Hybrid FSC Membrane for CO_2 Removal from Natural Gas: Experimental, Process Simulation, and Economic Feasibility Analysis

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The novel fixed-site-carrier (FSC) membranes were prepared by coating carbon nanotubes reinforced polyvinylamine/polyvinyl alcohol selective layer on top of ultrafiltration polysulfone support. Small pilot-scale modules with membrane area of 110–330 cm^2 were tested with high pressure permeation rig. The prepared hybrid FSC membranes show high CO_2 permeance of 0.084–0.218 m^3 (STP)/(m^2 h bar) with CO_2/CH_4 selectivity of 17.9–34.7 at different feed pressures up to 40 bar for a 10% CO_2 feed gas. Operating parameters of feed pressure, flow rate, and CO_2 concentration were found to significantly influence membrane performance. HYSYS simulation integrated with ChemBrane and cost estimation was conducted to evaluate techno-economic feasibility of a membrane process for natural gas (NG) sweetening. Simulation results indicated that the developed FSC membranes could be a promising candidate for CO_2 removal from low CO_2 concentration (10%) NGs with a low NG sweetening cost of 5.73E−3 \$/Nm^3 sweet NG produced. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 4174–4184, 2014

Keywords: fixed-site-carrier membranes, CO_2 removal, natural gas sweetening, process simulation, economic feasibility analysis

Introduction

To satisfy the increasing global energy demands and reduce greenhouse gas emissions, some alternative energy forms should be exploited. Natural gas (NG) is becoming one of the most attractive growing fuels for world primary energy consumption due to its availability, versatility and because it is a cleaner energy source compared to coal and crude oil.[1,2] However, raw NG in reservoirs or wells usually contains considerable amount of light and heavy hydrocarbons (HHCs), as well as the impurities of water, H_2S, CO_2, N_2, and helium even though it is relatively clean compared to other fossil fuels. These impurities must be removed at all NG plants to meet pipeline and fuel quality requirements. NG processing with dehydration and sweetening is usually conducted to produce sweet NG for fuels or other utilizations. First, raw NG should be dehydrated to a controlled water content to avoid formation of hydrates before transit to market, while NG sweetening is typically used to remove acid gases of H_2S and CO_2 to meet the legal requirements. CO_2 removal from NG is mandatory to meet NG network grid specifications because CO_2 can reduce heating value of NG, is corrosive, and easily forms hydrates that can clog equipment or damage pumps.[3] Moreover, removal of CO_2 from NG could additionally reduce CO_2 emissions to atmosphere. Different technologies such as chemical absorption,[4] pressure swing adsorption,[5–7] and membranes,[8–13] have been reported for CO_2 removal from NG. Decision on which technology should be used is mainly dependent on process condition, raw NG composition, capacity, and location. Although chemical absorption is still the state-of-the-art technology in this area, membrane systems possess many advantages such as small footprint, low capital, and operating costs, being environmentally friendly, and exhibiting process flexibility,[14] which show a great potential for CO_2 removal from NG. Moreover, membrane systems are quite flexible in CO_2 concentration in raw NG as reported by Baker and Lokhandwala.[15]

Commercial gas separation membranes for NG sweetening are mostly made from cellulose acetate (CA), cellulose triacetate (CTA), and polyimide. Among them, CA is widely used in UOP's membrane system.[15] CTA membrane systems using 16-in. hollow fiber modules have recently been successfully developed by Cynara-NATCO and installed in Thailand.[16] However, the challenges of commercial polymer membranes in high pressure NG sweetening such as relatively low separation performance and membrane plasticization direct to the development of novel, high performance composite membranes. The polyvinylamine (PVAm) fixed-site-carrier (FSC) membranes showed a high performance for CO_2/CH_4 separation at low pressure as reported by Deng et al.[17,18] However, high pressure is still challenging for this type of membrane as membrane plasticization and compaction are involved due to strong adsorption of CO_2 and HHC

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(benzene, toluene, ethylbenzene, and xylene, BTEX) in polymer matrix at high pressure. Moreover, carrier saturation and low water vapor content in high pressure gas stream will additionally reduce CO_2 permeance and CO_2/CH_4 selectivity. The feasible solutions to overcome membrane plasticization are cross-linking of membrane materials and development of membranes resistant to compaction. Deng et al.[19] and He and Hägg[11] used a physical cross-linking method (heat treatment) to increase mechanical strength of FSC membranes by controlling heating temperature $<120°C$, which can maintain membrane morphology and minimize extra production costs. Another potential approach is to develop the mechanically stronger membranes by adding inorganic nanoparticles into polymer matrix. Some literature has reported to increase mechanical strength of nanocomposite membranes by adding different inorganic particles such as TiO_2,[20] carbon nanotubes (CNTs),[21,22] and graphene.[23] Our previous work has already documented that CNTs reinforced PVAm/polyvinyl alcohol (PVA) blend FSC membranes could improve membrane performance, especially at high pressure operation.[11] Thus, high performance hybrid FSC membranes were produced using an optimized preparation condition in the current work. The prepared membranes were tested at high pressure up to 40 bar. The experimental data were used as input variables for process simulation.

Two key parameters, NG sweetening cost and CH_4 losses, are usually applied for techno-economic evaluation on membrane process, which depend on membrane performance and process operating condition. Membrane performances including CO_2 permeance and CO_2/CH_4 selectivity are mainly dependent on material physical properties and structures (controlled by membrane preparation condition), as well as operating condition. It is worth noting that process operating condition can be optimized by process design and simulation. Process design for CO_2 removal from NG by membrane systems depends on CO_2 concentration in feed stream, specific separation requirements, and plant location. Some literature investigated process feasibility of membrane systems for NG sweetening, examples are: Refs. 8,9,24–27. Hao et al. identified which process configurations (single stage or two stages connected in series) and CO_2-selective membranes would be the most economical processes for upgrading of NG containing different ranges of CO_2 concentrations.[26] Peters et al. conducted process simulation for CO_2 removal from NG using HYSYS.[25] They reported that a two-stage membrane system with a CO_2 permeance 0.3 m^3 (STP)/(m^2 h bar) and a CO_2/CH_4 selectivity 40 is comparable to that of amine process. CH_4 purity (98%) of sweet gas can achieve the gas sales standard ($<2\%$ CO_2 in sweet NG). CO_2 purity (90%) in permeate stream needs to be further improved for pipeline transportation and storage as a 10% non-CO_2 gas is needlessly compressed and will cost extra energy. The improvement can be achieved by process optimization. Ahmad et al. reported that process simulation with HYSYS integrated with a user defined unit operation,[27] and a double stage with permeate recycle membrane system was found to be the optimal configuration based on gas processing cost estimation. However, membrane performance (especially CO_2 permeance) was assumed to be independent of feed pressure in their work, but this should not be constant for most polymeric membranes at high pressure operation in reality. Hence, process simulation and optimization was conducted to evaluate process feasibility of the developed hybrid FSC membranes for high pressure NG sweetening based on experimental data from high pressure small pilot-scale module testing where the dependences of membrane performance on process conditions such as pressure, feed flow rate, and so forth were investigated.

