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Investigation on Nanocomposite Membranes for High Pressure CO_2/CH_4 Separation

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Abstract

The novel nanocomposite membranes were prepared for CO_2/CH_4 separation, and a good selectivity >30 at high pressure >30bar was obtained by testing a plate-and-frame module with a membrane area 110 cm^2. The Joule-Thomson effect was found to have negligible influence on the temperature drop inside the membrane module due to the very high heat transfer coefficient for the membrane materials, which is different from the HYSYS simulation results. The water permeance was determined to be higher compared to CO_2 permenace especially at high pressure, which indicated high water vapor content should be achieved in the feed gas to avoid the drying of the membrane and maintain high membrane separation performance in a real process. A two-stage membrane system was designed to purify CH_4 from a 50% CO_2/50% CH_4 gas mixture, and the CH_4 purity of 70% can be achieved in the 2nd stage. Process simulation using HYSYS integrated with ChemBrane indicated that a multi-stage membrane system is needed to achieve the industrial requirement on the production of sweet natural gas.

Highlight

- Development of novel nanocomposite membrane
- Joule-Thomson effect on membranes for CO_2/CH_4 separation
- Water permeation behavior through nanocomposite membrane
- Two-stage membrane system testing at high pressure

Introduction

CO_2 is one of the major contaminants in natural gas streams. The removal of CO_2 from high pressure natural gas stream is necessary prior to entering downstream units of the gas processing plants due to Health, Safety and Environment (HSE) concern, heating value specification, as well as plant and pipeline corrosion issues [1]. Chemical absorption is the state-of-the-art technology for CO_2 removal in on-shore/off-shore natural gas plants, but membrane system shows great potential in this application due to the advantages of smaller footprint, being environmentally friendly, and process flexibility [2-4]. Membranes for natural gas processing were first commercialized in the 1980s for CO_2 removal, and have been the dominant membrane gas separation process since then [5]. The commercial polymeric membranes for natural gas sweetening today are mostly made from cellulose acetate (CA, spiral-wound) and polyimides (PI, hollow fibers). CA membranes have relatively low CO_2/CH_4 selectivity under typical operating conditions in the field [6,7], but have fair-to-good tolerance to the contaminants such as benzene, toluene, ethylbenzene and xylene (BTEX) in natural gas streams [8,9] with relatively low cost. The PI membranes presented a little better performance with higher CO_2/CH_4 selectivity but are more sensitive to BTEX [10]. The use of membrane systems provides an economically and environmentally attractive way compared to the traditional amine absorption. However, the challenges related to membrane compaction and plasticization at high pressure operation directs to the development of novel membrane materials [11]. Wang et al. [12] and Suleman et al. [13] reviewed the latest technological advancements and major problems in polymeric membranes for CO_2/CH_4 separation, and pointed out that the feasible solution on the crosslinking of the membrane materials and/or introducing inorganic nanoparticles into the polymer matrix to enhance the mechanical strength at high pressure application. Different cross-linking methods such as thermal annealing, formation of semi-interpenetration polymer networks, and ultraviolet (UV) radiation have been discussed by Wind et al. [14]. They concluded that most of the preceding crosslinking methods involve the procedures that would be difficult to be applied in the commercial membrane manufacturing processes. Ma et al. reported that ester-crosslinked hollow fiber membranes can maintain a high CO_2 permeance under highly aggressive feed pressures up to 55 bar for a 50/50% CO_2/CH_4 feed gas without CO_2 plasticization [15]. Zhao et al. [16] reported the chemically cross-linked Matrimid® 5218 for CO_2 separation, which provided better mechanical properties, better flexibility for higher elongation at break, compared to their non-crosslinked precursors. He et al. [11,17] used a physical cross-linking method (heat treatment) to increase the mechanical strength of the fixed-site-carrier (FSC) membranes by controlling heating temperature <120°C, which can maintain membrane morphology and minimize production cost. Developing mixed matrix membranes (MMMs) and hybrid membranes is another potential approach to strength the mechanical stability. Adams et al. prepared a 50% (vol.) Zeolite 4A/polyvinyl acetate (PVAc) MMMs for CO_2 separation from natural gas [18]. They found that the prepared MMMs can approach the Robeson CO_2/CH_4 upper bound. Other type of Matrimid® 5218 based MMMs presented relatively good CO_2/CH_4 selectivity >50, and showed interesting for purification of natural gas [19,20]. The carbon nanotubes (CNTs) was added into the polyvinylamine (PVAm)/polyvinyl alcohol (PVA) blend membranes in

