Three Stage Membrane Process for CO_2 Capture from Natural Gas

Arshad Hussain

***Abstract*— This work is focused on a techno-economic analysis of a three stage membrane separation system for CO_2 capture from natural gas (without using any sweep gas or vacuum on the permeate side). The membrane used for CO_2 removal from natural gas is made of a thin PVAm (polyvinyl amine) and PVA (polyvinyl alcohol) blended membrane layer on a polysulfone support. The successful experimental results depicted that these fixed site carrier membranes can play a promising role in CO_2 capture from major industrial sectors like natural gas processing. Therefore, a viable process design associated with realistic CO_2 capture cost is inevitable for large scale applications. Simulation analysis is based on two cases describing two different natural gas (feed) flow rates and compositions. Analysis shows that it is possible to attain 90% CO_2 recovery and 90% purity at considerably lower gas processing cost, especially for Case A. Natural gas in Case B contains lower concentration of CO_2 hence 90% recovery is not feasible in this case. However, for 90% CO_2 purity and 75% recovery, it is feasible to employ this process at lower gas processing cost. The gas processing cost does not include any cost of feed pre-treatment such as removal of higher hydrocarbon and moisture and the recompression of permeate (containing 90% CO_2) up to desired CO_2 pipeline pressure.**

***Index Terms*— CO_2 capture, polymer membranes, techno-economic analysis, gas permeation**

I. Introduction

MEMBRANE based CO_2 capture processes offer a great potential for CO_2 capture, despite few limitations in terms of their sensitivity towards high temperature/pressure and severe process conditions. But membrane processes offer the benefit of their low capital investment, small footprints, ease of scale-up and low energy requirement. Process design and technical ease related to the process operation, along with CO_2 capture cost is a decisive factor while selecting the suitable capture technology.

This work can be considered as a contribution in strengthening the belief in CO_2/CH_4 membrane separation system capable to meet natural gas pipeline specifications (2 mol%) at significant lower methane loss compared to other studies [1-3]. A novel Fixed-Site-Carrier (FSC) membrane, a PVAm/PVA blend membrane, has been used in this study. In this blend membrane, PVAm has a high density of fixed amino groups which act as CO_2 transport carriers. The reversible reaction of CO_2 with amino carriers in PVAm facilitates the CO_2 transport and enhances the CO_2 permeability and CO_2/CH_4 selectivity [4-5]. This ultrathin PVAm/PVA blend layer (0.3 μm) supported on a polysulfone membrane has been evaluated and the experimental results revealed its suitability for CO_2/CH_4 separations. The selectivity up to 45 and the permeance up to 0.3 m^3 (STP)/m^2.bar.h at 2 bar has been recorded. However, in this analysis a selectivity of 40 and permeance 0.1 m^3 (STP)/m^2.bar.h has been used. The technical viability of membrane based CO_2 capture process has been investigated by using a three stage membrane process to meet natural gas pipeline requirement (2% CO_2) and confine the methane loss in permeate below 2%. The influence of CO_2 composition in feed (natural gas) and feed pressure on methane loss, membrane area, energy required and gas processing cost has been investigated.

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II. Principle of Gas Separation by Membranes

The principle of membrane gas separation depends on the membrane material, process conditions and the gas components in the mixture. The governing flux equation for gas permeation (eq. 1) is based on Fick's law where the driving force is the difference in partial pressures over the membrane. The flux, J (m^3 (STP)/m^2h), is expressed as,

$$\frac{q_{p,i}}{A_m} = \frac{q_p y_{p,i}}{A_m} = J_i = \frac{P_i}{l}\left(p_h x_i - p_l y_i\right) \quad (1)$$

where q_p is the volumetric flow rate of the permeating gas (i) (m^3 (STP)/h), P_i is the permeability of gas component i (m^3(STP)m/(m^2.h.bar)), l is the thickness of the membrane (m), p_h and p_l are pressure on the feed and permeate sides (bar), x_i and y_i are the fractions of component i on the feed and permeate sides, respectively, and A_m (m^2) is required membrane permeation area. The general definition of permeability (P) of gases through membrane is defined as product of diffusion, D (m^2/s) and solubility, S (m^3(STP)/m^3.bar) coefficients for gas in the membrane material.

$$P = D.S \quad (2)$$

$$\alpha = \frac{P_i}{P_j} \quad (3)$$

$$R = \theta.y_i / x_i \quad (4)$$

The intrinsic membrane selectivity "α" is estimated by ratio of the pure gas permeabilities (P_i , P_j),

III. CO_2 Capture by a Membrane Separation Process

A sketch of membrane separation process is depicted in

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Fig. 1. Apart from feed composition and temperature, pressure ratio (ψ), between the upstream (p_h) and downstream (p_l) pressure over membrane is an important process variable when using polymeric membranes. Recovery of desired component (in this work $i = CO_2$) by a membrane separation process is calculated by eq. 4.

