Thin SAPO-34 Membranes Synthesized in Stainless Steel Autoclaves for N₂/CH₄ Separation

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KEYWORDS: SAPO-34 membranes; stainless steel autoclave; N₂/CH₄ separation; cooling effects.

Abstract

SAPO-34 membranes were synthesized in stainless steel autoclaves and Teflon autoclaves with water bath, ice/water bath and flowing water cooling towards N₂/CH₄ separation. The best membrane displaying unprecedented N₂ permeance of ~2,600 GPU and N₂/CH₄ separation selectivity of 7.4 was prepared in the stainless steel autoclave with a water bath cooling. A more selective membrane with a N₂/CH₄ selectivity of 8.6 and N₂ permeance of ~2,150 GPU was also prepared in the stainless steel autoclave but with an ice/water bath cooling. The heat flux rate of the stainless steel autoclaves during membrane preparation was ~two orders of magnitude higher than that of the membranes prepared in conventional Teflon autoclaves. The higher heat flux rate decreased the gel temperature faster, and slowed the kinetics of crystal growth. The slow crystal growth rate during the cooling translated into thinner and more permeable membranes. These SAPO-34 membranes may have great potential for economic N₂ rejection from natural gas.

1 Introduction

N₂ is a significant impurity in many natural gas wells and has to be removed because it decreases the energy content of the gas, as approximately 14% U.S. natural gas wells contains >4% N₂ [1]. However, the U.S. natural gas pipeline specification requires inert gases, such as N₂, to be less than 4% [1]. Natural gas processing requires a cost effective technology to reject the N₂. Currently, an energy-intensive cryogenic distillation process is employed to separate N₂ from natural gas, but this technology 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 process, a more energy-efficient membrane separation technology is needed. Thus, the challenge becomes to develop membranes with enhanced N₂/CH₄ separation performance. N₂-selective membranes are favored over CH₄-selective membranes due to the costly recompression process of low-pressure CH₄ in the permeate side to reach the pipeline pressure. The state-of-the-art N₂-selective polymeric membranes exhibit a N₂/CH₄ selectivity of only 5 and low N₂ permeance of only 20 GPU (Gas Permeation Unit, 1 GPU = 3.348 × 10⁻¹⁰ mol/(m²·s·Pa)), as shown in the “Robeson” plot [3].

Recently, inorganic materials have also been made into N₂-selective membranes and shown potential for N₂/CH₄ separation since the performances are above the so-called upper bound observed for polymers [3]. A carbon molecular sieve (CMS) membrane has been reported by Koros group [4]. These CMS membranes displayed N₂/CH₄ selectivity of 7.7 and N₂ permeability of 6.8 barrers (1 barrer = 10⁻¹⁰ cm³ (STP)·cm/(cm²·s·cmHg)) at 24 °C. Li et al. [5] reported continuous SAPO-34 membranes on stainless steel supports with a N₂/CH₄ selectivity of 4 at 22 °C and N₂ permeance 63 GPU.

SAPO-34 membranes are more attractive in N₂ rejection process due to their high N₂ permeance. SAPO-34 is a silicoaluminophosphate microporous molecular sieve having the composition Si_xAl_yP_zO₂ where x, y and z represent the mole fraction of silicon, aluminum and phosphorous range from 0.01-0.98, 0.01-0.60, and 0.01-0.52, respectively, with x + y + z = 1 [6]. The SAPO-34 structure is formed by substituting silicon for phosphorous in the AlPO₄, which has a neutral framework and exhibits no ion exchange capacity [7]. The SAPO-34 membranes have been successfully employed for CO₂/CH₄ separation [8-32]. However, the separation of N₂/CH₄ mixtures using SAPO-34 membranes is much more challenging than the CO₂/CH₄

separation, because the kinetic diameters of N_2 (0.36 nm) and CH_4 (0.38 nm) differ by less than 5% and N_2 absorbs more weakly than CH_4 on SAPO-34 [24].