the previous work [3,11]. The initial testing on the lab-scale membranes presented a very promising separation performance for CO$_2$/CH$_4$ separation at high pressure (up to 40bar). It was reported that process operating parameters significantly influenced the module performance. Thus, bench-scale module testing without sweep gas was conducted in this work to document the nanocomposite membrane performance in a more realistic way. Moreover, understanding the water transportation behavior inside the membrane matrix and Joule-Thomson (J-T) effect is crucial to identify the optimal process operation condition for natural gas sweetening. The objective of this work was to develop a novel high performance nanocomposite membrane for CO$_2$ removal from moderate pressure natural gas, and identify the requirement on the appropriate pre-treatment.

Experimental

Preparation of nanocomposite membranes

Carbon nanotubes (CNTs, VGCF-X (D/L, 15 nm/3 μm) [11] reinforced nanocomposite membranes were prepared by coating a thin selective layer with controlled thickness on the top the commercial polysulfone (PSf) flat-sheet support (MWCO 20K, purchased from Alfa Laval)-See Figure 1. A certain amount of CNTs (1 wt.%) were added into the polymer solution and mixed by an ultrasonic mixer. Sonicated solution was then filtered using a syringe with a hydrophilic filter (Acrodisc® 5 μm) to remove any contaminants, polymer particles and the aggregated or not completely dispersed CNTs. The filtered solution was evenly casted on the top of the PSf supports. The nascent membranes were dried overnight in a vacuum oven, and then thermally cross-linked at 95 [11]. A 30 cm × 30 cm large flat-sheet nanocomposite membrane was prepared for the bench-scale module testing. The prepared nanocomposite membrane has a thin selective layer <1micron as shown from the SEM image (right in Figure 1: Using A Hitachi S-3400N scanning electron microscopy).
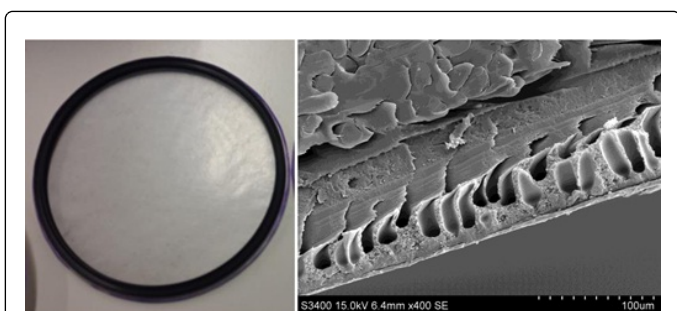

Figure 1: CNTs reinforced nanocomposite membranes.

Membrane performance testing

The membrane separation performance was measured by gas permeation testing. The prepared large flat-sheet membrane was cut into several sheets with a specific size (diameter, 12 cm), and each membrane area is 110 cm^2 (see left image in Figure 1). The high pressure bench-scale module (designed by PHILOS from South Korea involves three sheets (membrane area: 110-330 cm^2) that can be operated individually or in other configurations such as parallel, series, and cascade [3]. The modules were then tested with the high pressure gas permeation rig [17]. The permeate gas composition was analyzed by a gas chromatograph (GC, from SRI Instruments Inc.), and the flow rate in feed and permeate were controlled/measured by Bronkhorst mass flow controller/meters. The gas permeance (m^3 (STP)/(m^2.h.bar)) of component i(Pi) is calculated by

$$P_i = \frac{J_i}{\Delta p_i} = \frac{J_i}{\left(\bar{x}_i p_F - y_i p_P\right)} \tag{1}$$