Where y_i and x_i are the mole fractions of CO_2 in permeate and feed and stage cut $\theta = Q_p/Q_f$ being the ratio of permeate flow rate to the feed flow rate.

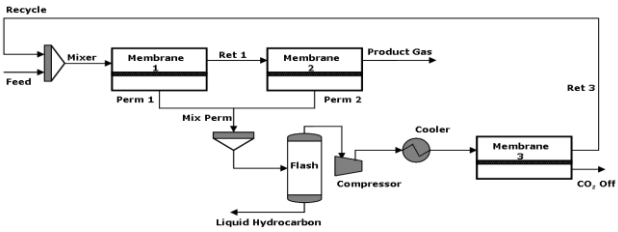

Fig. 1. Simplified two stage membrane separation process (without sweep flow)

IV. Process Conditions and Simulation Method

The CO_2 concentration in natural gas can vary from 5-40% depending on the source [6], methane always being the major component. Natural gas also contains significant amounts of ethane, some propane, butane and 1–3% of other higher hydrocarbons [7]. In contrast to many other studies, where a binary CO_2/CH_4 [8-9] or tertiary $CO_2/CH_4/H_2S$ mixture is considered, two real natural (classified as Case A and Case B). The gas compositions and process conditions for both natural gas mixtures are given in Table I & II. However, the nominal concentrations of H_2S, NO_x and ash have been ignored in the gas mixture. The feed (natural) gas flow rates (in both cases) are relatively smaller compared to existing membrane systems (100-700 MMSCFD) for natural gas sweetening [10-11]. It is worth mentioning here that membrane systems for natural gas sweetening are typically favoured for small size applications (less than 5 MMSCFD) and remote applications. This supports the idea of employing membrane system for natural gas sweetening in this analysis. Membrane and amine absorption system become competitive for a size of 5-50 MMSCFD [11-12].

The heat integrated structure of simulated process is shown in the Fig. 2a. The feed gas initially at 90 bar and 50°C is mixed with retentate from stage 3 (Ret3) and then fed to the first membrane stage. First membrane stage enables 50% trimming of CO_2 and thus remaining CO_2 containing stream (Ret1) is fed to stage 2. The retentate from stage 2 (Ret 2) contains less than 2% CO_2 and is sent to pipeline as product gas at 89 bar. Pressure on the permeate side is varied to see its influence on the required membrane area and energy. The temperature of permeate from stage 1 and stage 2 decreases due to high pressure drop across the membrane (depending on the applied pressure ratio across the membrane) and fair amount of higher hydrocarbons in the permeate liquefy. Therefore, permeate from stage 1 and stage 2 are mixed in a mixer and fed to a flash vessel where higher hydrocarbons are collected at the bottom and the vapour product enriched with CO_2, methane and some amount of other hydrocarbons is compressed, cooled and then fed to stage 3 for final enrichment of CO_2 in permeate from stage 3. The retentate from stage 3 is compressed to 90 bars and recycled back to stage 1 as feed. Permeate from stage 3 contains 90% CO_2 which can be stored for further processing and storage. Heat exchangers are used to economize the energy consumption. Cooling water is circulated in the heat exchangers to lower the temperature of compressed gas streams. It is obvious from Case B data (Table I) that natural gas stream contains only methane and CO_2, however saturated with water like Case A. Hence the process flow diagram for Case B is similar to Case A, except without a flash vessel.

TABLE I
Gas Compositions and Process Conditions for Case A and Case B

Case A		Case B	
Feed flow rate, MMSCFD =	0.35	Feed flow rate, MMSCFD =	2.48
Feed pressure, bar =	90	Feed pressure, bar =	115
Feed temperature, °C =	60	Feed temperature, °C =	8
Feed composition	mol %	Feed composition	mol %
CO_2 =	9.5	CO_2 =	2.9
CH_4 =	72.4	CH_4 =	97.1
C_1-C_6 =	18	H_2O	Saturated
H_2O	Saturated		

Gas Processing Cost (GPC) calculations are based on the values assigned to the selected process/economic parameters which might differ considerably for different evaluators. In this analysis, GPC defined as the cost per MSCF (1000 Standard Cubic Foot) of product, is based on three cost components; Total Plant Investment cost (TPI), Variable Operating & Maintenance cost (VOM) and the methane lost in permeate (CH_4Loss). Table II shows the values of economic and process parameters along with calculation methodology.