Generally, the SAPO-34 membranes are prepared in autogenous pressure autoclaves by hydrothermal treatment. Teflon-lined autoclaves have been conventionally employed for SAPO-34 membrane synthesis [8-14, 16-20, 22-29, 31-43]. The reported thinnest SAPO-34 membrane was $\sim 2.3 \mu m$ with N_2 permeance of 860 GPU for N_2/CH_4 separation [43] and the N_2 permeance of 1200 GPU for doubled silicon content in the gel to obtain the N_2/CH_4 selectivity of 9-11.2 by using high-aspect-ratio seeds. Zong et al. [42] prepared SAPO-34 membranes by diluted gels with increased crystallization temperature with a N_2/CH_4 selectivity of 7.2 and N_2 permeance as high as 1,300 GPU at 23 °C.

Microwave (MW) treatment has been used to synthesize SAPO-34 membranes employing Teflon liners [15, 21, 44, 45]. Chew et al. [44] prepared 1-2 μm thick membrane with 3 layers after MW heating at 200 °C for 2 h, but no separation performance was shown. Chew et al. [45] also prepared H-SAPO-34 with 3-4 μm thickness for CO_2/CH_4 separation after MW heating at 200 °C for 2 h, which had CO_2 permeance of ~ 1700 GPU. Liu et al. [21] showed SAPO-34 membranes prepared by microwave-assisted heating at 180 °C for 2 h to obtain a thickness of $\sim 3 \mu m$, in which no permeation test was carried out. Shi [15] prepared 9-10 μm thick SAPO-34 membranes with CO_2 permeance of 1,075 GPU for the CO_2/CH_4 separation. In these previous studies, the highest N_2 permeance that has been achieved is 2,600 GPU, but with a poor selectivity of only 2.3 using $Al(OH)_3$ as alumina source [41]. However, to compete with the cryogenic distillation, a further increase of the N_2/CH_4 selectivity or the N_2 permeance is needed to reduce the N_2 rejection cost.

In the current study, we compared the separation performance of SAPO-34 membranes towards the N_2/CH_4 separation synthesized in the teflon lined autoclaves vs the stainless steel autoclaves. We also investigated the cooling effects of the autoclaves after membranes synthesis by applying water bath cooling, ice/water bath cooling and flowing water cooling, respectively. Our resultant SAPO-34 membranes separated N_2 from CH_4 with N_2 permeance as high as $\sim 2,600$ GPU with N_2/CH_4 selectivity of 7.4 prepared in the stainless steel autoclave with water bath cooling. A more selective membrane with a N_2/CH_4 selectivity of 8.6 and N_2 permeance of $\sim 2,100$ GPU was also prepared in the stainless steel autoclave, but with an ice/water cooling.

2 Experimental Methods

2.1 Membrane Preparation

The SAPO-34 membranes were prepared by secondary seeded growth method inside the surface of porous α -Al₂O₃ tubes. The supports (Inopor GmbH) have an inside diameter of 0.7 cm and an outside diameter of 1.1 cm and are asymmetric within the inner layer, which has a pore size of 100 nm. To avoid bypass during permeation measurements, the ends of 6-cm-long, tubular supports were sealed with a glazing compound (Envision Glaze Clear IN1001, Duncan) to provide a sealing surface for O-rings, which was calcined at a heating rate of 1 °C/min and a cooling rate of 1 °C/min with a final hold at 950 °C for 5 min. Before synthesis, the supports were boiled in deionized water for 30 minutes. This cleaning step was carried out three times. The cleaned supports were then dried at 100 °C overnight.

2.1.1 Synthesis of SAPO-34 Seeds

The synthesis gel used to grow the SAPO-34 seed crystals had a molar ratio of 1.0 Al₂O₃: 2.0 P₂O₅: 0.6 SiO₂: 4.0 TEAOH: 150 H₂O. To prepare the seeds, aluminum isopropoxide (Al(i-C₃H₇O)₃, Aldrich 99.99%) and deionized water were mixed for 1 h to form a homogeneous solution, followed by addition of phosphoric acid (H₃PO₄, Sigma-Aldrich 85 wt.% aqueous solution) for another 2-h stirring, and then Ludox AS-40 colloidal silica (40% wt.% suspension in water) was added, and the resulting solution was stirred for another 3 h. Finally, tetraethylammonium hydroxide (TEAOH, Aldrich 35 wt.% aqueous solution) was added, and the resultant solution was stirred overnight at room temperature (~22 °C). The gel was then placed in the Teflon liner 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 min to collect the seeds, which were followed by deionized water washing. The process was repeated three times, and the resulting seeds were dried overnight at 100 °C.

