

Optimization of membrane unit for removing carbon dioxide from natural gas

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Abstract

The aim of this paper is to find out the optimum configuration and design variables for the asymmetric membrane-based separation of carbon dioxide from natural gas for meeting the pipeline specification of 2% carbon dioxide. For this purpose, optimization of gas processing cost of the membrane unit having up to three stages is performed based on a fundamental model of the unit. It shows that there is no unique configuration that is always optimum irrespective of the values of carbon dioxide concentration and natural gas price. However, within certain ranges of the carbon dioxide concentration and the natural gas price, the optimum configuration may be unique and the minimum gas processing cost can be achieved by adjusting only the number of modules in each stage and the compressor power. In most cases, there is no significant cost difference between the two and three staged optimum configurations and the choice of a configuration may depend on engineering assessment.
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1. Introduction

Removal of carbon dioxide increases the calorific value and transportability of the natural gas. Carbon dioxide content in the natural gas obtained from gas or oil well can vary from 4 to 50%. On the other hand, purged gas from a gas-reinjected EOR (enhanced oil recovery) well can contain as much as 90% carbon dioxide. Before a natural gas rich in carbon dioxide can be transported, it must be pre-processed so as to meet the typical specification of 2–5% carbon dioxide. To meet such a specification, the natural gas is most commonly treated with an aqueous alkanolamine solution in absorption columns. The major advantages of the amine treatment are that it is a widely commercialized technology in which the hydrocarbon loss is almost negligible. However, the capital and operating cost shoots up very rapidly as the concentration of carbon dioxide in feed gas increases. An alternate technology for separation of carbon dioxide from the natural gas is based on the membrane.

Membrane consists of a polymer film that allows some molecules to permeate faster than other molecules. Molecules

with higher diffusivity (or, lower size) and higher solubility in the film can permeate faster. Thus, carbon dioxide, hydrogen sulfide and water vapor can permeate faster than hydrocarbon molecules through cellulose acetate and many other similar polymeric membranes. To achieve high gas separation efficiency, the membrane is cast in an asymmetric form with very thin membrane film supported on a thick and porous polymeric layer on one side. Furthermore, membrane modules are fabricated in a very compact form as hollow fibers or spirally wound sheet. The residual feed stream from such a module is called the product or retentate, while the stream built up through permeation is called the permeate. For high-capacity applications, a membrane process unit can consist of multiple stages, each stage being constituted of one or more parallel modules and with internal recycling between stages. Apart from the modules, a membrane unit also requires pre-filter and pre-heater to prevent harmful deposit of dust, droplets and condensate on the membrane surface.

The membrane separation is normally associated with lower capital and operating costs than the amine treatment unit unless the area requirement is too high. With too large membrane area, a major concern is the loss of hydrocarbon to the permeate side via slow permeation. It is known that such a loss can be minimized by compressing the permeate and then recovering the hydrocarbons in a separate stage. However, this

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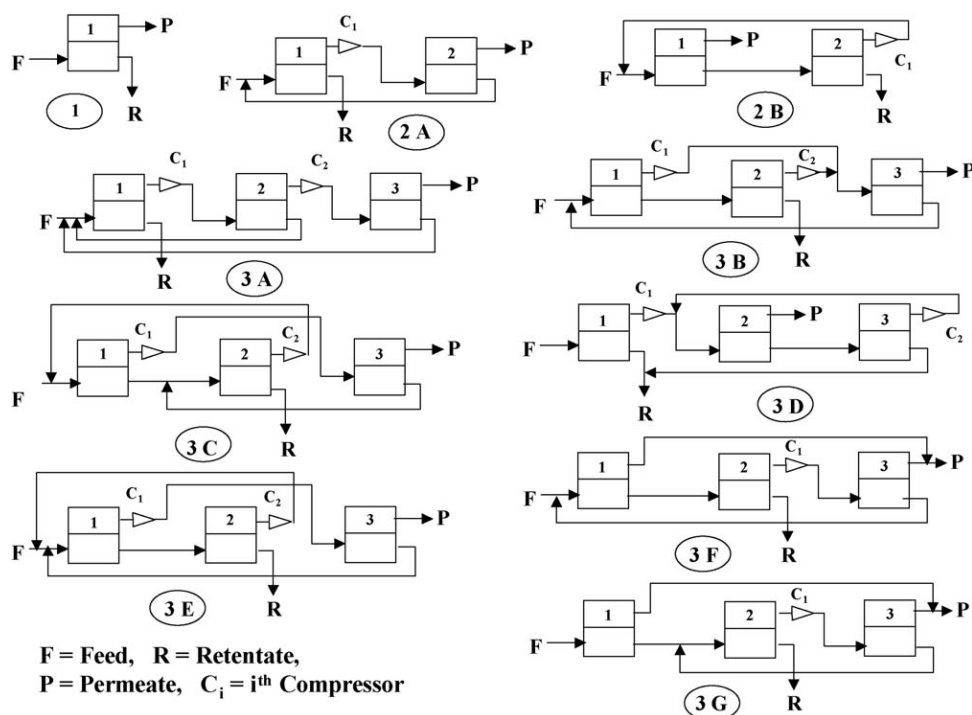


Fig. 1. Some probable optimum configurations of a membrane unit.

increases capital and operating costs of the membrane unit. Many studies have been performed in order to minimize these costs and make the membrane technology commercially viable. It has been suggested [1–3] that a feed gas with high carbon dioxide partial pressure (say, above 15 atm) can be treated in a hybrid unit. A pre-membrane unit will remove bulk of the carbon dioxide taking advantage of the high driving force for permeation. The product stream from the membrane unit can then be post-treated in an amine unit to meet the pipeline specifications. As described below, many reviews and studies have been reported on the optimal design of membrane-only unit for various gas separation applications including removal of carbon dioxide from the natural gas.