Experimental

Materials

Commercial polysulfone (PSf) flat-sheet ultrafiltration membranes (MWCO 20K) were purchased from Alfa Laval. The commercially available high molecular weight polyvinyl amine (PVAm, MW 340K) was purchased from BASF, and further purified in the lab with a specific procedure as reported by Sandru et al.[28] 90+% hydrolyzed polyvinyl alcohol (PVA, MW 72K) was purchased from Merck Schuchardt. The nanoparticles of CNTs VGCF-X (*D*/*L*, 15 nm/3 μm) were provided by SHOWA DENKO K. K. The CNTs have a bulk density and surface area of 0.08 g/cm^3 and 270 m^2/g, respectively.

Preparation of FSC membranes

Inorganic nanoparticles (CNTs) reinforced PVAm/PVA blend FSC membranes were prepared in this work to improve the mechanical strength and reduce compaction issue at high pressure operation. A 0.5 wt % CNTs was added into a 5 wt % PVAm aqueous solution and mixed by an ultrasonic mixer, and a 5 wt % PVA aqueous solution was subsequently added into and completely mixed with the CNTs/PVAm solution. PSf 20K support was placed over steel support and fixed by steel frame. The prepared polymer solution was casted on the top of support to coat an even selective layer with a predetermined thickness as reported by Deng and Hägg.[18] Heat treatment for membrane cross-linking was then performed at 95°C for 45 min to increase mechanical strength, separation performance, and stability.

Gas permeation testing

Membrane separation performance is characterized by high pressure gas permeation testing. High pressure small pilot-scale module (designed by PHILOS in South Korea) involves three sheets (membrane area of each sheet is 110 cm^2) that can be operated in parallel or individually (see Figure 1). This module can also be designed as two-stage cascade system by connecting the retentate of first sheet to the feed of second sheet. Moreover, module was operated in a countercurrent flow pattern, and tested without leakage up to 40 bar in high pressure permeation setup. All gas permeation measurements are conducted at 30°C and a permeate pressure of 1 bar without sweep gas, and the experimental conditions are listed in Table 1. Gas composition in the permeate stream was analyzed by a gas chromatograph (GC, SRI Instruments), and flow rate in feed and permeate sides were measured by mass flow controllers (EL-Flow®, Bronkhorst High-Tech B.V.). The gas permeance [m^3 (STP)/(m^2 h bar)] of component *i* (P_i) is calculated by

$$P_i = \frac{J_i}{\Delta p_i} = \frac{\frac{q}{A} y_i}{\bar{x}_i p_F - y_i p_P} \tag{1}$$

$$\bar{x}_i = \frac{x_{F,i} - x_{R,i}}{\ln\left(\frac{x_{F,i}}{x_{R,i}}\right)} \tag{2}$$

where J_i and $\bar{x}_i$ are flux [m^3 (STP)/(m^2 h)] and logarithm average of feed component *i*, respectively. p_F and p_P are feed and permeate pressure (bar). $x_{F,i}$ is feed concentration

Figure 1. Small pilot-scale plate-and-frame module for high pressure testing.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of component i. $x_{R,i}$ and y_i are retentate and permeate concentration of component i, respectively, which can be measured by GC. q is the permeate volume flow (m^3 (STP)/h). A is the effective membrane area (m^2). The experimental errors of all measurements for gas permeance were estimated by the method for propagation of errors as described by Skog et al.[29] According to Eq. 1, the standard deviation of gas permeance can be estimated on the basis of permeate volume flow, driving force, and membrane area. The error of q, Δp, and A are estimated to be 2%, 3%, and 2.8%, respectively. Therefore, a typical experimental error for gas permeance was calculated to be ±4.6%. The permselectivity of gas mixture ($\alpha_{i/j}$) is calculated by

$$\alpha_{i/j}=\frac{P_i}{P_j} \tag{3}$$

The membrane performance of CO_2 permeance and CO_2/CH_4 selectivity are used as input variables for process simulation. Moreover, stage-cut (θ), CO_2 recovery (R_{CO_2}), and CH_4 losses are calculated based on the following equations

$$\theta=\frac{q_P}{q_F}\times 100\% \tag{4}$$

$$R_{CO_2}=\frac{q_P\times y_{CO_2}}{q_F\times x_{F,CO_2}}\times 100\% \tag{5}$$

$$CH_4\text{losses}=\frac{q_P\times y_{CH_4}}{q_F\times x_{F,CH_4}}\times 100\% \tag{6}$$

where q_P and q_F are gas flow in feed and permeate streams. y_{CO_2} and y_{CH_4} are composition of CO_2 and CH_4 in permeate stream, respectively.

Results and Discussion

Process operating parameters

A small pilot-scale module M1 mounted with the developed hybrid FSC membranes (membrane area: 110 cm^2) was tested at different feed pressures from 10 to 40 bar using synthetic mixed gases of 10 and 50 mol % CO_2 in balance CH_4 to investigate the influences of process operating parameters on membrane separation performances. A constant feed flow of 3000 NmL/min was humidified (RH 100%) and fed into membrane module at 30°C without sweep gas, and the experimental results are shown in Table 2. It can be found that CO_2 permeance decreases with increase of feed pressure due to membrane compaction and less facilitated transport contribution. Carrier saturation and lower water vapor contents at high pressure additionally lead to the decreases of CO_2/CH_4 selectivity due to a more significant reduction in CO_2 permeance compared to CH_4 permeance (dominated only by solution diffusion mechanism). Thus, different CO_2 permeances should be used in process simulation when feed pressure is varied, which has not been considered in other literature.[25] Figure 2 shows the dependence of CO_2 flux on feed pressure at different CO_2 content feed gas. It was also found that CO_2 flux still increases with feed pressure at a low CO_2 feed concentration (10 mol %) due to a much significantly increase of driving force compared to reduction of CO_2 permeance. However, for high CO_2 feed concentration (50 mol %), CO_2 flux increases with feed pressure up to 20 bar, and starts to decrease afterward even though driving force is still increasing owning to much less contribution from both facilitated transport and solution-diffusion with carrier saturation (at lower pressure for higher CO_2 content feed gas) and membrane compaction (reduction on CO_2 solubility and diffusion coefficient, as well as a less water vapor content inside membrane). It indicates that optimal operating pressure should be identified in a specific application. Moreover, it was also found that feed CO_2 concentration will significantly influence membrane separation performance at same feed pressure (see Table 2), which is directly related to separation requirements such as CH_4 purity and methane losses.