2.1.2 Preparation of Membrane Gels

The synthesis gel for SAPO-34 membranes had a molar ratio of 1.0 Al₂O₃: 1.0 P₂O₅: 0.3 SiO₂: 1.0 TEAOH: 1.6 DPA: 300 H₂O. To prepare the gel, Al(i-C₃H₇O)₃ and deionized water were stirred for 1 h to form a homogeneous solution, followed by addition of H₃PO₄ into the gel for another 2-h stirring, and 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 45-50 °C for 4 days before it was used for membrane growth.

2.1.3 Preparation of SAPO-34 Membranes

The inside surface of the supports was seeded by rubbing with the SAPO-34 seeds. The outside surface of the supports was wrapped with Teflon tape to avoid growth of membranes on the outside surface and the seeded supports were placed in an autoclave filled with the synthesis gel. Two supports were placed in one autoclave with the synthesis gel ~0.5 cm above the top of the supports. The SAPO-34 membranes were prepared in two different autoclaves, Teflon liner autoclaves (4744 General Acid Digestion Vessel, 45 mL, Parr Instrument) and stainless steel autoclaves (4713 General Purpose Pressure Vessel, 45 mL, Parr Instrument), to make a comparison of their separation performance. Hydrothermal treatment was carried out in a conventional oven at 230 °C for 6 h. After the synthesis, the autoclaves were taken out from the oven and cooled in water bath for 25 min, ice/water bath for 25 min and flowing tap water for 15 min down to room temperature, respectively. The membranes were then taken out and washed for 15 min with flowing tap water and dried at 100 °C for ~2 h. The membranes were then calcined at 400 °C for 4 h with heating and cooling rates both at 0.8 °C/min under a vacuum environment (pressure of 10 Pa).

2.2 Characterization

Crystals collected from the bottom of the autoclaves after membrane synthesis were analyzed by powder X-ray diffraction (PXRD) using a Siemens Kristalloflex 810 diffractometer operating at 30 kV and 25 mA with Cu K α 1 radiation ($\lambda=1.54059$ Å). Selected SAPO-34 membranes were broken and analyzed by scanning electron microscope (SEM, JEOL JSM-7000F).

2.3 Gas Permeation Measurement

Mixture permeations were measured in a flow system, as described earlier [41]. The membrane was mounted in a stainless steel module and sealed at each end with silicone O-rings. The pressure on permeate and retentate sides of the membrane was independently controlled by back pressure regulators. Fluxes were measured using a bubble flow meter. A pre-mixed 50/50 N₂/CH₄ gas was used as feed gas. The total feed flow rate was 100 standard cubic centimeters per minute (sccm). Further increasing of the flow rate to 200 sccm, 400 sccm and 600 sccm did not increase separation performance, indicating that 100 sccm has eliminated concentration

polarization. The testing temperature was room temperature, the feed pressure was 223 kPa, and the trans-membrane pressure drop was 138 kPa. The compositions of the feed, retentate and permeate streams were measured, after reaching 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.

The permeance of the component i , P_i , was calculated using:

$$P_i = \frac{J_i}{\Delta p_{\ln,i}} \quad (1)$$

where J_i is the flux through the membrane for component i . For the cross-flow configuration, one component preferentially permeates through the membrane, so the partial pressures in the feed and retentate sides are quite different. Therefore, a log-mean pressure drop, $\Delta p_{\ln,i}$, was calculated by:

$$\Delta p_{\ln,i} = \frac{(p_{f,i} - p_{r,i})}{\ln[(p_{f,i} - p_{p,i})/(p_{r,i} - p_{p,i})]} \quad (2)$$

where $p_{f,i}$, $p_{r,i}$, and $p_{p,i}$ are partial pressures for component i , in feed, retentate, and permeate sides, respectively. The permeability is defined as the permeance multiplied by membrane thickness. The separation selectivity, $\alpha_{i/j}^{sep}$, is the ratio of the permeances of components i and j in the mixture.

3 Results and Discussion

3.1 Membrane Synthesis and Characterization

The SAPO-34 seeds for membrane preparation consisted of nanosheet crystals. The lengths and widths of these crystals were between 200 and 800 nm, respectively, and thicknesses were between 50 and 220 nm. XRD confirmed the typical CHA topology of SAPO-34. The XRD patterns (Figure 1) of the SAPO-34 crystals collected from the bottom of the autoclaves after membrane synthesis were essentially identical for the stainless steel and the Teflon autoclaves with different cooling methods and all peaks matched with those from the simulated SAPO-34. Moreover, the crystallinity did not show any significant change for the two types of employed autoclaves or different cooling methods.