An excellent review on economics of applications of gas separation membranes has been provided by Spillman [3]. The author has shown the two-stage and three-stage configurations (e.g., configurations 2A and 3G in Fig. 1) that are more economical than the single stage configuration for carbon dioxide removal from natural gas. For applications in which the permeate stream is to be recompressed for further use (e.g., EOR application and hydrogen recovery from purge gas), the author has described how permeate can be generated at different pressures in a two-stage series configuration in order to minimize the permeate recompression cost. Configurations 2A and 3G was considered for treatment of natural gas containing 8–11% carbon dioxide [4] and EOR application for well-head gas containing 30–50% carbon dioxide [5], respectively.

Many authors have described rigorous optimization-based approach to select the optimal process configuration and other operating conditions for membrane units. Bhide and Stern [6] identified configuration 3G as the optimum choice for the feed

carbon dioxide concentration range 5–40% when natural gas price is 75 USD/K N m³ (~2 USD/MMBTU) and asymmetric cellulose acetate membrane is used. Qi and Henson [7] also identified configuration 3G as the best choice for the feed carbon dioxide concentration range 5–95% and the natural gas price range 30–100 USD/K N m³ when a membrane similar to asymmetric cellulose acetate is used. For natural gas price range 10–30 USD/K N m³, a different two-stage configuration (e.g., configuration 2B in Fig. 1) was found to be more economical. On the other hand, the authors identified another different three-stage configuration (e.g., configuration 3E in Fig. 1) to be most economical choice for the feed carbon dioxide concentration range 0–50% when the permeate carbon dioxide concentration is restricted above 95%, in addition to the usual product concentration constraint of 2% carbon dioxide. Hao et al. [8] compared five different non-recycle configurations with two different types of asymmetric membranes for reducing carbon dioxide from 0–40% to 2% and hydrogen sulfide concentrations from 0–10% to 4 ppmv. Assuming the same natural gas price as in [6], they found the optimum configuration to be a CO₂-selective membrane in the first stage in series with a H₂S-selective membranes in the second stage.

In some gas processing applications, recovery of certain components through permeate stream is the most desired objective. For these applications, different innovative design configurations like CMC (continuous membrane column) and CRC (counter-current recycle cascade) have been proposed [9–10]. However, these configurations are not economical in natural gas treatment, where the processing objective is to produce natural gas with low concentrations of pollutants as the product stream [11]. Hence, it is beyond the scope of this paper to elaborate

and compare these configurations with the multi-stage configurations discussed above. The purpose of the present study to find out the optimum configuration and design variables for the membrane-based separation of carbon dioxide from natural gas for meeting the pipeline specification of 2% carbon dioxide. For simplicity, the economic objective used here does not account for the removal of hydrogen sulfide (as in sour natural gases), recompression of permeate (as in EOR application), any constraint on the permeate concentration and use of membrane other than the asymmetric cellulose acetate membrane. Under these conditions and at natural gas price >30 USD/K N m³, some of the earlier studies [6,7] have clearly singled out configuration 3G as the best for almost the entire range of carbon dioxide concentration in the natural gas. The present study intends to examine this further by using a rigorous process model, a comprehensive economic analysis model and the current values of the natural gas price as well as other cost parameters. The findings of this study is expected to be valuable in view of the increasing number of membrane-based natural gas processing plants that are due to be built worldwide. Section 2 describes the model used, optimization procedure, the basis and the limitations of the study performed. Important results of the study are presented and discussed in the next two sections.

2. The model, optimization, basis and limitations of the study

The rigorous model used in this study is described in details in Appendix A. Optimization is performed to find the best configuration and design variables so that the GPC (gas processing cost) is minimum subject to the satisfaction of product specification (e.g., 2% carbon dioxide in the product gas). GPC is a very convenient economic parameter for evaluating the design of membrane unit since this term includes not only the capital investment cost (i.e., costs of membrane and compressor) and operating cost (i.e., costs of running compressor, replacing membrane and labor) of the unit but also the loss incurred due to the permeation of hydrocarbons. It may be noted that the choice of economic evaluation parameters is user specific. In other words, one may like to compare various variables depending on his perspective. Thus, if capital cost is a major concern, one may like to compare membrane area and/or compression power. On the other hand, if energy cost is very high, one may like to compare the values of compression energy. Since this work is intended to yield generalized results on economic optimization of membrane-based carbon dioxide removal from natural gas, GPC has been found to be the most convenient economic parameter for evaluation. The GPC calculations performed in this study are described in details in Appendix B.

Optimization variables are number of stages, number of modules in each stage, permeate exit pressure of each stage, compression ratio of permeate from each stage and network variables, like, the division of feed flow into various stages and the divisions of retentate/permeate flows from each stage to other stages as well as to unit's outlets. In order to get the best starting point (or, equivalently the best unit configuration) that will facilitate the use of rigorous optimization, extensive initial

Table 1
Base condition for optimization

Membrane module specification	0.2032 m diameter (1 m × 18.5 m × 0.008 m channels) spirally wound cellulose acetate membrane
Feed flow	35 K N m ³ /h
Feed inlet pressure and temperature	50 kg/cm ² and 25 °C
Feed components	CO ₂ and CH ₄
Permeate exit pressure	1.5 kg/cm ²
CH ₄ permeance	4.5E−06 cm ³ (STP) cm ^{−2} s ^{−1} cmHg ^{−1}
CO ₂ /CH ₄ selectivity	20
Cost of CH ₄ in natural gas	226 USD/K N m ³

search is done. Given the number of stages of the unit, the initial search will evaluate the value of optimization objective for all feasible unit configurations based on the discrete values of the optimization variables. Once the best configuration is identified, rigorous nonlinear optimization is performed to find the best design variables for the same configuration. This optimizer uses the well-known BFGS (Broyden–Fletcher–Goldfarb–Shanno) algorithm and varies the optimization variables so as to minimize an optimization objective that includes the scaled deviations of product concentrations from their upper limits apart from the scaled GPC:

$$f_{op} = \left(\frac{\text{GPC}}{0.1 \sum_{i=1}^{n_c} x_{f_{ex_i}} C_i} \right) \left[1 + w_c \sum_{i=1}^{n_c} \left(\frac{x_{f_{ex_i}} - x_{f_{ex_{lim}}}}{x_{f_{ex_{lim}}}} \right)^2 \right] \quad (1)$$

where f_{op} is the optimization objective, GPC the gas processing cost per unit volume of product, C_i the cost of i th component per unit volume, $x_{f_{ex_i}}$ the mole fraction of i th product component, $x_{f_{ex_{lim}}}$ the upper limit of mole fraction of i th product component and w_c is the weight or relative importance of concentration deviation.