Membrane capacity

Membrane capacity was investigated by testing of module M2 at 30°C and 30 bar using different feed flow rates, and the membrane performance are summarized in Table 3. At a low feed CO_2 concentration (10 mol %), CH_4 purity in retentate can reach the requirements using a single stage membrane unit (e.g., 96%) at a low feed flow rate (high stage-cut) as shown in Figure 3a, but CH_4 losses are quite high, which needs to be partly recovered using a second-stage membrane unit. CO_2 purity in permeate is usually around 50–60% as shown in Figure 3b, which should be further purified to meet the requirement for pipeline

Table 1. Membrane Modules and Gas Permeation Testing Conditions[a]

Module	Membrane Area (cm^2)	Feed CO_2 Concentration (%)	Feed Pressure (bar)	Feed Flow Rate (NmL/min)
M1 (single sheet)	110	10	10–40	3000
	110	50	10–40	3000
	110	50	6	100–1500
M2 (three sheets in parallel)	330	10	30	500–3000

[a] All experiments were conducted at 30°C and permeate pressure of 1 bar.

Table 2. Membrane Separation Performance at Different Feed Pressures

Membrane Performance	Feed CO_2 Composition (%)	Feed Pressure (bar)			
		10	20	30	40
CO_2 permeance [m^3 (STP)/(m^2 h bar)]	10	0.218	0.162	0.113	0.084
	50	0.143	0.088	0.055	0.033
CO_2/CH_4 selectivity	10	34.7	27.4	22.0	17.9
	50	28.0	24.6	18.2	11.0

transportation and storage or injection back to reservoirs. Thus, for a specific membrane area of 0.033 m^2 in this work, the maximum NG flow that can be treated is 500 NmL/min at 30 bar and 30°C in order to achieve >96% CH_4 purity in retentate. Based on these results, one could predict the required membrane area for processing of a given NG capacity. However, at such a small pilot-scale module, the effective membrane area may be smaller compared to the calculated membrane area, especially at a low feed flow rate due to a relatively bad flow pattern for gas permeation. Thus, a larger membrane module with a bigger membrane area and better flow pattern should be designed and tested in future work.

At a high feed CO_2 concentration (50 mol %), single stage membrane unit (e.g., module M1) can achieve a high CO_2 purity in permeate (>90%) at 6 bar and 30°C as shown in Figure 4, while CH_4 purity in retentate cannot meet the requirement of NG network grid (>96% CH_4), and needs to be further purified using a second stage or multistage membrane unit. Therefore, different process configurations should be designed in process simulation for CO_2 removal from different NG sources such as common NG wells (relatively low CO_2 concentration) and enhanced gas recovery fields (high CO_2 concentration).

Process Simulation and Economic Feasibility Analysis

Process design

Proper pretreatment is critical to the performances of all membrane systems. Improper pretreatment may lead to a significant performance decline. When sour NG is processed by a membrane system, most CO_2 and small part of CH_4 will pass through membrane to permeate side, and leave most part of CH_4 and relatively impermeable HHC in retentate stream. The retentate gas will probably enter into phase envelop due to the increase of HHC concentration and Joule–Thomson effect as documented by Baker and Lokhandwala.[15] This type of condensation will damage most instruments and/or membranes. Hence, a suitable pretreatment is definitely required. One of feasible solutions is to control dew point by heating feed gas to a certain level and removing most condensable components such as water and HHC. Heating feed gas sufficiently can keep retentate temperature above dew point even when cooled by Joule–Thomson expansion as reported by Baker and Lokhandwala.[15] This is more important for a high pressure feed gas contains a high CO_2 content where temperature drop can be very significant to cause condensation.[30] Water and condensable HHCs C4+ are usually removed by dehydration with glycol absorption combined with cooling and condensation. In addition, temperature swing adsorption is often used to remove small amounts of C12+ hydrocarbons with dry-bed adsorption. Different pretreatment processes need to be designed in NG plants where different contents of CO_2, HHCs, and trace impurities exist. The pretreated NG can be fed into membrane systems for CO_2 removal subsequently.

Process design of a membrane system for CO_2 removal from NG is mainly dependent on the following factors[15]:

1. Membrane separation performance of CO_2 permeance (related to membrane unit cost) and CO_2/CH_4 selectivity (related to methane losses)
2. Feed CO_2 concentration and product requirement (CH_4 purity and other components in the sweet NG)
3. Location of NG plants (onshore or offshore)

Membrane separation performance mainly depends on process configuration, and some literature has already reported optimization of process configuration in a specific separation process.[25,26,31–34] A single-stage membrane unit is usually designed to investigate the influence of process operating parameters such as pressure ratio, feed composition, and capacity. In this work, a single-stage membrane unit (Figure 5a) was designed for comparison of experimental data with simulation results, and to verify the reliability of the membrane transport model used in ChemBrane.

A two-stage cascade membrane system related to the permeate stream was designed for processing of sour NG containing a relatively low CO_2 concentration (e.g., 10 mol %) as shown in Figure 5b. The sweet NG is produced in the first stage retentate stream. It is worth noting that multimembrane units in series connection can be designed in the first stage to ensure high water vapor content in gas stream with rehumidification in between (a relatively high operating temperature could also increase water vapor content as reported in our previous work[35]). The permeate stream needs to be further purified in the second stage to achieve a high CO_2 purity (>95%) for storage or injection back to reservoir. Recycling retentate stream in the second stage can reduce

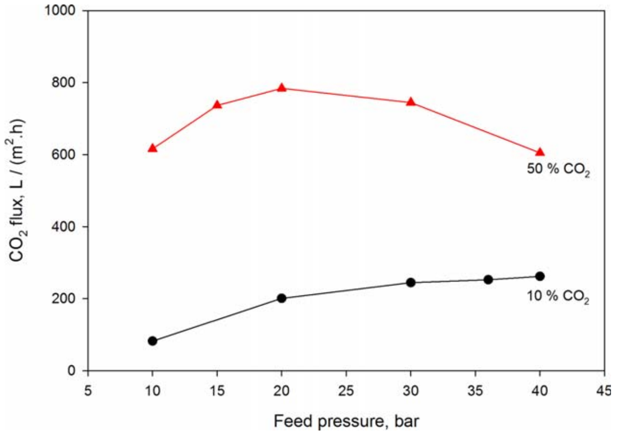

Figure 2. Dependence of CO_2 flux on the feed pressure at 30°C.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 3. Gas Separation Performances at Different Feed Flow Rates[a]

	Feed Flow Rate (NmL/min)					
Membrane Performance	500	700	1000	1500	2000	3000
CO_2 permeance [m^3 (STP)/(m^2 h bar)]	0.023	0.029	0.034	0.044	0.056	0.066
CO_2/CH_4 selectivity	9.2	11.2	12.8	15.3	17.3	19.4

[a] Tested at 30°C and 30 bar with a 10% CO_2 feed gas.