Figure 1. XRD patterns of SAPO-34 crystals collected from the bottom of the membrane gels employing different cooling methods: (a) stainless steel autoclave and (b) teflon liner autoclave. For comparison, the simulated XRD pattern for pure SAPO-34 crystals is shown.

Table 1. Comparison of membrane thickness and membrane surface crystal size of the SAPO-34 membranes prepared in the stainless steel autoclaves and teflon autoclaves cooled with water bath, ice/water bath and flowing water, respectively.

Autoclave	Cooling methods	Crystal size (μm)	Membrane thickness (μm)
Stainless steel	Water	0.5-3.0	1.9
	Ice/water	0.4-3.2	2.1
	Flowing water	0.4-2.5	1.7
Teflon	Water	0.3-4.2	2.8
	Ice/water	0.7-4.9	3.4
	Flowing water	0.3-4.1	3.0

After been tested for gas mixture permeation, selected SAPO-34 membranes were broken and analyzed by SEM. SEM images of the membrane top surface (Figure 2 left column) showed that the zeolite crystals for the SAPO-34 membranes were well-intergrown. Cross-sectional SEM images of the membranes (Figure 2 right column) clearly showed dense zeolite layers on the top of the supports. The thickness of the zeolite layer and the crystal sizes on the surface of the membrane were analyzed by SEM measuring tool, and are summarized in Table 1. *The SAPO-34 membranes prepared in the stainless steel autoclaves showed thickness of 1.7-2.1 μm , which were thinner than those displayed by membranes prepared in the teflon autoclaves (thickness of 2.8-3.4 μm).* For the stainless steel and teflon liner autoclaves, the thickness did not vary significantly with the cooling methods.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 2. Top (left column) and cross-sectional views (right column) of SEM of the SAPO-34 membranes prepared in: (a) stainless steel autoclaves cooled with water bath, (b) stainless steel autoclaves cooled with ice/water bath, (c) stainless steel autoclaves cooled with flowing water, (d) teflon autoclaves cooled with water bath, (e) teflon autoclaves cooled with ice/water bath and (f) teflon autoclaves cooled with flowing water.

In addition, the largest membrane crystal size of those membranes prepared in the stainless steel autoclaves was 2.5-3.2 μm , which was also smaller than those prepared in the Teflon autoclaves with crystal size of 4.1-4.9 μm . The crystals collected from the bottom of the autoclaves after membrane synthesis were also analyzed by the SEM, as shown in Figure 3. The largest crystal size for the stainless steel autoclaves was $\sim 2.3 \mu\text{m}$ and the Teflon autoclaves was 4.3 μm , which were in the range of the membrane surface crystal size distribution. Smaller crystal sizes are more likely to form thin membranes [43], which supports well the thinner membranes formed in the stainless steel autoclaves vs the teflon liners.

Figure 3. SEM images of the SAPO-34 crystals collected from the bottom of the autoclaves after membrane synthesis prepared in: (a) the stainless steel autoclaves and (b) the teflon autoclaves cooled with ice/water bath.

3.2 Gas Permeation Properties

Membranes prepared in different autoclaves with different cooling methods were used to separate a premixed 50/50 N_2/CH_4 mixture as described in experimental section. The separation results at 23°C for these membranes are shown in Figure 4. The detailed separation results are summarized in Table 2. From Figure 4(a), the N_2/CH_4 selectivities did not show any significant trend between the stainless steel autoclaves and the Teflon autoclaves. The largest selectivity of 8.6 for the stainless steel autoclave was for the ice/water bath cooling, while for the teflon