In the above, GPC per unit volume of product is scaled with respect to its expected minimum value that is assumed to be 10% of the product value per unit volume. On the other hand, the deviation in product concentration from upper limit is scaled by the same limit. When product concentration is above its upper limit, the weight of concentration deviation is set to a high value so that the same concentration can decrease to a feasible lower value. However, when the product concentration is below the upper limit, appropriate measures should be taken so that it does not decrease too much since a lower product concentration is synonymous to a higher membrane area (or, higher capital cost). In this case, therefore, the weight of concentration deviation is set to a low but non-zero value so that too much decrease in product concentration can be penalized also.

As an illustration, for a two-stage network with basic inputs as in Table 1 and 5 vol.% carbon dioxide in feed gas, three of the many feasible sets of optimization variables are tabulated in Table 2. The best configuration was found to be the set 3 in the same table since it corresponds to the lowest value of GPC. Rigorous optimization of the variables of set 3, using the objective

Table 2

Finding optimum set of variables for a two-stage network and 5 vol.% CO₂ in natural gas at the base condition

	Set of optimization variables			Optimum set
	Some feasible sets			
	1	2	3	
Fraction of feed going to stage 1	0	1	1	1
Product from going to stage 1	Exit	Exit	Exit	Exit
Product from going to stage 2	Exit	Stage 1 and exit	Stage 1	Stage 1
Permeate from going to stage 1	Exit	Stage 2	Stage 2	Stage 2
Stage 2 permeate from going to	Stage 1	Exit	Exit	Exit
Stage 1 permeate exit pressure (kg/cm ²)	1.5	1.5	1.5	1.79
Stage 2 permeate exit pressure (kg/cm ²)	1.5	1.5	1.5	1.5
Stage 1 permeate compression ratio	1	33.33	33.33	27.89
Stage 2 permeate compression ratio	33.33	1	1	1
Stage 1 number of modules	26	118	121	164
Stage 2 number of modules	114	25	19	10
GPC (USD/K N m ³ product)	7	7	6	5

function shown in Eq. (1) above, resulted in the optimum set as shown in the last column of same table.

The basic process condition of the study is shown in Table 1. The feed and permeate conditions chosen are the typical ones for a medium sized plant. As mentioned earlier, only asymmetric CA (cellulose acetate)-based commercial membrane modules will be used in this study. These spirally wound modules have a life span of 4 years, a diameter of 0.2032 m (8 in.), feed and permeate channel lengths of 1.0 and 18.5 m, respectively (i.e., membrane area 37 m²) and channel thickness of 0.008 m. The characteristics of the membrane are assumed to be same as described in Lee et al. [12] and reasonable values of friction factors for pressure drop calculations were also assumed. Current cost of hydrocarbon (or, methane) in natural gas as shown in Table 1 was obtained from the energy related websites [13–14].

The optimization results of a membrane unit depend on the feed conditions, membrane properties and economic parameters. Optimized configuration may be substantially different for different feed composition. The cost parameters that go into the dominant terms of the gas processing cost can also significantly influence the choice of unit configuration. Change in feed flow rate, feed pressure and membrane characteristics also have some influence in the choice of optimum unit configuration. The objective of the present study is limited to establishing the optimum configuration and operating condition of the membrane unit for various concentrations (5–90%) of carbon dioxide and expected fluctuations (113–339 USD/K N m³) in the natural gas price subject to the product specification of 2% carbon dioxide.

For simplicity, the single stage configuration considered in this study would be without any recycle of the product or permeate since earlier studies have not revealed any significant benefit of such recycling as compared to the optimum configuration [6–7]. Furthermore, as in earlier studies, more than three stages will not be considered here. The other limitations of the present study, as mentioned earlier, are non-consideration of hydrogen sulfide removal, recompression of outgoing permeate and constraint on the permeate concentration. Furthermore, as explained in Section 1, configurations like CMC and CRC need not be considered in the present study.

3. Results

As mentioned above, the single staged configuration considered here is a unique configuration with no internal recycle of retentate or permeate stream, while multiple staged configurations can have internal recycle streams with compression of the recycled permeates. Some of the multi-stage recycle configurations, including the ones examined in earlier studies [3,6,7], are illustrated in Fig. 1. It is emphasized here that the present study compares not only these configurations but also all other feasible multi-staged recycle configurations (up to three stages as mentioned above).