CH_4 losses to a few percent (<2%) as required in most NG processing plants. Although a two-stage cascade membrane system related to retentate stream was designed for processing of NG with a high feed CO_2 concentration (e.g., 50 mol %). CH_4 purity in retentate stream of the first stage cannot reach >96% as fuels or merging into NG network grid, which needs to be further purified in the second stage membrane unit. CO_2 purity in the first stage permeate stream can easily achieve >90% (if membrane has a CO_2/N_2 selectivity of 20–30), and can be optionally further purified or injected back to gas wells and transported to storage sites. The permeate stream in the second stage is then recycled back to the feed stream in first stage to achieve a low methane loss (<2%) as shown in Figure 5c.

Simulation basis

Raw NG produced from gas wells or oil reservoirs has different range of composition depending on well type, depth, and location, which usually contains primary methane and certain amount of light and heave hydrocarbons as well as the impurities of CO_2, H_2S, and inert gases (N_2 and He). However, only the main components of CO_2 and CH_4 were considered after pretreatment to simplify process simulation in this work. Light hydrocarbons such as C_2H_6 and C_3H_8 were found by Uddin[36] to be less permeable compared to CH_4 in our PVAm-based FSC membranes. C2/C3 has relatively low solubility in this membrane compared to methane due to the hydrophilic FSC selective layer and a glassy PSf support. Moreover, water vapor influences on FSC membrane performance has not been fully explored, dry-base composition is used in this work. The simulation basis was chosen based on experimental data from high pressure gas permeation testing and processing requirements as listed in Table 4. It was worth noting that moderate feed pressure of 20–40 bar used in process simulation was decided on the basis of small pilot-scale testing condition, which might be lower compared to most NG fields where it usually should

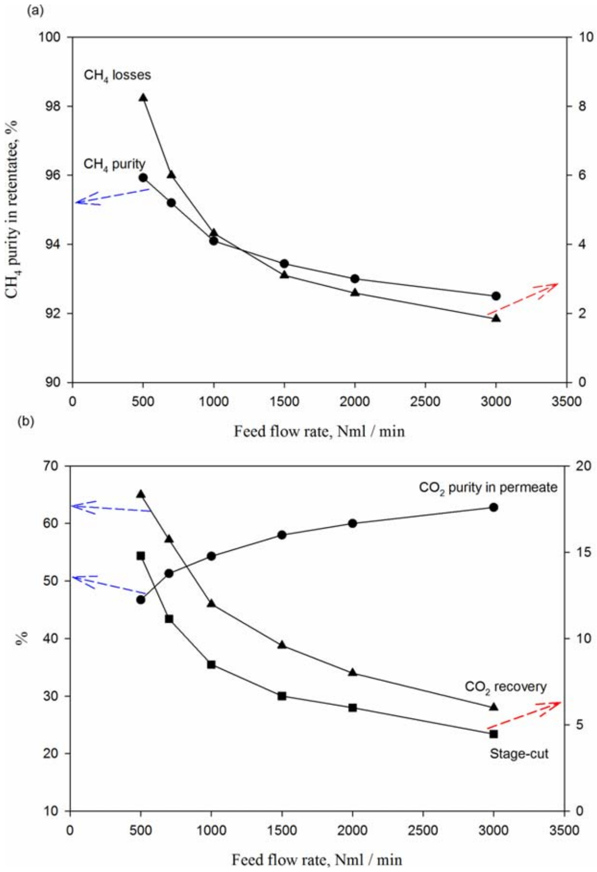

Figure 3. Dependence of the separation performance on the feed flow at 30 bar and 30°C, tested with 10%CO_2−90%CH_4.

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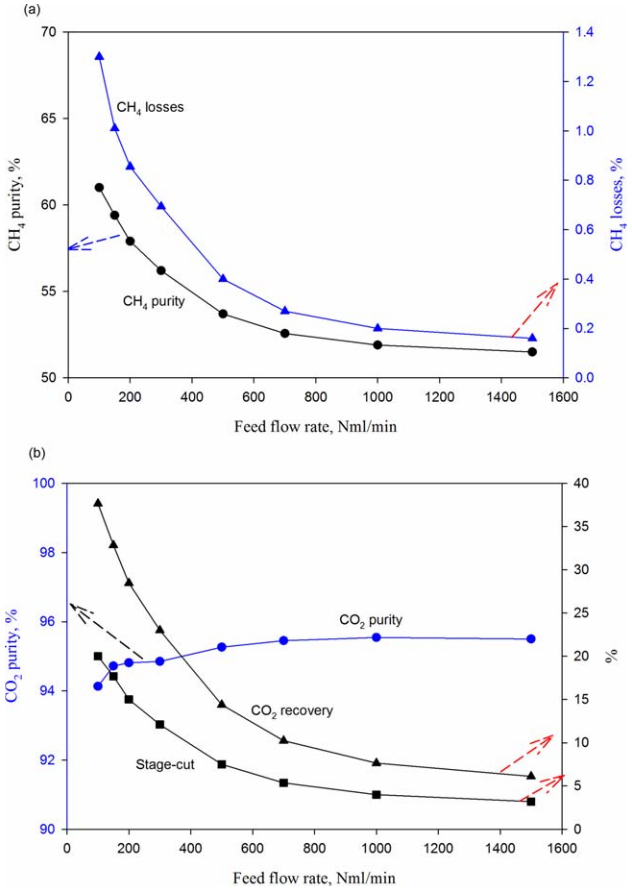

Figure 4. Dependence of the separation performance on the feed flow rate at 6 bar and 30°C, tested with 50%CO_2−50%CH_4.