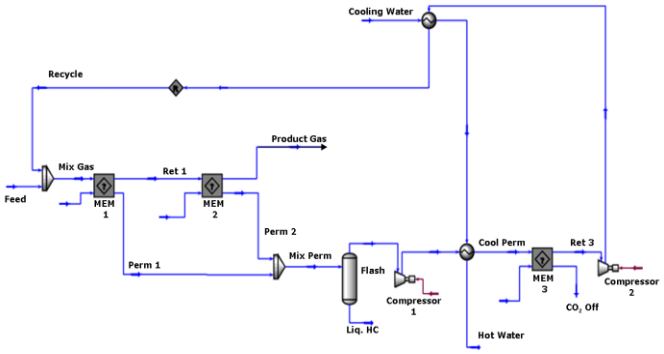

Fig. 2a. Hysys process flow diagram for 3-stage (Case A) membrane integrated natural gas sweetening without using any sweep or vacuum on the permeate side.

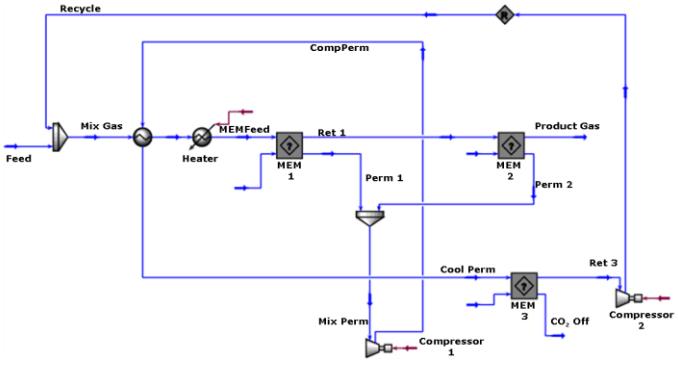

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Fig. 2a. Hysys process flow diagram for 3-stage (Case B) membrane integrated natural gas sweetening without using any sweep or vacuum on the permeate side.

The gas processing cost does not include the cost of permeate (~ 90% CO_2) re-compression to desired pipeline pressure. It is worth mentioning here that gas processing cost can differ substantially by changing the process parameters given in Table II. The membrane area and the required energy impart substantial influence on the gas processing cost which can be seen in the results presented in subsequent paragraphs for different process conditions.

V. Results and Discussion

This simulation analysis is started with the influence of permeate side pressure on the CO_2 purity and recovery for fixed membrane area. It can be seen in Figure 3 that by increasing the permeate side pressure, both CO_2 purity and recovery decreases, however, later decreases significantly. This figure reveals that for the specified area, CO_2 recovery and purity can be attained more than 80% only if the pressure on the permeate side is kept below 10 bar. Figure 3 shows that by increasing permeate side pressure both specific required energy and Gas Processing Cost (GPC) decrease. In fact cost of required energy has considerable impact on the GPC. Hence, less energy consumption results in less Gas Processing Cost. Figure 4 (which is a counterpart of Figure 3) shows that demand for high CO_2 purity and recovery results in higher energy consumption (due to lower permeate side pressure) which yields the higher gas processing cost in turn.

If it is desired to achieve 90% CO_2 purity and recovery then as evident from Figure 3, it is only possible by either decreasing the pressure on permeate side or increasing the membrane area. Figures 5 & 6 show the required membrane area, required energy and GPC plotted against pressure on the permeate side (permeate pressure only in first two stages as the pressure on stage 3 is kept 1 bar constant for all cases) respectively. It can be concluded from Figures 5&6 that to achieve 90% purity and recovery, more membrane area and energy is required as the pressure on permeate side increases. The gas processing cost (GPC) is strongly influenced by the required membrane area and required energy. Therefore, a cumulative influence of membrane area and energy is obvious in terms of rise in gas processing cost (Figure 6).