Single staged configuration is always associated with the highest gas processing cost due to the losses of hydrocarbons through the permeate exit. Configurations 2A and 3A result in the lowest losses of hydrocarbons through the permeate exit, though they require highest compressor powers, among the two and three staged configurations respectively. They are likely to be the optimum configuration at low concentrations of carbon dioxide since the amounts of permeate generated for being recycled and compressed would be small. On the other hand, configurations 2B and 3G require lowest compressor powers, though they result in the highest losses of hydrocarbons through the permeate exit, among the two and three staged configurations, respectively. They are likely to be the optimum configuration at high concentrations of carbon dioxide since the amounts of permeate generated for being recycled and compressed would be large. The hydrocarbon loss and requirement of compressor power for the other three-stage configurations (e.g., 3B to 3F) fall in between those of configurations 3A and 3G. They are likely to be the optimum configurations at intermediate concentrations of carbon dioxide. Hydrocarbon loss, compression power requirement and GPC of various configurations are quantitatively compared in Table 3 for the specific case of 20 vol.% carbon dioxide in natural gas under the base condition. Clearly, the single stage (configuration 1) incurs the highest hydrocarbon loss among all the configurations. Furthermore, as expected, configurations 2A and 3A result in the lowest loss of hydrocarbons through the permeate exit, though they require highest

Table 3

Comparison of the important outputs of various configurations for a specific case of 20 vol.% CO₂ in natural gas at the base condition

	Configuration									
	1	2A	2B	3A	3B	3C	3D	3E	3F	3G
CH ₄ loss (% of CH ₄ in feed)	16	2.2	4.7	0.8	2.1	1.5	2.2	2.0	2.7	3.5
Compression power (kW/0.746 or HP)	0	2509	2033	3932	2551	2784	2534	2661	2419	2204
GPC (USD/K N m ³ product)	44	16	21	19	17	16	17	17	17	18

Table 4

Optimum configuration and GPC (USD/K N m³ product) at the base condition

Natural gas (CH ₄) price (USD/K N m ³)			CO ₂ (vol.%)								
			5	10	15	20	30	40	50	60	90
226	One stage	GPC	17	31	38	44	53	60	67	74	113
		Configuration	2A	2A	2A	2A	2A	2A	2B	2B	2B
	Two stages	GPC	5	10	13	16	22	29	37	47	80
		Configuration	3A	3A	3B	3C	3D	3E	3F	3G	3G
	Three stages	GPC	5	10	13	16	22	29	35	43	77

compressor powers, among the two and three staged configurations, respectively. The opposite of this is true for configurations 2B and 3G.

At the base condition (see Table 1), rigorous optimization was performed for various concentrations of carbon dioxide. As explained earlier, Table 2 shows some of the feasible sets of optimization variables identified during initial search as well as the optimum set obtained for a particular case. The optimum configurations found along with the optimum GPC for single-stage, two-stage and three-stage configurations are shown in Table 4. While single-stage configuration is uneconomical over the entire range of carbon dioxide concentrations, GPC of both two-stage and three-stage optimum configurations are almost equal to each other with only marginal differences (≤ 4 USD/K N m³) in few places. This is visually depicted in Fig. 2. Optimization at the base condition also reveals the differences between the extreme configurations as explained in the last paragraph. Thus, while configurations 2A and 3A are the preferred ones at low carbon dioxide concentrations, configurations 2B and 3G are the optimum ones at high carbon dioxide concentrations, and con-

figurations 3B to 3F are best only at specific intermediate carbon dioxide concentrations.

Both Table 4 and Fig. 2 show that some configurations (e.g., 2A, 2B, 3A and 3G) remain optimum within certain ranges of carbon dioxide concentrations. However, for the same optimum configuration, optimum decision (or, optimization) variables would be different for different carbon dioxide concentration in the natural gas. This is illustrated in Table 5 for the two stage optimum configurations.

Large changes in some economic parameters, like, the costs of natural gas, membrane module, compressor and compression energy can affect the optimization results. Based on the available information [9,10], significant future changes can be expected in the unit cost of natural gas. Hence, it would be quite interesting to study the effect of the natural gas price on the unit optimization. To limit the scope of the study, two specific scenarios are considered, viz., the one in which the price decreases by half and the other in which the price doubles. The optimum configurations thus found along with the optimum GPC (in USD/K N m³ product) for the two extreme scenarios are shown in Table 6. As was observed for the base condition, the differences of optimum GPC between two-stage and three-stage configurations are insignificant (≤ 4 USD/K N m³) in most of the cases optimized. A higher difference of 6 USD/K N m³ is seen only for the case of natural gas price 339 USD/K N m³ when feed carbon dioxide concentration is 90%. For natural gas price higher than the base condition, it is more important to prevent loss of hydrocarbons through permeate. Hence, configurations 2A and 3A that minimize such loss remain optimum for a wider range of low carbon dioxide concentration. On the other hand, if natural gas price falls below the base condition, relative importance of compression power increases even at low carbon dioxide concentration. This is why configuration 2A remain optimum for a narrower range and configuration 3D replaces configuration 3A as the optimum configuration for the low carbon dioxide concentrations. Furthermore, configurations 2B and 3G that minimize

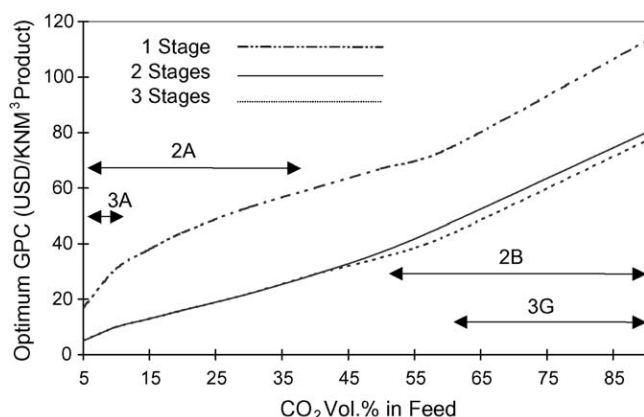


Fig. 2. GPC of optimum configurations at the base condition.