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

where J_i is the flux [m3(STP)/(m^2.h)] of component i. p_F and p_P are feed and permeate pressure (bar), and $x_{F,i}$ is the feed concentration of component i. $x_{R,i}$ and y_i are the retentate and permeate concentration of component i, respectively, which were measured by GC. q is the permeate volume flow (m3 (STP)/h), and A is the effective membrane area (m2). The selectivity is the ratio between the gas permeances of different compounds. According to eq. (1), the standard deviation of gas permeance can be estimated on the basis of permeate volume flow rate, driving force and membrane area, and a typical experimental error for gas permeance was calculated to be ± 4.6% [3]. Moreover, the CH$_4$ loss is calculated based on the following equations,

$$CH_4 \quad loss = \frac{q_P \times y_{CH4}}{q_F \times x_{F,CH4}} \times 100\% \tag{3}$$

where q_P and q_F are the gas flow rate in feed and permeate streams (Nml/min). $y_{CO}2$ and $y_{CH}4$ are the CO$_2$ and CH$_4$ contents in the permeate stream.

Results and Discussion

Membrane material performance

A single module mounted the prepared membrane (membrane area of 110 cm^2) was tested with a 3000Nml/min 10 vol.%CO$_2$-90 vol.%CH$_4$ mixed gas at 30°C and different feed pressures. The membrane system run at a low stage-cut, and the results are shown in Table 1. The CO$_2$/CH$_4$ selectivity >30 was found within the testing pressure window ranges 10-30bar. The CO$_2$ permeance decrease with the increase of feed pressure due to the less water content in the feed gas stream and the low relative humidity (RH) in the retentate at higher pressure. The developed nanocomposite membranes showed good separation performance at operating pressure up to 30bar, but the gas permeance decreases with the increase of feed pressure. Thus, other alternative membrane materials (e.g. Carbon membranes) should be pursued for high pressure (60-90bar) natural gas sweetening in the future work.

Experimental condition				Membrane performance		
Feed pressure, bar	Temperature °C	Feed flow, Nml/min	Retentate RH, %	CO$_2$ permeance, m^3(STP)/ (m^2·h·bar)	CH$_4$ permeance, m^3(STP)/ (m^2·h·bar)	CO$_2$/CH$_4$ selectivity

10	30	3000	84	0.302	0.00775	39
20	30	3000	77	0.183	0.00528	34.6
30	30	3000	70	0.112	0.00343	32.7

Table 1: Membrane performance tested with a 10%CO$_2$-90%CH$_4$ mixed gas without sweep gas.