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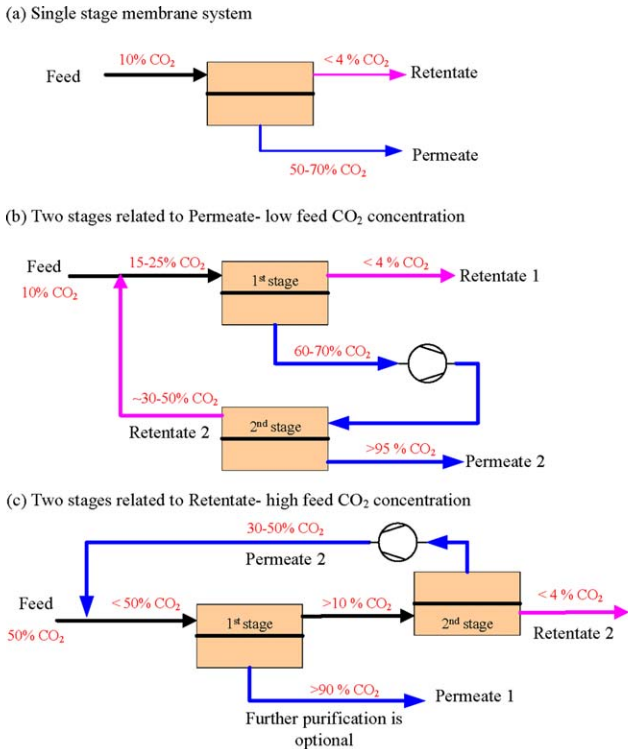

Figure 5. Schematic diagrams of different process configurations: (a) single stage; (b) two stages related to permeate; (c) two stages related to retentate.

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be 60–90 bar. Scenario A is conduced to compare HYSYS simulation results with experimental data, and to validate the membrane model used in ChemBrane. Scenario B is to document process feasibility of membrane systems for CO_2 removal from a 5e+5 Nm^3/h NG plant (with 10% CO_2 in feed). CH_4 purity (>96%) and methane losses (<2%) were chosen as separation target. While Scenario C is studied to evaluate techno-economic feasibility of CO_2 removal from a 5000 Nm^3/h NG plant (with 50% CO_2 in feed). All scenarios were simulated by Aspen HYSYS integrated with an in-house program (ChemBrane[37]) at feed temperature 30°C and permeate pressure 1 bar.

Table 4. Simulation Basis of CO_2 Removal from High Pressure Natural Gas Processes

	Scenarios		
Parameters	A	B	C
Feed flow (Nm^3/h)	0.03–0.18	5E+5	5000
Feed CO_2 composition (%)	10	10	50
First stage feed pressure (bar)	30	40	20
Permeate pressure (bar)	1	1	1
Feed temperature (°C)	30	30	30
CO_2 and CH_4 permeance	Table 3	Table 2	Table 2
CO_2 purity (%)	–	>95	>90
CO_2 recovery (%)	–	>60	>90
CH_4 purity (%)	–	>96	>96
CH_4 losses (%)	–	<2	<8
Membrane area (m^2)	0.033	Optimized	Optimized
CO_2 compression[a] (bar)	–	110	110

[a] Compress to 75 bar and pump to 110 bar.

Table 5. Natural Gas Sweetening Cost Estimation with Membrane System

Category	Parameter	Value
Capital expenditure (CAPEX)	Membrane skid cost ($C_{BM,\ M}$)	35 $\$/\text{m}^2$
	Compressor, pump cost ($C_{BM,i}$)	Eq. 7
	Total capital cost (C_{TM})	Eq. 8
Annual operating expenditure (OPEX)	Labor cost (LC)	15 $\$/\text{h}$
	Electricity cost (EC)	0.07 $\$/\text{kWh}$
	OPEX	LC + EC
Annual capital related cost (CRC)[a]	$0.2 \times C_{TM}$	
NG sweetening cost[b]	(CRC + OPEX)/annual sweet NG production ($\$/\text{m}^3$) sweet NG	
Other assumptions	Membrane lifetime	5 years
	Project lifetime	25 years
	Operating time	7500 h/year
	Compressor and pump efficiency	85%

[a] Covering depreciation, interest and maintenance.
[b] CH_4 losses cost is not included.

Cost estimation

Major equipment cost in a process (e.g., compressor, pump, and membrane unit) was used for estimation of capital expenditure (CAPEX), which provides the accuracy in the range of −25 to 40%, and typically for the preliminary feasibility evaluation of different processes. The bare module cost (C_{BM}) accounts to purchase cost (C_p^0) of equipment in base conditions (i.e., carbon steel material and near ambient pressure), and a multiplying bare module factor (F_{BM}) is applied to consider specific equipment type, specific materials of construction, and operating pressure. Thus, the bare module cost of each piece of equipment is calculated by

$$C_{BM}=C_p^0 F_{BM} \tag{7}$$

An excel program of CAPCOST 2008 is used to estimate capital cost based on the equipment module approach.[38] The total capital cost (C_{TM}) includes contingency and contractor fee in addition to direct and indirect cost, which is calculated as follows

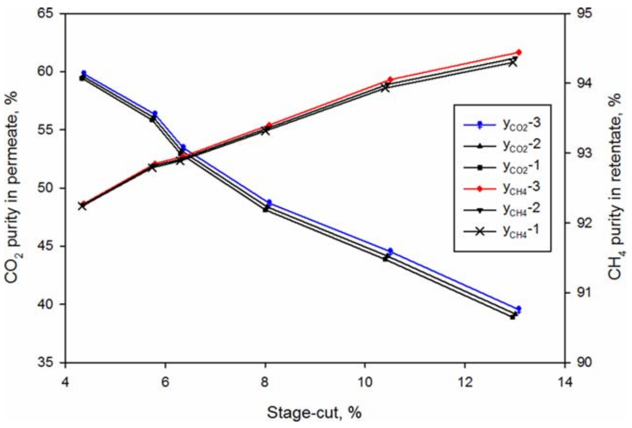

Figure 6. Effect of stage-cut and flow pattern on the permeate CO_2 purity and retentate CH_4 purity at 30 bar and 30°C, (1) cocurrent; (2) cross-flow; (3) countercurrent.

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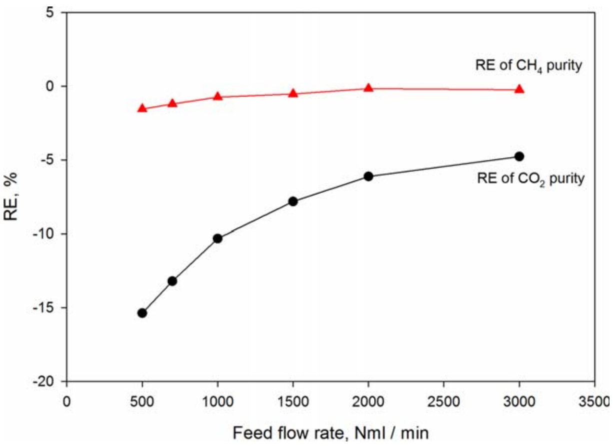

Figure 7. Comparison between the experimental and simulation results using a countercurrent model.