Table 5

Dependence of optimum decision variables of two stage configurations at the base condition on feed CO₂ concentration

	CO ₂ (vol.%)								
	5	10	15	20	30	40	50	60	90
Optimum configuration	2A	2A	2A	2A	2A	2A	2B	2B	2B
Optimum variables									
Stage 1 permeate exit pressure (kg/cm ²)	1.79	2.03	1.5	1.58	1.5	1.5	1.5	1.5	1.5
Stage 2 permeate exit pressure (kg/cm ²)	1.5	1.5	1.5	1.5	1.62	1.5	1.5	1.5	1.5
Stage 1 permeate compression ratio	27.9	24.6	30.0	31.7	33.3	33.3	1	1	1
Stage 2 permeate compression ratio	1	1	1	1	1	1	33.3	33.3	33.3
Stage 1 number of modules	164	234	253	260	288	285	125	75	109
Stage 2 number of modules	10	26	32	44	47	56	140	250	25
Compression power (kW/0.746 or HP)	1018	1551	2155	2509	3679	4437	1300	5285	233

Table 6

Optimum configuration and GPC (USD/KN m³ product) at lower and higher prices of natural gas

Natural gas (CH ₄), price (USD/KN m ³)			CO ₂ (vol.%)								
			5	10	15	20	30	40	50	60	90
113	Two stages	Configuration	2A	2A	2A	2A	2B	2B	2B	2B	2B
		GPC	5	8	11	14	18	22	25	28	50
	Three stages	Configuration	3D	3D	3D	3D	3G	3G	3G	3G	3G
		GPC	5	8	11	14	18	22	25	28	49
339	Two stages	Configuration	2A	2A	2A	2A	2A	2A	2A	2B	2B
		GPC	7	11	16	18	25	32	41	50	100
	Three stages	Configuration	3A	3A	3A	3E	3B	3C	3C	3G	3G
		GPC	5	10	14	18	25	32	42	54	106

compression power remain optimum for a wider range of high carbon dioxide concentration.

As in case of base condition, Table 6 shows that some configurations (e.g., 2A, 2B, 3A, 3D and 3G) remain optimum within certain ranges of carbon dioxide concentrations at a particular price of natural gas. Some configurations remain optimum not only within certain ranges of carbon dioxide concentrations but also for the entire range of natural gas price (113–339 USD/KN m³). For example, configurations 2A and 2B remain optimum within carbon dioxide vol.% ranges 5–20 and 60–90, respectively, irrespective of the natural gas price.

Results in Tables 4 and 6 also show that optimum GPC increases monotonically with increase in the carbon dioxide concentration in feed, or equivalently, with increase in the difference of carbon dioxide concentrations between feed and product. This is graphically presented in Fig. 3. The figure shows that there is

a more rapid increase in the optimum GPC beyond a difference of 50% CO₂ between feed and product.

4. Discussion

The present study clearly does not identify any specific configuration to be the best for the entire range of carbon dioxide concentrations and the expected range of natural gas price. This is contradictory to the earlier studies, which identified a particular configuration (e.g., configuration 3G) to be optimal for a wide range of carbon dioxide concentration. Such a difference has arisen due to the use of different process model, economic model, economic parameters (including the natural gas price) and optimization strategy in the present study.

It was found that some configurations remain optimum within certain ranges of the carbon dioxide concentration in the natural gas and the natural gas price. Within such ranges, minimum gas processing cost can be achieved by adjusting the decision variables (e.g., number of modules in each stage and the compressor power). This study was done for a particular natural gas flow (i.e., unit capacity). For any change in the unit capacity, all the results remain same except that there will be proportional changes in the membrane area in each stage and the power for each compressor system compressing a particular permeate stream. It is to be noted here that these capacity-related changes only imply that each stage or each compressor system needs to handle different flow rates at different capacities while achieving the same degree of separation or compression ratio, respectively.

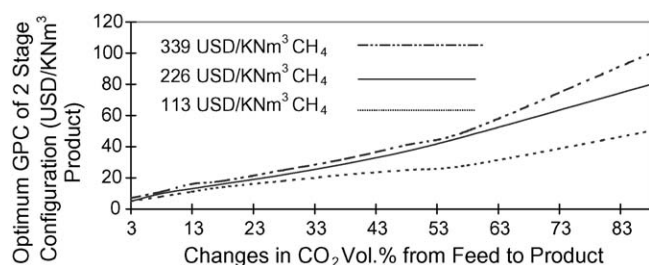


Fig. 3. Optimum GPC of two stage configurations vs. change in CO₂ concentration between feed and product.

For example, a doubling of unit capacity as compared to the base case would double the flow rate of all the external and internal streams. Hence, without redoing the optimization, one can say that there will be two-fold increases of the membrane area of each stage and the required power of each compressor system. Commercial membrane modules being small and compact, it is easy to change the total membrane area of any stage incrementally by adding or removing modules arranged in parallel. Using compressors in parallel, it is also possible to alter the compression power as per the capacity requirement. Hence, when a membrane unit is designed, enough flexibility can be added to the design in order to handle future changes in carbon dioxide concentration in the natural gas, natural gas price and unit capacity [4].

Optimization at different natural gas prices reveals that there is marginal difference ($\leq 4 \text{ USD/K N m}^3$) between the optimum GPC of two-stage and three-stage configurations in most of the cases optimized. Hence, in these cases, either of them might be used and the choice of a configuration is rather dependent on engineering assessment. A two-stage configuration has fewer internal recycles and compressors so that it is much simpler than a three-stage configuration. The second advantage of a two-stage optimum configuration is that it remains optimum for wider ranges of feed carbon dioxide concentration and natural gas price than any three-stage configuration. Hence, when carbon dioxide concentration or natural gas price changes, the unit can still be run optimally by changing only the number of modules in each stage and the number of compressor stages as predicted by the unit optimizer. However, in EOR applications, more than two stages with inter-stage dew point control unit are commonly used in order to prevent condensation of heavy hydrocarbons on the membrane [5].