Similar analysis (like case A) has been carried out for case B by keeping the total membrane area constant (350 m^2). Figure 7 shows that for this area, it is not possible to achieve 80% recovery even if the permeate side pressure is 5 bar (unlike Figure 3). It is evident from figure 8 that more specific energy is required for Case B. In contrary to Case A, natural gas in Case B has less CO_2 and higher feed flow rate (7 times higher than case A), which ultimately requires more membrane area. Though required specific energy has a strong influence on the gas processing cost but in Figure 8, this influence is significantly dampened due to higher feed flow rates and lower CO_2 recovery, *however as expected gas processing cost decreases as the permeate side pressure increases.* For case B, it has been further investigated that

TABLE II
Economic and Process parameters for Gas Processing Cost (GPC)

Total Plant Investments (TPI)	
Total Membrane Module Cost (MC)	
Installed Compressor Cost (CC)	$ 8650 X (HP/η)0.82
Fixed Cost (FC)	MC+CC
Base Plant Cost (BPC)	1.12 X FC
Project Contingency (PC)	0.2 X BPC
Total Facilities Investment (TFI)	BPC+PC
Start-up Cost (SC)	0.10 X VOM
Total Plant Investments (TPI)	TFI+SC
Annual Capital related Cost (CRC)	0.2 X TPI
Annual Variable Operating & Maintenance Cost (VOM)	
Contract & Material Maintenance Cost (CMC)	0.05 X TFI
Local Taxes & Insurances (LTI)	0.015 X TFI
Direct Labor Cost (DL)	$15/h
Labor Overhead Cost (LOC)	1.15 X DL
Membrane Replacement Cost (MRC)	$2.5/ft2 of membrane
Utility Cost (UC)	$0.07/kWh
Annual Variable Operating & Maintenance Cost (VOM)	CMC+LTI+DL+LOC+MRC+UC
Annual Cost of CH4 Loss in Permeate (CH4LS)	
Annual Natural Gas Lost (NGLS)	365 X OSF X (Qf X x_CH4_Qf) X (Qp X x_CH4_Qp)
Methane Loss (CH4LS)	NGLS X NHV X NWP
Gas Processing Cost ($/MSCF), GPC	(CRC+CH$LS+VOM)/[365 X OSF X Qf X (1-SCE) X 1000]
Other Assumptions	
Membrane Life (t)	4 years
Wellhead price of crude Natural Gas (NWP)	$4/MMBTU
Heating Value of Natural Gas (NHV)	1066.8 MMBTU/MMSCF
Stage Cut Equivalent (SCE)	Permeate flow rate (Qp)/Feed flow rate (Qf)
On Stream Factor (OSF)	96%
Compressor Efficiency (eta)	0.85

how membrane area, specific required energy and gas processing cost would change if CO_2 purity in permeate is kept constant (90%) and CO_2 recovery is varied from 50% to 75%. As expected, Figure 9 shows that more membrane area is required if CO_2 recovery is set 75%. Similarly, Figure 10 shows that for 75% recovery, less specific energy is required. Figure 11 shows the comparison of GPC for 50% and 75 recovery. As mentioned earlier, required membrane area and specific energy has strong influence on the gas processing cost. This combined influence of required membrane area and specific energy on gas processing cost (GPC) is replicated in Figure 11, showing that gas processing cost is bit higher if higher CO_2 recovery is desired.

Figure 6 shows that for case A, GPC is about 0.5 $/MSCF when permeate side pressure is set around 5 bar and methane

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loss in permeate is about 0.5%. From Figure 11 for case B, it can be seen that for permeate side pressure around 5 bar, GPC is about 0.14 $/MSCF and methane loss is about 0.25% for 75% recovery. These values are significantly lower than the results presented in [13]. It is worth mentioning here that feed flow rate taken in this analysis (Table 1) is far less than the flow rates taken in [13].

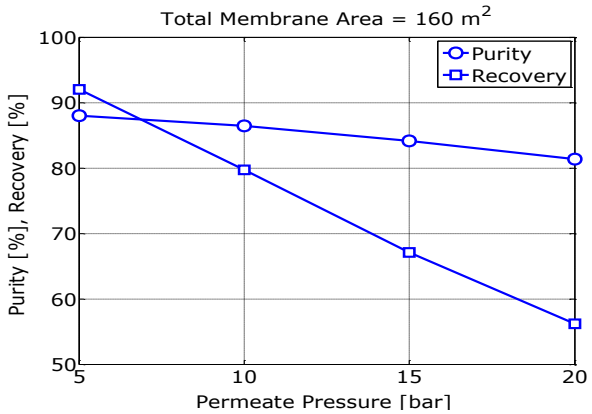

Fig. 3. CO_2 purity and recovery vs. permeate pressure (in first two stages) case A.