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$$C_{TM} = 1.18 \sum_{i=1}^{n} C_{BM,i} \tag{8}$$

where n is total number of individual units. A chemical engineering plant cost index of 585.7 for equipment is adopted for all inflation adjustments. Table 5 shows the cost models and parameters for NG sweetening. A membrane skid cost of 35 \$/m^2 was decided to estimate membrane unit cost by considering the relatively cheap materials for large-scale production on PVAm/PVA blend FSC membranes. However, considering specific materials required for membrane modules and valves at high pressure operation, sensitivity analysis on membrane skid price was additionally studied in Scenario B. Membrane lifetime is considered as 5 years and replacement cost is estimated as 20% of membrane unit cost. Bare module cost for compressor and pump is estimated by Eq. 7, while total capital cost is calculated by Eq. 8. The annual capital related cost (CRC) is assumed to be 20% of total capital cost. For operating expenditure (OPEX), only electricity and labor costs are considered to simplify operating cost estimation based on the literature.[25,26] Finally, NG sweetening cost is estimated by

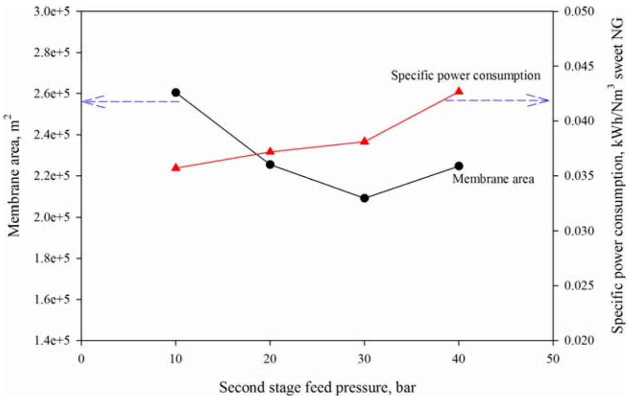

Figure 9. Dependence of specific power consumption, membrane area, and sweetening cost on the feed pressure of the second stage membrane unit.

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$$\begin{aligned}\text{NG sweetening cost} &= (\text{CRC}+\text{OPEX})\\ &/\text{annual sweet NG production, } \$/\text{m}^3\end{aligned} \tag{9}$$

NG sweetening cost is applied to evaluate economic feasibility of membrane processes.

Membrane transport model validation

Different flow patterns in ChemBrane, (1) cocurrent, (2) crossflow, and (3) countercurrent were investigated for simulation of Scenario A using a single-stage membrane system, and the results are shown in Figure 6. It can be concluded that countercurrent model showed the best separation performance both for CO$_2$ purity in permeate and CH$_4$ purity in retentate. Thus, countercurrent flow pattern was chosen for process optimization and feasibility analysis. The relative error (RE) is applied to compare the simulation results with the experimental data, and to validate membrane transport model in ChemBrane, which is calculated by

$$\text{RE}_i = \frac{x_{\text{sim.},i} - x_{\exp.,i}}{x_{\exp.,i}} \times 100\% \tag{10}$$

where $x_{\text{sim.},i}$ and $x_{\text{exp.},i}$ are the simulation and experimental composition of gas component i. Figure 7 indicates that the

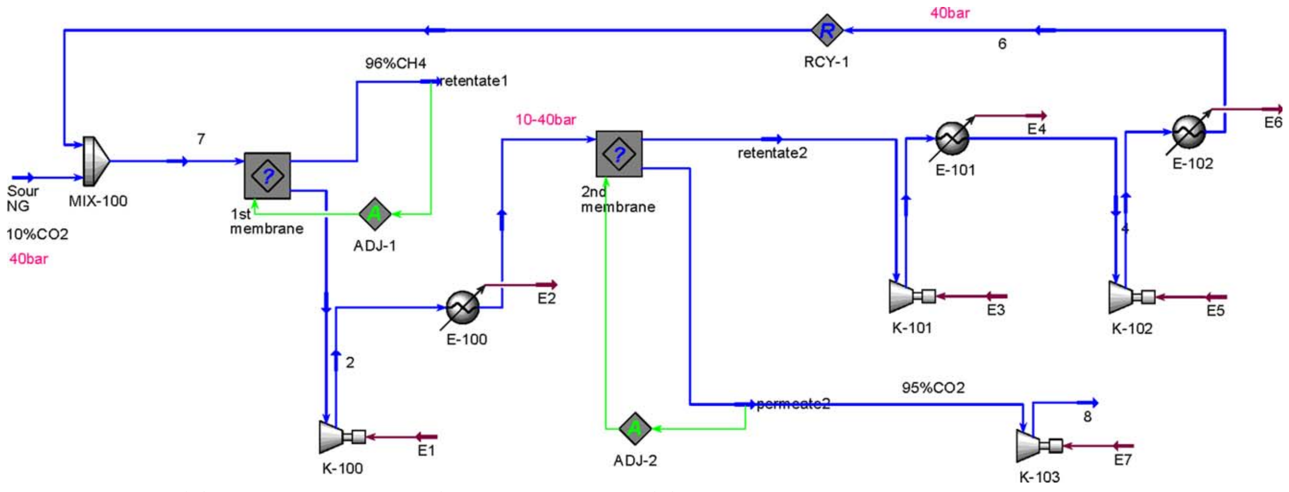

Figure 8. PFD of CO$_2$ removal from a NG containing 10% CO$_2$ using membrane systems.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 6. Simulation Results of Scenario B

Parameters	Simulation Results W/ CO_2 Capture	 W/O CO_2 Capture
Sweet NG productivity (Nm^3/h)	4.67E+05	4.67E+05
CH_4 purity in sweet NG (%)	96.08	96.08
CH_4 losses (%)	0.35	0.35
CO_2 purity (%)	95.01	–
CO_2 recovery (%)	63.65	–
Specific power consumption (kWh/Nm^3) sweet NG	3.63E−02	2.43E−02
Total membrane area (m^2)	2.62E+05	2.62E+05
NG sweetening cost ($\$/Nm^3$) sweet NG	5.73E−03	4.22E−03

Table 7. Simulation Results of Scenario C with High CH_4 Losses

Parameters	Simulation Results W/ CO_2 Capture	 W/O CO_2 Capture
Sweet NG productivity (Nm^3/h)	2.31E+03	2.31E+03
CH_4 purity in sweet NG (%)	96.09	96.09
CH_4 losses (%)	7.66	7.66
CO_2 purity, %	92.54	–
CO_2 recovery (%)	96.39	–
Specific power consumption (kWh/Nm^3) sweet NG	0.25	4.24E−02
Total membrane area (m^2)	8.21E+03	8.21E+03
NG sweetening cost ($\$/Nm^3$) sweet NG	4.50E−02	1.89E−02
Membrane unit footprint[a] (m^3)	2.74	

[a] Assuming 0.03 m^3 per hollow fiber module ($D = 20$ cm, $H = 1$ m, packing density 3000 m^2/m^3), needs 91 modules.