5. Conclusion

In this paper, economic optimization of membrane-based process for separation of carbon dioxide from natural gas was studied over a wide range of feed carbon dioxide concentration and natural gas price. Feasible configurations of the two-stage and three-stage membrane units, including the ones reported in previous publications, were compared and the best configuration was optimized further to find the design variables. The results show that the optimum configuration is not a unique one but depends on the ranges of feed carbon dioxide concentration and natural gas price. It is discussed how one can incorporate enough flexibility to the design of a membrane unit in order to handle future changes in carbon dioxide concentration in the natural gas, natural gas price and unit capacity. Although the two-stage optimum configuration is found to have almost the same economy as the three-stage optimum configuration, some practical advantages of both the configurations are mentioned.

Appendix A. Process model

A simplified diagram of the flows around an asymmetric gas membrane is shown in Fig. A1.

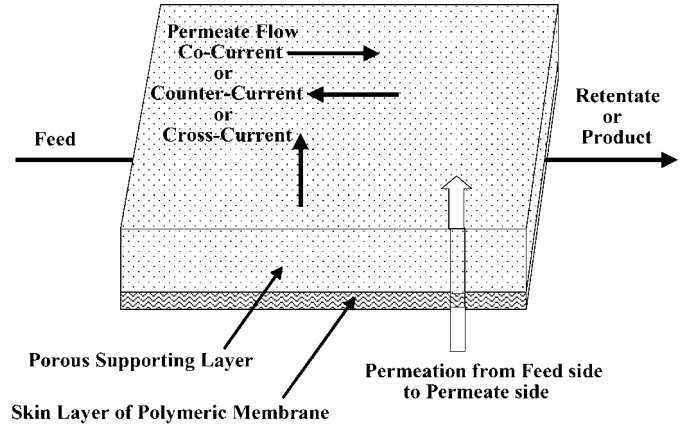


Fig. A1. Simplified diagram of flows around the membrane.

A.1. Mass balance

The component balance equations are adopted from Pan [15]. Thus:

- feed side:

$$0 = \text{in} - \text{out} - \text{permeation from feed to permeate side} \\ (\text{steady-state mole balance})$$

$$\text{or } 0 = -\frac{d(Fx_{fi})}{dx} - (A_x dx) \left(\frac{Q_i}{t} \right) (P_f x_{fi} - P_p x_{mi}) \\ \text{or } \frac{d(F_r x_{fi})}{dS} = \alpha_i (\beta x_{fi} - \gamma x_{mi}) \quad (\text{A1})$$

- membrane skin:

$$0 = \text{in} - \text{out} \quad (\text{steady-state mole balance})$$

$$\text{or } 0 = d(Fx_{fi}) - (dF)x_{mi} \quad \text{or } \frac{d(F_r x_{fi})}{dF_r} = x_{mi} \quad (\text{A2})$$

where F is the bulk molar flow rate on feed side, x_f the bulk mole fraction on feed side, x_m the mole fraction at the interface between the membrane and the porous layer on permeate side, x the distance from inlet in the feed flow direction, A_x the membrane area per unit distance (x), Q the permeability, t the thickness of membrane's skin layer, P_f the pressure on feed side, P_p the pressure on permeate side, $F_r = F/F_{en}$, F_{en} the value of F at entrance, S (dimensionless membrane area) the $A_x x P_{fen} (Q_r/t)/F_{en}$, P_{fen} the value of P_f at entrance, Q_r/t the reference value of permeance (any reasonable value can be chosen), $\alpha = (Q/t)/(Q_r/t)$ the selectivity, $\beta = P_f/P_{fen}$ and $\gamma = P_p/P_{fen}$.

Dividing Eq. (A1) by Eq. (A2) gives:

$$\frac{dF_r}{dS} \left(\frac{x_{mi}}{\alpha_i} \right) = -(\beta x_{fi} - \gamma x_{mi}) \quad (\text{A3})$$

Taking summation of Eq. (A3) for all components gives:

$$\frac{dF_r}{dS} = -\frac{\beta - \gamma}{x_{mav}} \quad (\text{A4})$$

where

$$x_{m_{av}} = \sum_{i=1}^{n_c} \frac{x_{m_i}}{\alpha_i}$$

where n_c is the number of component.

Eq. (A1) can now be written as

$$\begin{aligned} \frac{d(F_r x_{f_i})}{dS} &= F_r \frac{dx_{f_i}}{dS} + x_{f_i} \frac{dF_r}{dS} = -\alpha_i(\beta x_{f_i} - \gamma x_{m_i}) \\ \text{or } \frac{dx_{f_i}}{dS} &= \frac{1}{F_r} \left[\frac{x_{f_i}(\beta - \gamma)}{x_{m_{av}}} - \alpha_i(\beta x_{f_i} - \gamma x_{m_i}) \right] \end{aligned} \quad (A5)$$

x_{m_i} required in Eq. (A5) can be expressed explicitly using Eqs. (A3) and (A4) as follows:

$$\begin{aligned} -\frac{\beta - \gamma}{x_{m_{av}}} &= -\frac{\alpha_i(\beta x_{f_i} - \gamma x_{m_i})}{x_{m_i}} \\ \text{or } x_{m_i} &= (\beta x_{m_{av}}) \frac{\alpha_i x_{f_i}}{\beta - \gamma + \gamma \alpha_i x_{m_{av}}} \end{aligned} \quad (A6)$$

$x_{m_{av}}$ required in Eqs. (A4)–(A6) can be expressed implicitly through summation of Eq. (A6) for all components, i.e.:

$$x_{m_{av}} = \frac{1}{\beta \sum_{i=1}^{n_c} \alpha_i x_{f_i} / (\beta - \gamma + \gamma \alpha_i x_{m_{av}})} \quad (A7)$$

Integration of differential–algebraic Eqs. (A4)–(A7) would give total molar flow and mole fractions at various points on the feed side including the exit point. The total molar flow and mole fractions at permeate exit point can then be calculated as follows:

$$P_{ex} = F_{en} - F_{ex}, \quad x_{p_{ex}} = \frac{F_{en} x_{f_{en}} - F_{ex} x_{f_{ex}}}{P_{ex}} \quad (A8)$$

where P is the bulk molar flow on permeate side, x_p the bulk mole fraction on permeate side, and subscripts en and ex are the entrance and exit values, respectively.

