Figure 6 compares our SAPO-34 membranes to polymer membranes presented in “Robeson” plot [4] for the N₂/CH₄ separation. The SEM thicknesses were used in the calculation of N₂ permeabilities (permeance $\times$ membrane thickness) for our SAPO-34 membranes. The data points for the SAPO-34 membranes are significantly above the upper bound.

Figure 6. Comparison to membranes presented in Robeson plot [4] for N₂/CH₄.

The synthesized SAPO-34 membranes are viable for economic N₂ rejection in natural gas processing, especially for small nitrogen-contaminated gas wells where cryogenic distillation costs about \$2.40/MSCF for a plant capacity of 1 MMSCF/day. Note that many small N₂-contaminated gas wells have been shut in for lack of suitable small-scale nitrogen rejection technology. Lokhandwala et al. [20] reported the development of methane-selective membranes with high permeances and methane/nitrogen selectivities of approximately 3–3.5 for treating natural gas containing high concentrations of nitrogen. They concluded that multi-step/multi-stage membrane systems were the lowest cost nitrogen removal technology in many applications despite the design complexity and compression requirements.

The synthesized SAPO-34 membranes are N₂-selective. Aspen HYSYS software was used to model a **one-stage membrane process** for N₂/CH₄ separation. The major economic evaluation bases are: 1) \$4 per MSCF gas price to plant, 2) 4% N₂ in the residue gas, 3)

membrane module costs of \$400/m² in a skid, and 4) membrane lifetime of 15 years. Membrane technology competes most directly against cryogenic distillation. One-stage membrane process is simple, contains no rotating equipment, and requires minimal maintenance.

Figure 7 shows the N₂ rejection costs as a function of N₂ permeance for membranes with N₂/CH₄ selectivities of 8 and 15. Note that the costs here include membrane processing cost and the revenue loss due to the CH₄ loss to the permeate. For both selectivities, the costs decrease sharply as the N₂ permeance increases from 100 to 500 GPU. As the N₂ permeance increases further, the costs decrease more slowly. Therefore, it is critical to develop membranes with N₂ permeances approaching or exceeding 500 GPU to reduce the N₂ rejection cost.

Figure 7. N₂ rejection cost as a function of N₂ permeance for membranes with N₂/CH₄ selectivities of 8 and 15. The N₂ feed concentration is 15 vol.%.

The N₂ permeances for the SAPO-34 membranes prepared in the current study were as high as 1,200 GPU. The membranes also had moderate N₂/CH₄ selectivities. The economic evaluation indicates the cost would be approximately \$0.90/MSCF (Figure 7) if our SAPO-34 membrane technology is used for N₂ rejection in the natural gas processing. Our membranes show significant cost advantage over polymeric membranes, carbon molecular sieve membranes, the SAPO-34 membranes reported by Wu et al. [8] (~\$1.50/MSCF as shown in Figure 7) and the SSZ-13 membranes [8] (greater than \$3.20/MSCF due to the low N₂ permeance of 66 GPU).

Moreover, this cost is only 38% the benchmark technology cryogenic distillation for a plant capacity of 1 MMSCF/day (~\$2.40/MSCF).

4 Conclusions

Diluted gels and increased crystallization temperature resulted in thinner SAPO-34 membranes and thus higher permeances for N₂/CH₄ separation. The membranes separated N₂ from CH₄ with N₂ permeance as high as 1,300 GPU and selectivity of 7.4 at 23°C for a 50/50 N₂/CH₄ mixture. Furthermore, membranes were reproducible and effectively separated gas mixtures having low N₂ content which are relevant compositions of natural gas. This separation performance is superior to those of the state-of-the-art membranes. These SAPO-34 membranes are viable for economic N₂ rejection in natural gas processing.

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