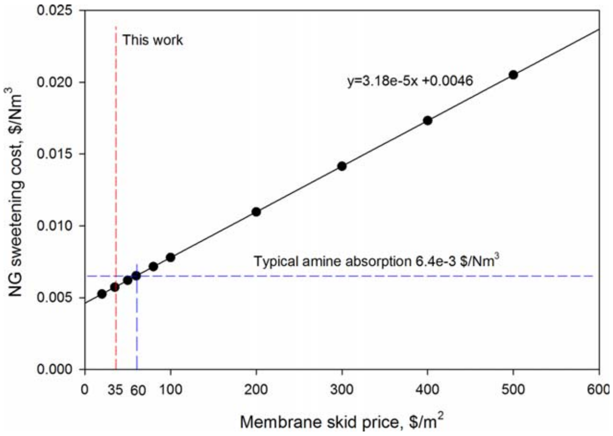

Figure 10. Sensitivity analysis on NG sweetening cost vs. membrane skid price.

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membrane model used in the simulation gives a good prediction compared to the experimental data with a maximum RE of 1.5% for CH_4 purity in retentate and 15% for CO_2 purity in permeate.

Techno-economic feasibility analysis

The main equipment of compressors, pumps, and membrane units are designed, arranged, controlled, and operated in a particular way to remove CO_2 from high pressure NG to meet the specific requirements (see Table 4). It was found that single stage membrane unit (Scenario A) cannot accomplish the separation requirements based on experimental testing and above discussion. Thus, a two-stage membrane system was then designed for process feasibility analysis, and cost minimization on NG sweetening was applied to process optimization.

NG with a Low CO_2 Concentration. The process flow diagram (PFD) of Scenario B with a low feed CO_2 concentration (10 mol %) is shown in Figure 8. Feed pressure in the first stage is set to 40 bar, and retentate stream (retentate1) contains >96% CH_4 is the product of sweet NG. Permeate stream (permeate1) is then compressed (K-100 or multistage compressors) from 1 bar to a given pressure (10–40 bar) optimized based on cost minimization. Process simulation was conducted with a two-stage membrane system to achieve a specific separation requirement of CH_4 purity > 96%, a methane loss < 2%, and a CO_2 purity > 90%. The main power consumption is located in the recompression of the first stage permeate and the second stage retentate as well as the compression of captured CO_2 for pipeline transportation. The dependence of specific power consumption and required membrane area on the second stage feed pressure is shown in Figure 9. It can be seen that specific power consumption mainly depends on feed pressure in the second stage membrane unit, and more power (higher operating cost) is usually needed to be operated at high pressure.

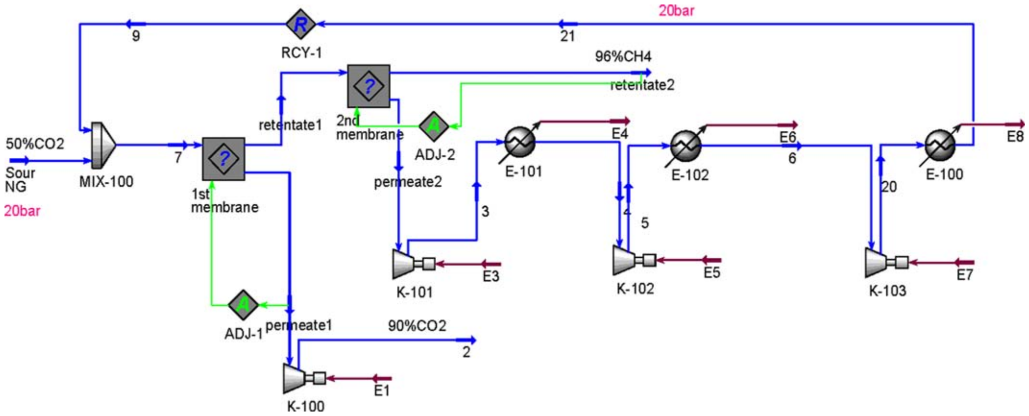

Figure 11. PFD of CO_2 removal from a NG containing 50% CO_2 using membrane systems with high methane losses.

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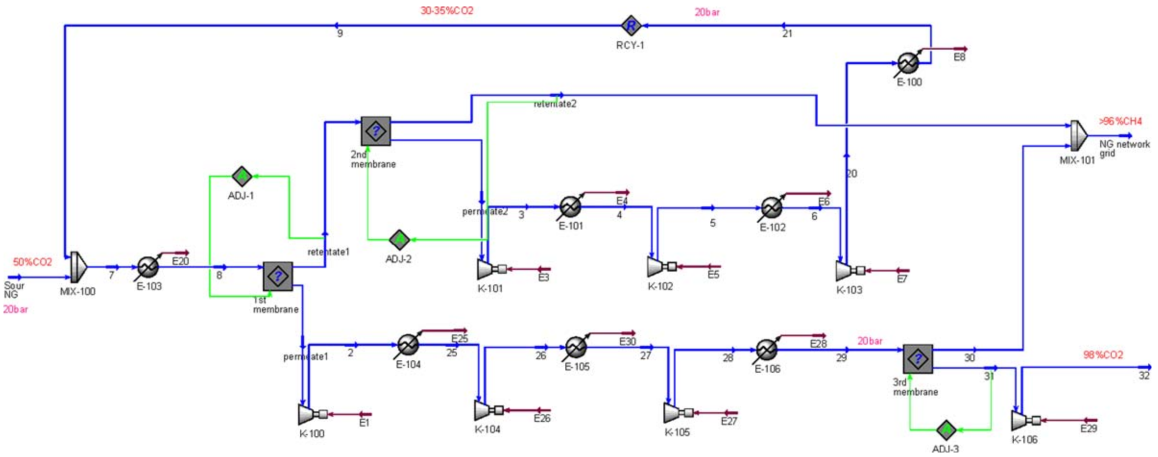

Figure 12. PFD of CO_2 removal from a NG containing 50% CO_2 using membrane systems with low methane losses.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