A.2. Pressure equations

In this work, rigorous pressure drop equations have been developed for both the feed and the permeate sides. These equations account for the additional effects of change in fluid velocity due to permeation across the membrane and frictional loss due to membrane internals. From steady-state continuity (fluid mass balance) equation:

$$\begin{aligned} 0 &= \frac{dF}{dx} = \frac{d(u_f A_f \rho_f / M_{f_{av}})}{dx} = \left(\frac{A_f}{M_{f_{av}}} \right) \left(\rho_f \frac{du_f}{dx} + u_f \frac{d\rho_f}{dx} \right) \\ \text{or } d \left(\frac{u_f^2}{2} \right) &= u_f du_f = \left(\frac{M_{f_{av}}}{A_f} \right) \left(\frac{u_f}{\rho_f} \right) dF - u_f^2 d(\ln(\rho_f)) \end{aligned}$$

where u_f is the bulk velocity on feed side, A_f the flow area on feed side, ρ_f the bulk density on feed side and $M_{f_{av}}$ is the average bulk molecular weight on feed side.

The above equation implies that change in kinetic energy results from changes in both mass and pressure. Usually, pressure drop across a membrane module is small (usually less than 1% of the total pressure), while the yield of permeate is quite

high (usually higher than 10% of the total feed). Hence, the second term is negligible as compared to the first term. The above equation, therefore, reduces to

$$d \left(\frac{u_f^2}{2} \right) = \left(\frac{M_{f_{av}}}{A_f} \right) \left(\frac{u_f}{\rho_f} \right) dF$$

Substituting above in the mechanical energy balance equation gives:

$$\begin{aligned} 0 &= \frac{dP_f}{\rho_f} + d \left(\frac{u_f^2}{2} \right) + \left(\frac{2u_f^2}{d_f} \right) \delta_f dx \\ \text{or } \frac{dP_f^2}{dx} &= 2P_f \frac{dP_f}{dx} = - \left(\frac{2M_{f_{av}}}{A_f} \right) P_f u_f \frac{dF}{dx} - \left(\frac{4}{d_f} \right) u_f^2 P_f \rho_f \delta_f \end{aligned}$$

where d_f is the equivalent diameter for flow on feed side, $\delta_f = \delta_{f_s} + K_{f_e} d_f^2 / Re_f$, δ_{f_s} the skin friction factor on feed side (a known function of Re_f), K_{f_e} the a parameter for additional friction on feed side due to internals, Re_f the feed side Reynold's no. = $d_f F_r F_{en} M_{f_{av}} / \mu A_f$ and μ is the viscosity of gas.

Expressing u_f in terms of molar flow and ρ_f in terms of pressure, the above equation further simplifies to

$$\begin{aligned} \frac{dP_f^2}{dx} &= - \left(\frac{2M_{f_{av}} Z_{f_{av}} R T F}{A_f^2} \right) \frac{dF}{dx} - \left(\frac{4M_{f_{av}} Z_{f_{av}} R T F^2}{d_f A_f^2} \right) \delta_f \\ \text{or } \frac{d\beta^2}{dS} &= -UC_P \left[\left(\frac{2M_{f_{av}} Z_{f_{av}} R T F_{en}^2}{A_f^2 P_{f_{en}}^2} \right) F_r \frac{dF_r}{dS} \right. \\ &\quad \left. + \left(\frac{4M_{f_{av}} Z_{f_{av}} R T F_{en}^3}{d_f A_f^2 P_{f_{en}}^3 A_x(Q_r/t)} \right) F_r^2 \delta_f \right] \end{aligned} \quad (A9)$$

where $Z_{f_{av}}$ is the average bulk compressibility factor on feed side, R the ideal gas constant, T the system temperature and UC_P (unit conversion factor) = $P(M/LT^2)^{-1}$ (P , M , L and T being units of pressure, mass, length and time).

In the same way as for the feed side, permeate side pressure drop can be expressed by the following equation:

$$\begin{aligned} \frac{dP_p^2}{dy} &= - \left(\frac{2M_{p_{av}} Z_{p_{av}} R T P}{A_p^2} \right) \frac{dP}{dy} - \left(\frac{4M_{p_{av}} Z_{p_{av}} R T P^2}{d_p A_p^2} \right) \delta_p \\ \text{or } \frac{d\gamma^2}{dT} &= -UC_P \left[\left(\frac{2M_{p_{av}} Z_{p_{av}} R T F_{en}^2}{A_p^2 P_{f_{en}}^2} \right) P_r \frac{dP_r}{dT} \right. \\ &\quad \left. + \left(\frac{4M_{p_{av}} Z_{p_{av}} R T F_{en}^3}{d_p A_p^2 P_{f_{en}}^3 A_y(Q_r/t)} \right) P_r^2 \delta_p \right] \end{aligned} \quad (A10)$$

where y is the distance from inlet in the permeate flow direction, A_y the membrane area per unit distance (y), A_p the flow area on permeate side, d_p the equivalent diameter for flow on permeate side, $\delta_p = \delta_{p_s} + K_{p_e} d_p^2 / Re_p$, δ_{p_s} the skin friction factor on permeate side (a known function of Re_p), K_{p_e} the parameter for additional friction on permeate side due to internals, Re_p the permeate side Reynold's no. = $d_p P_r F_{en} M_{p_{av}} / \mu A_p$, $M_{p_{av}}$ the average bulk molecular weight on permeate side, $Z_{p_{av}}$ the average bulk compressibility factor on permeate side, $P_r = P/F_{en}$ and $T = A_y y P_{f_{en}}(Q_r/t) / F_{en}$ the dimensionless membrane area.