autoclave, the largest selectivity of 9.2 was for flowing water cooling. Figure 4(b) clearly shows that membranes prepared in the stainless steel autoclaves displayed much higher N_2 permeance than those prepared in the teflon autoclaves. For the water bath cooling, the N_2 permeance in the stainless steel autoclave was ~ 2.2 times of that in the teflon autoclaves. For the ice/water bath, the N_2 permeance in the stainless steel autoclave was ~ 1.2 times of that in the teflon autoclaves. For the flowing water cooling, N_2 permeance in the stainless steel autoclaves was ~ 1.5 times of that in the teflon autoclaves. Membranes prepared in stainless steel autoclaves displayed separation indices π in the 0.34-0.46 mol/(m²·s) range; while those prepared in the teflon liners showed separation indices of 0.23-0.27 mol/(m²·s). Separation index π [$\pi = N_2$ permeance $\times$ (selectivity-1) $\times$ permeate pressure] has been used as a reliable quantitative parameter to predict zeolite membrane performance and reproducibility [31]. Figure 4(c) shows that the separation indices π of the membranes prepared in the stainless steel autoclave were almost twice of that prepared in the teflon liner autoclaves.

Table 2. N_2/CH_4 separation performance of the SAPO-34 membranes prepared in the stainless steel autoclaves and the teflon autoclaves cooled with water bath, ice/water bath and flowing water, respectively.

Autoclave	Cooling methods	Separation Selectivity α	N_2 permeance (GPU)	Separation index π (mol/(m ² ·s))
Stainless steel	Water	7.4 ± 1.2	2591 ± 242	0.46 ± 0.04
	Ice/water	8.6 ± 0.3	2143 ± 90	0.46 ± 0.04
	Flowing water	8.0 ± 0.8	1728 ± 158	0.34 ± 0.01
Teflon	Water	7.9 ± 0.2	1189 ± 134	0.23 ± 0.02
	Ice/water	6.2 ± 1.8	1801 ± 361	0.25 ± 0.04
	Flowing water	9.2 ± 0.1	1160 ± 6	0.27 ± 0.00

*. Two membranes were prepared at each condition. Average permeances, selectivities and separation indices are presented. All the +/- values are standard deviations.

(a)

(b)

(c)

Figure 4. Separation performance comparison between the stainless steel autoclave and the teflon autoclave with different cooling methods: (a) separation selectivities (α), (b) N_2 permeance and (c) separation index (π).

Comparing the separation performance of the membranes prepared in the stainless steel autoclaves vs the teflon liners, is clear that the stainless steel autoclaves promoted better membrane performance than those in the teflon liners, especially for N₂ permeance. The enhanced N₂ permeance can be explained by a simple one-dimensional Fourier heat law analysis:

$$q_x = -k \frac{dT}{dx} \quad (3)$$

where q_x is the heat flux rate, W/m², k is the material's conductivity, W/(m·K), and dT/dx is the temperature gradient, K/m. Table 3 compares the calculations of the two different types of autoclaves employed for membrane synthesis. Since the flowing water cooling approach includes a convection component in the overall heat transfer process, it was not included in the calculation. The heat flux rate of the stainless steel autoclaves during membrane preparation was ~ two orders of magnitude higher than that of the membranes prepared in the teflon liners. During the heating stage of membrane preparation, the stainless steel autoclaves took shorter time to reach to the final temperature, which was critical during the SAPO-34 membranes synthesis. Li et al. [23] suggested that small AFI impurities may be present especially in lower temperature regions. Therefore, the lower temperature was more favorable for the synthesis of the AFI impurities. In principle, the stainless steel autoclaves can largely reduce this staying (lag) time in the low temperature regime and promote the synthesis of pure SAPO-34. Furthermore, during the cooling stage, the larger heat flux rate can decrease the gel temperature faster, which consequently slows down the kinetics of crystal growth. The slow growth rate during the cooling step, led to a decrease of the membrane thickness (which was experimentally confirmed by SEM, Figure 2). For the stainless steel autoclaves, the heat flux rate of the ice/water bath cooling was 10% higher than that of the water bath, but there were not significant change on the final membrane thickness. This same behavior was observed for the membranes synthesized in the teflon liners. In the heat analysis, we have assumed a constant water bath temperature (this is a reasonable assumption, since the water bath temperature changed slightly < 1 °C) during the cooling stage since the weight of the gel and the mass of the autoclaves was negligible compared to that of the cooling water.

Table 3. Comparison of heat flux rate during the cooling stage after membrane synthesis for the stainless steel autoclaves and the teflon autoclaves.