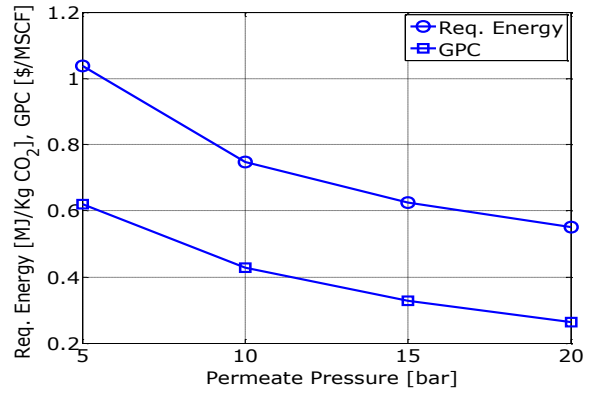

Fig. 4. Permeate side pressure vs. required energy and GPC (Gas Processing Cost).

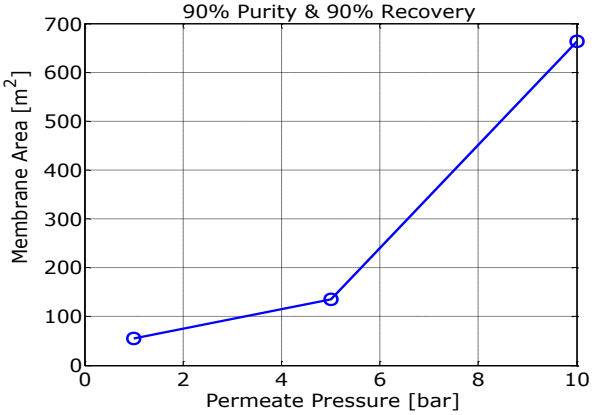

Fig. 5. Permeate side pressure vs. required membrane area to attain 90% purity & recovery.

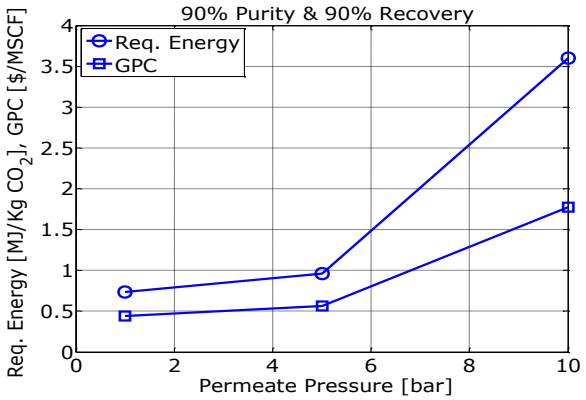

Fig. 6. Permeate side pressure vs. required energy and GPC to attain 90% purity & recovery.

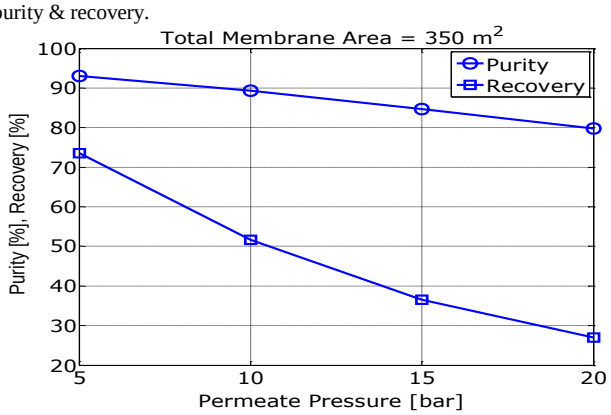

Fig. 7. CO_2 purity and recovery vs. permeate pressure (in first two stages) case B.