Investigation on Joule-Thomson effect

Temperature may decrease inside a membrane module when condensable gases (e.g., CO$_2$) pass through a membrane from the high pressure feed side to the low pressure permeate side due to the Joule-Thomson (J-T) effect. HYSYS simulation integrated with ChemBrane was conducted (Simulation basis: area 330 cm^2, PCO$_2$=0.066 m^3 (STP)/(m^2.h.bar), SCO$_2$/CH$_4$=19.4, feed flow 3000 Nml/min 10%CO$_2$-90%CH$_4$, sweep flow 50 Nml/min, permeate pressure 1.2bar) to predict temperature drop over a membrane using generic ComThermo package with Sour Peng-Robinson model in the vapor phase (see Figure 2). The results showed that permeate temperature decreased to 13.6°C at a feed temperature and pressure 30°C and 30 bar, respectively. Thus, the water vapor may condense inside the membrane matrix and/or on the membrane surface, which can potentially form a water film and decrease the gas separation performance. A gas stream with a high CO$_2$ concentration transport through a membrane at high pressure may present a much significant temperature drop. Therefore, the feed line side should be super-heated to avoid water condensation inside the membrane and on the membrane surface as illustrated in Figure 3.
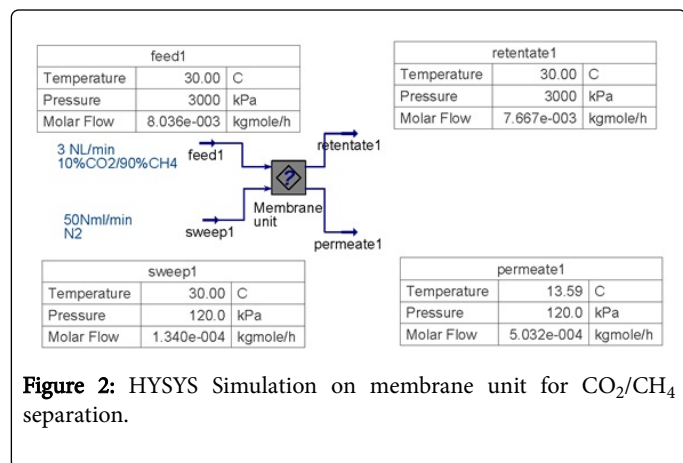

Figure 2: HYSYS Simulation on membrane unit for CO$_2$/CH$_4$ separation.

If the system was operated at 30°C, the feed stream should be pre-heated to >45°C so that the temperature inside membrane module is higher than the dew point even with the J-T effect as illustrated in Figure 3. A thermocouple was inserted into the module to measure the temperature inside the membrane module. The sensor was initially put under the ceramic support inside the module, but no temperature difference was detected as the ceramic support is too thick which could hinder the heat transfer. Thus, the temperature drop inside the membrane matrix does not immediately influence the temperature on the bottom of the support. Therefore, the sensor was then directly installed in the permeate side of the membrane to detect the exact permeate temperature. However, there is still no temperature difference found. It was suspected that membrane material has very high heat transfer coefficient, and thus difficult to detect the

temperature drop in a real process. Employing the computational fluid dynamics (CFD) modelling to simulate the temperature profile inside matrix should be conducted to further validate this experimental results in the future work.
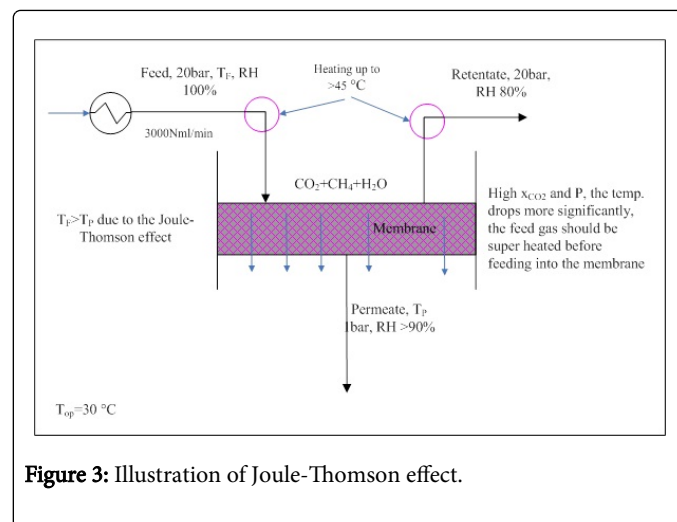

Figure 3: Illustration of Joule-Thomson effect.