Autoclaves	k (W/(m·K))	Wall thickness (cm)	q_x (W/m ²)	
			Water bath (22 °C)	Ice/water bath (0 °C)
Stainless steel	16	0.29	1.15E6	1.27E6
Teflon	0.25	0.64	0.81E4	1.98E4

3.5 Comparison with Literature and Potential for N₂ Rejection in Natural Gas Processing

Table 4 compares N₂/CH₄ selectivities and N₂ permeances for the SAPO-34 membranes prepared in this study vs other N₂-selective inorganic membranes reported in the literature. Among these materials, the SAPO-34 membranes prepared in the current study showed *the highest N₂ permeance, which is the critical factor to reduce the nitrogen separation costs in natural gas processing as discussed below.* The previous “Robeson” plots [42, 43] showed that the data points were significantly above the upper bound, near to the right corner. To clearly compare these results, Robeson plots were not included.

Table 4. Comparison of inorganic membranes employed for N₂/CH₄ separation.

Material	Separation Selectivity	N ₂ permeance (GPU)	Thickness (μm)	Ref.
Carbon molecular sieve	7.7	~0.1	70 ± 15	[46]
SSZ-13	13	66	7.8	[11]
SAPO-34	5-7	300	2.0-3.0	[11]
SAPO-34	8	500	6.2	[41]
SAPO-34	5.7-11.3	281-1,200	2.3	[43]
SAPO-34	6.5-7.4	880-1,300	3.0-4.2	[42]
SAPO-34 prepared in the stainless steel autoclaves	7.4-8.6	1,728-2,591	1.7-2.1	This study
SAPO-34 prepared in the teflon autoclaves	6.2-9.2	1,160-1,801	2.8-3.4	This study

Figure 5 shows the N_2 rejection costs as a function of N_2/CH_4 selectivity for membranes with N_2 permeance of 500 GPU, 1,000 GPU and 2,000 GPU. The detailed cost simulation process is described elsewhere [41]. The costs here has included membrane processing cost and the revenue loss due to the CH_4 loss to the permeate side. For all the N_2 permeance, the costs decrease sharply as the N_2/CH_4 selectivity increasing from 6 to 12. As the N_2/CH_4 selectivity increases further, the costs decrease slowly. The N_2 permeances for the SAPO-34 membranes prepared in the current study were as high as 2,600 GPU. The economic evaluation indicates that the projected N_2 separation cost would be approximately \$0.60/MSCF (Figure 5) if these SAPO-34 membranes were to be used for N_2 rejection in the natural gas processing. This cost is lower than the best reported SAPO-34 membranes (Huang et al. [43] (~\$0.70/MSCF) and Zong et al. [42] ~\$0.90/MSCF). Moreover, this cost represents only ~25% the benchmark technology cryogenic distillation for a plant capacity of 1 MMSCF/day (~\$2.40/MSCF) and 75% for a plant capacity of 20 MMSCF/day (~\$0.8/MSCF).

Figure 5. N_2 rejection cost as a function of N_2/CH_4 selectivity for membranes with N_2 permeance of 500 GPU, 1000 GPU and 2000 GPU.

4 Conclusions

SAPO-34 membranes were synthesized in stainless steel autoclaves and teflon autoclaves with water bath, ice/water bath and flowing water cooling for N_2/CH_4 separation. The synthesis in the stainless steel autoclaves cooled with a water bath, ice/water bath and flowing water cooling resulted in thinner SAPO-34 membranes (as compared to the teflon liners) and thus into higher permeances for N_2/CH_4 separation, and slightly improved N_2/CH_4 selectivities. The

membranes separated N₂ from CH₄ with unprecedented N₂ permeance as high as 2,600 GPUs and a N₂/CH₄ selectivity of 7.4 and 2,100 GPUs and a selectivity of 8.6 at 23 °C for a 50/50 premixed N₂/CH₄ gas. The heat flux rate of the stainless steel autoclaves during membrane preparation was ~ two orders of magnitude higher than that of the membranes prepared in conventional teflon liners. The higher heat flux rate slowed down the kinetics of crystal growth, translating into thinner and more N₂ permeable membranes. To our best knowledge, the observed separation performance is superior to any the state-of-the-art membranes employed to separate N₂ from CH₄. If scaled-up, these SAPO-34 membranes are potentially viable for economic N₂ rejection in natural gas processing.

Acknowledgements

The work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0000247.

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Graphical Abstract