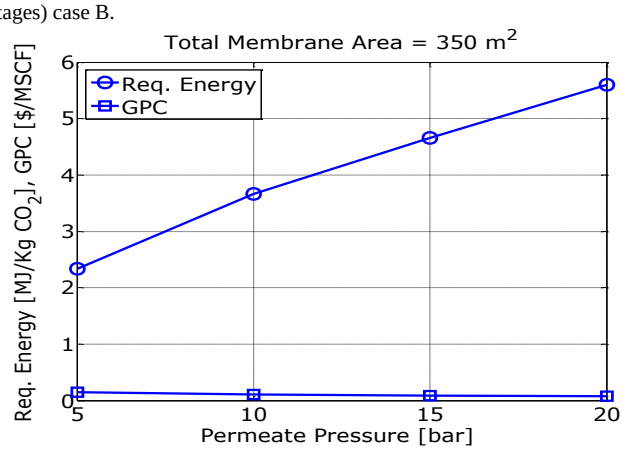

Fig. 8. Permeate side pressure vs. required energy and GPC for case B.

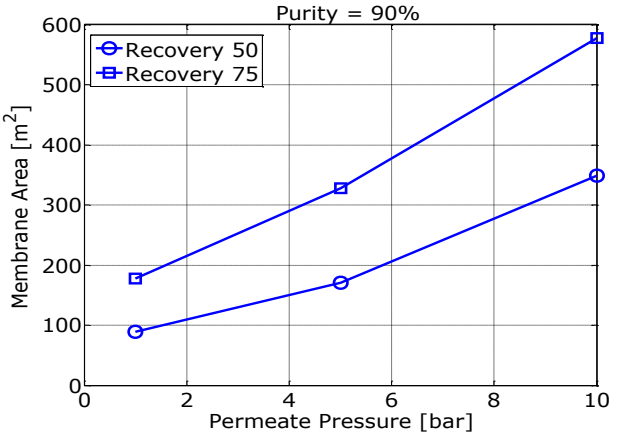

Fig. 9. Permeate side pressure vs. required membrane area for 50% & 75% recovery.

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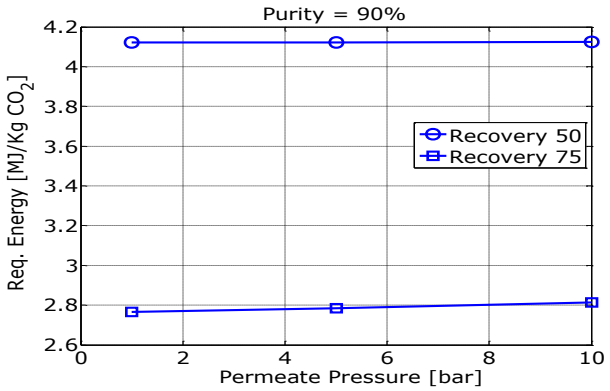

Fig. 10. Permeate side pressure vs. required energy for 50% and 75% recovery.

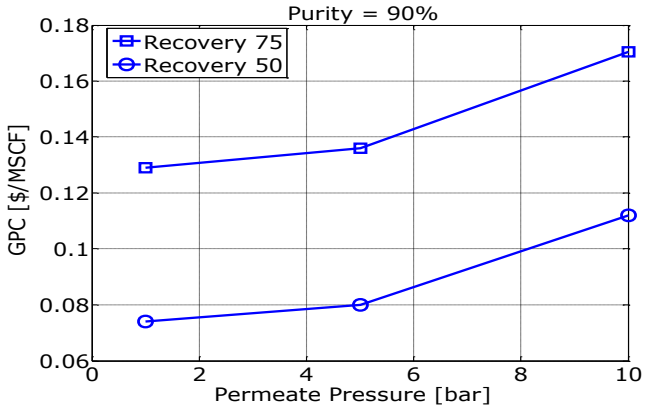

Fig.11. Permeate side pressure vs. GPC for 50% and 75% recovery.

VI. Conclusions

A three stage membrane separation system for CO_2 capture from natural gas (without using any sweep gas or vacuum on the permeate side) is viable. Simulation analysis is based on two cases describing two different natural gas (feed) flow rates and compositions. Analysis shows that it is possible to attain 90% CO_2 recovery and 90% purity at considerably lower gas processing cost, especially for Case A (higher CO_2). Natural gas in Case B (lower CO_2) contains lower concentration of CO_2 hence 90% recovery is not feasible in this case. However, for 90% CO_2 purity and 75% recovery, it is feasible to employ this process at lower gas processing cost. The gas processing cost does not include any cost of feed pre-treatment such as removal of higher hydrocarbon and moisture and the recompression of permeate (containing 90% CO_2) up to desired CO_2 pipeline pressure.

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