Water vapor permeation

Deng et al. reported that membrane performance of the PVAm/PVA blend FSC membranes significantly depended on the relative humidity in the gas streams [21], and higher CO$_2$ permeance was found at a high relative humidity due to the enhanced contributions from facilitated transport mechanism where CO$_2$ reacts with the amino functional groups in the swelled (humidified) membranes. The influences of water vapor content (calculated from the relative humidity at a given pressure and temperature) on the membrane performance was reported in the previous work [11]. The lower absolute water vapor content decreases at higher feed pressure could cause the reduction on CO$_2$ permeance besides the membrane compaction and carrier saturation. Water permeation of the prepared membrane (110 cm^2) was tested at 30°C and different pressures (sweep gas 50 Nml/min at 1.2bar), and the results are shown in Table 2 and Figure 4. It can be found that both CO$_2$ flux and water flux increase with the increase of feed pressure. It was worth noting that the water vapor permeance was found to be much higher compared to the CO$_2$ permeance, especially at high pressure. Therefore, high water vapor content in a gas stream should be achieved to avoid the drying of the membranes at high stage cut operation-this will be the challenges related to process design and operation.

Feed pressure	Flux, L/(m^2·h)		Permeance, m^3(STP) /(m^2·h·bar)		Selectivity	
	CO$_2$	H$_2$O	CO$_2$	H$_2$O*	CO$_2$/CH$_4$	H$_2$O/CO$_2$

1.5	26.3	1.28	0.544	0.53	59.7	1
2	34.1	1.78	0.495	0.74	55.1	1.5
3	51	2.6	0.432	1	48.4	2.3
4	67	3.7	0.339	1.54	44.6	3.9
5	82.2	4.43	0.335	1.85	42.2	5.2
6	96.4	5.48	0.334	2.29	40.4	6.9
8	122.7	6.85	0.289	2.92	37.8	10.1
10	147.4	8.39	0.257	3.52	36.1	13.7
15	198.7	11.46	0.212	4.36	32.2	20.6

*H_2O permeance is calculated based on water flux and water vapor pressure difference between the feed and permeate sides.

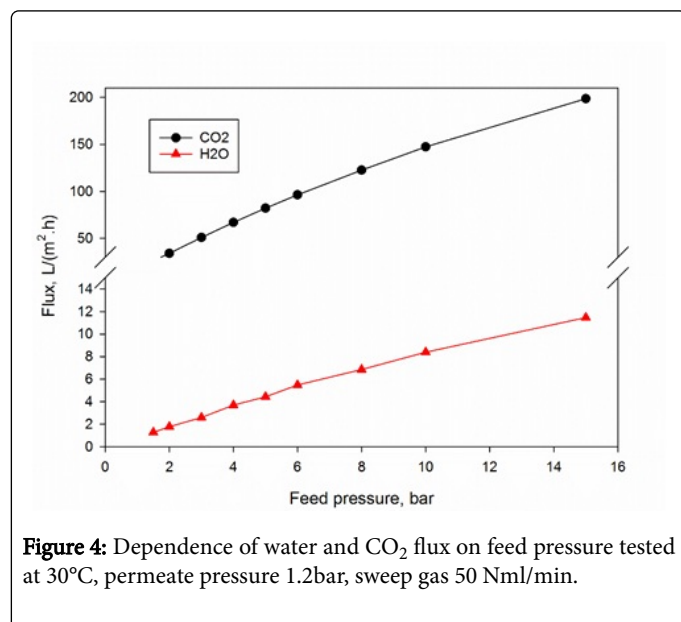**Table 2:** Membrane separation performance tested at 30°C.

Figure 4: Dependence of water and CO_2 flux on feed pressure tested at 30°C, permeate pressure 1.2bar, sweep gas 50 Nml/min.