For co-current flow of feed and permeate, Eqs. (A4)–(A10) can be integrated simultaneously. However, for counter-current and cross-current flows of permeate, it is not possible to do the same. In these cases, feed and permeate side equations are to be solved consecutively. Due to coupled nature of the two sets of equations, it would be needed to guess the variables on one side and solve equations on both sides repeatedly till the guessed variables converge. For simplicity, permeate flow direction is divided into a number of grids and the permeate pressure in each grid is assumed to be uniform. Starting with a guessed distribution of permeate pressure, the feed and permeate side equations are solved consecutively and repeatedly (i.e., as in the successive substitution algorithm) to ensure that the iterated variables converge. This gives rise to the inner layer of iterations in the solution of model equations. The outer layer of iterations in the solution of model equations originates from the fact that the pressure at the closed end of permeate channel is never known. It is rather the permeate exit pressure that is normally specified. This introduces an iterative procedure in the model solution since the permeate exit pressure is to be fitted to its specified value by varying the closed-end pressure of permeate.

As mentioned earlier, a membrane unit may be constituted of multiple stages and each stage may contain multiple modules. Modules of a stage are arranged in parallel. Therefore, for each stage, it is sufficient to solve the model equations for a single module only. Pressure and concentrations remaining same, the exit flow rates from a stage are obtainable by simply multiplying the flow rate of a module with the number of modules. However, model equations are to be solved for every stage. When multiple streams mix, the total flow rate, component flow rates and pressure of the mixed stream are calculated, respectively, by the overall mass balance, component mass balances and overall momentum balance. The momentum balance takes into account the transfer of excess kinetic energy or pressure from one stream to the other. Variables corresponding to recycled streams between stages will be initially unknown. Values of these are assumed initially and then converged by the successive substitution method.

Appendix B. Gas processing cost

Hao et al. [8] have recently published a comprehensive economic analysis model for the membrane-based gas separation units. This economic model has been adopted here in a simplified form. It account for the following costs:

1. Initial capital costs of membrane modules and compressors.
2. Operating costs for running compressors, regular replacement of membrane modules (after a certain period of service) and labor.
3. Cost of hydrocarbons lost through the permeate stream (assuming this stream is useless).

The values of various cost related parameters (other than the natural gas price) have been adopted from Ref. [8]. It may be noted that some of these parameters (like, the membrane, compressor and energy costs) are substantially different from earlier

studies [6,7]. Substituting all relevant values, the cost equations become:

$$\text{GPC} = \frac{\text{CRC} + \text{LRC} + \text{ORC}}{(F_{\text{en}})(22.4)(1 - \text{SC})(24)(365)(F_{\text{os}})} \quad (\text{A11})$$

where GPC is the gas processing cost (USD/N m³ product), CRC the capital related cost (USD/year), LRC the material loss related cost (USD/year), ORC the operation related cost (USD/year), F_{en} the feed flow at entrance (kg mol/h), SC the stage cut defined as the ratio of permeate to feed flow and F_{os} is the (plant's on-stream factor)=0.96:

$$\text{CRC} = \frac{\text{TFC}}{F_{\text{cp}}}, \quad \text{TFC} = C_{\text{m}}(n_{\text{m}}^{\text{T}}) + C_{\text{c1}} \sum_{i=1}^{n_{\text{com}}} \text{HP}_i C_{\text{c2}},$$

$$\text{HP}_i = (3.0973e - 03) \left[(P_{\text{ci}} Z_{\text{p}_{\text{ci}}} T) \left\{ \frac{n_{\text{sc}_i} \gamma_{\text{s}}}{(\gamma_{\text{s}} - 1)} \right\} \left(\frac{1}{\eta_{\text{com}}} \right) \right] \\ \times [r_{\text{p}_i}^{(\gamma_{\text{s}} - 1)/n_{\text{sc}_i} \gamma_{\text{s}}}],$$

$$\text{LRC} = (F_{\text{en}})(22.4)(\text{SC})(24)(365)(F_{\text{os}}) \sum_{i=1}^{n_{\text{c}}} C_i x_{\text{p}_{\text{ex}_i}},$$

$$\text{ORC} = (\text{HP}^{\text{T}})(0.746)(C_{\text{e}})(24)(365)(F_{\text{os}}) + \frac{(C_{\text{mr}})(n_{\text{m}}^{\text{T}})}{L_{\text{m}}} \\ + (C_1)(8)(365)(F_{\text{os}})(n_1)(F_{\text{en}})(22.4)$$

where TFC is the total facility cost (USD), HP_i the energy requirement i th compressor, F_{cp} the (capital payout period)=5 years, C_{m} the (cost per module)=108 USD/m² (~10 USD/ft²)=3996 USD/module, n_{m}^{T} the total number of modules, C_{c1} and C_{c2} (constants relating to compressor cost in USD)=8650 and 0.82, n_{com} the number of compressors in the unit, P_{ci} the molar flow of permeate entering i th compressor (kg mol/h), $Z_{\text{p}_{\text{ci}}}$ the compressibility factor of permeate entering i th compressor, T the temperature (K), n_{sc_i} the number of stages of i th compressor, r_{p_i} the compression ratio of i th compressor, γ_{s} the specific heat ratio of feed, η_{com} the fractional compressor efficiency, C_{CH_4} the cost of natural gas or CH₄ (USD/N m³), $x_{\text{p}_{\text{exCH}_4}}$ the volume fraction of CH₄ at permeate exit point, HP^{T} the total energy requirement of compressor's = $\sum_{i=1}^{n_{\text{com}}} \text{HP}_i$, C_{e} the (compressor's energy cost)=0.07 USD/kWh, C_{mr} the (replacement cost per module)=54 USD/m² (~5 USD/ft²)=1998 USD/module, L_{m} the (life of membrane element)=4 years, C_1 the (cost of labor)=15 USD/h and n_1 the (number of labors required at a time)=34 for each 1 MN m³/h capacity (~1 for each 25 MMSCFD capacity).

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