But increasing driving force reduces required membrane area, and thus decreases membrane cost. Therefore, minimization of NG sweetening cost should be applied to optimize operating condition. A minimum cost of 5.73E−3$ per Nm^3 produced sweet NG was found at a feed pressure of 10 bar in the second stage membrane unit to achieve the given separation requirements (i.e., CH_4 purity > 96%, CH_4 losses < 2%, and captured CO_2 purity > 95%) as shown in Table 6, which is relatively lower compared to amine absorption of 0.18 \$/mscf product (i.e., 6.4E−3 \$/ Nm^3) as reported by Peters et al.[25] If CO_2 transport and reinjection is not required, the processing cost can be further reduced to 4.22E−3 \$/Nm^3 sweet NG produced as indicated in Table 6. However, the price of membrane skid for high pressure NG sweetening is still uncertain. Thus, membrane skid prices from 20 to 500 \$/m^2 are conducted for sensitivity analysis. Figure 10 shows the dependence of NG sweetening cost on membrane skid price. It can be found that membrane systems are competitive to amine absorption if membrane price < 60 \$/m^2. Although NG processing cost will be higher if membrane price is higher than 60 \$/m^2, low environmental impact and smaller footprint of membrane system still provides a good alternative for NG sweetening. It is worth noting that required membrane area for a 5e+5 Nm^3/h NG plant is about 2.6e+5 m^2. To reduce the footprint of membrane unit, hollow fiber or spiral wound modules are required instead of using plate-and-frame module that has been tested in the lab- and bench-scale. Moreover, simulation basis chosen from the experimental data on our FSC membranes is to provide guidelines for material performance requirement and process integration. Any other types of membrane materials with such or even high performance should be viable for NG sweetening.

NG with a High CO_2 Concentration. The PFD of Scenario C with a high feed CO_2 concentration (50 mol %) is shown in Figure 11. Feed pressure in the first stage is set to 20 bar and retentate stream (retentate1) is further sent to the feed stream in the second stage (second membrane).To achieve a low methane loss, permeate stream (pemeate2) in the second stage is then recompressed (K-101, K-102, and K-103) from 1 to 20 bar, and recycled back to mix (MIX-100) with sour NG. The main power consumption includes the recompression of the second stage permeate and reinjection of CO_2 to gas wells (or transport of the captured CO_2 to the storage sites). The simulation results are given in Table 7, the specific power consumption is estimated to 0.25 kWh/Nm^3 sweet NG produced, which is much higher compared to Scenario B (3.63E−2 kWh/Nm^3 sweet NG in Table 6). However, power consumption can be brought down to 4.24E−2 kWh/Nm^3 sweet NG produced by excluding CO_2 transportation and reinjection (i.e., W/O CO_2 capture in Table 7). The NG sweetening cost is estimated to be 4.50E−2 \$ /Nm^3 sweet NG produced, but methane loss of 7.66% in this process is quite high, which can be reduced by partly recovering CH_4 from the first stage permeate stream using an extra membrane unit (as shown in Figure 12). Stream (permeate1) is compressed (K-100, K-104, and K-105) to 20 bar and sent into the extra membrane unit (third membrane). The retentate stream (30) is mixed (MIX-101) with stream (retentate2) as products. Stream (31) contains high purity CO_2 is compressed (multistage compression from K-106) to 110 bar for pipeline transportation. The simulation results are shown in Table 8, it was found that methane losses are now brought down to 1.91%, but the specific NG sweetening cost is increased to 5.72E−2 \$ /Nm^3 sweet NG produced (∼30% increase). Moreover, the footprint of membrane unit also increases about 25% from 2.74 to 3.43 m^3 (estimated by hollow fiber modules with packing density

Table 8. Simulation Results of Scenario C with Low CH_4 Losses

Parameters	Simulation Results W/ CO_2 Capture	 W/O CO_2 Capture
Sweet NG productivity (Nm^3/h)	2.45E+03	2.45E+03
CH_4 purity in sweet NG (%)	96.11	96.11
CH_4 losses (%)	1.91	1.91
CO_2 purity (%)	97.94	–
CO_2 recovery (%)	96.17	–
Specific power consumption (kWh/Nm^3) sweet NG	0.34	0.17
Total membrane area (m^2)	1.03E+4	1.03E+4
NG sweetening cost (\$/Nm^3) sweet NG	5.72E−02	3.55E−02
Membrane unit footprint[a] (m^3)	3.43	

[a] Assuming 0.03 m^3 per hollow fiber module ($D = 20$ cm, $H = 1$ m, packing density 3000 m^2/m^3), needs 114 modules.

$3000\ m^2/m^3$). The increases of footprint and power consumption may not offset the relatively low methane losses. Thus, in offshore NG plants, process with relatively high CH_4 losses could be an economical way instead of pursuing much low CH_4 losses. It was found that integration of CO_2 capture unit significantly increased NG processing cost, and EOR process by reinjecting captured CO_2 back to gas/oil fields could be one of the most promising and economical ways in NG processing plants.

Conclusions

The CNTs reinforced FSC membranes were prepared by coating a PVAm/PVA selective layer on the top of the MWCO 20K PSf supports. The prepared membranes showed a good CO_2/CH_4 separation based on high pressure pilot-scale module testing. The operating parameters of feed pressure, feed CO_2 concentration, and feed flow rate were found to significantly influence membrane performance. Both CO_2 permeance and CO_2/CH_4 selectivity decrease with increase of feed pressure, especially at high pressure up to 40 bar. The experimental results also indicate that developed FSC membranes could accomplish a specific separation requirement with a CH_4 purity $> 96\%$ at a high stage-cut when feed gas is $10\%CO_2-90\%CH_4$, but a second stage membrane unit is required to achieve low methane loss ($<2\%$).

Based on experimental data, process simulation using HYSYS integrated with ChemBrane was conducted for CO_2 removal from high pressure NG. ChemBrane was documented to be a good model for simulation and prediction of gas transport through the developed FSC membranes. Two-stage membrane systems were designed to evaluate process feasibility for CO_2 removal from different NG sources. The simulation results indicated that membrane systems could be a potential candidate for CO_2 removal from a NG contains a low CO_2 concentration (10 mol %) based on cost estimation. The processing cost of $5.73E-3$ \$/Nm^3 sweet NG produced is found to be lower compared to a typical amine system. Moreover, membrane systems for CO_2 removal from high CO_2 concentration (50 mol %) NG were additionally evaluated. The NG sweetening cost is found to be much lower if relatively high CH_4 losses ($\sim8\%$) are acceptable, which indicates that the values for extra gas recovered may not offset the increased weight, footprint, and power consumption typically in offshore site.

Although the developed FSC membranes showed a nice potential application in high pressure NG sweetening based on small pilot-scale testing and process simulation, the membrane performance needs to be further improved especially at high pressure operation. Influences of water vapor on FSC membrane performance should be documented in future work. Moreover, membrane durability testing by exposed to a real NG field where it usually contains the impurities of H_2S and some other HHCs should be further conducted before bringing the membranes into a large-scale demonstration or commercial applications.

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