Two-stage membrane system

The high pressure bench-scale module involves three sheets that can be operated individually, or in parallel, series and cascade configurations. Testing with different membrane areas from a single sheet (110 cm^2) to the whole module (330 cm^2) at 10 bar and 30°C was reported by He et al. [11]. Both CO_2 permeance and CO_2/CH_4 selectivity decrease with the increase of membrane area, and a better performance was reported in the vacuum operation compared to the sweep gas operation. In order to test the actual membrane separation capability for CO_2 removal from natural gas, a two-stage membrane system related to the retentate was designed (see Figure 5) and tested at

30°C and 10bar with different feed flow rates (a synthetic gas mixture: 50% CO_2-50% CH_4) without sweep gas. The CH_4 purity was improved from 50% to 70% at feed flow of 300-500 Nml/min as shown in Table 3. Further purification using extra stages is usually required to achieve the separation requirement of CH_4 purity >96%. Moreover, the methane loss was found relatively high, recycling of the first stage permeate is needed to meet the requirement of low methane loss (i.e. <2%). The experimental results provided the input for process design on a full-scale natural gas sweetening plant using membrane technology.
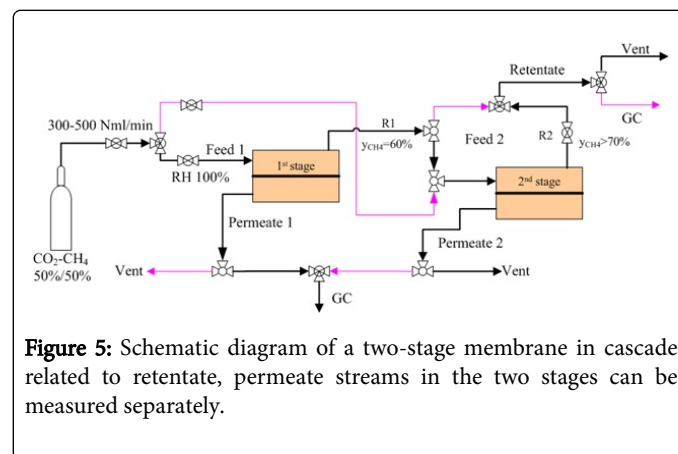

Figure 5: Schematic diagram of a two-stage membrane in cascade related to retentate, permeate streams in the two stages can be measured separately.

Conclusions

The high performance nanocomposite membranes were prepared for CO_2/CH_4 separation at high pressure. The high CO_2/CH_4 selectivity >30 was tested out at the feed pressure up to 30bar with acceptable CO_2 permeance. This high separation performance attributes to the combination of the Fickian diffusion and facilitated transport contribution from the developed membranes. However, the facilitated transport contribution is significantly dependent on the available carrier amount and water vapor content. Thus, the membrane performance was still found to decrease with the increase of feed pressure due to the lower water vapor content in the gas stream. Moreover, the water permeance was quite higher, especially more than one order of the CO_2 permeance at high pressure. Thus, how to maintain high water vapor content at high pressure operation is crucial, and will be a challenge to engineering design. The membrane materials were found to have high heat transfer coefficient and the Joule-Thomson effect has negligible influence on temperature drop inside membrane module. The testing results from the two-stage cascade membrane system with bench-scale modules indicated that CH_4 purity was improved from 50% to 70%, and the membrane performance in the second stage was better due to a lower feed CO_2 concentration. The experimental results indicated that multi-stage membrane system related to the retentate is need to achieve high CH_4 purity in the sweet natural gas when processing a high CO_2 content (e.g. 50%) sour natural gas, which could be used to guide the process design in commercial applications.

Feed flow, Nml/min	1st stage			2nd Stage			Total CH$_4$ loss, %
	PCO$_2$, Nm^3/(m^2·h·bar)	SCO$_2$/CH$_4$	Retentate CH$_4$ purity, %	PCO$_2$, Nm^3/(m^2·h·bar)	SCO$_2$/CH$_4$	Retentate CH$_4$ purity, %	

| 500 | 1.17E-01 | 27.3 | 58.8 | 0.145 | 32.3 | 70.4 | 3.8 |
| 300 | 8.54E-02 | 30.8 | 60.8 | 0.00958 | 35.2 | 73.4 | 4.1 |

Table 3: Separation performance of a two-stage cascade membrane unit.

Acknowledgements

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