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Membrane Area Sensitivity Analysis to Achieve Higher CO_2 Outlet Concentration

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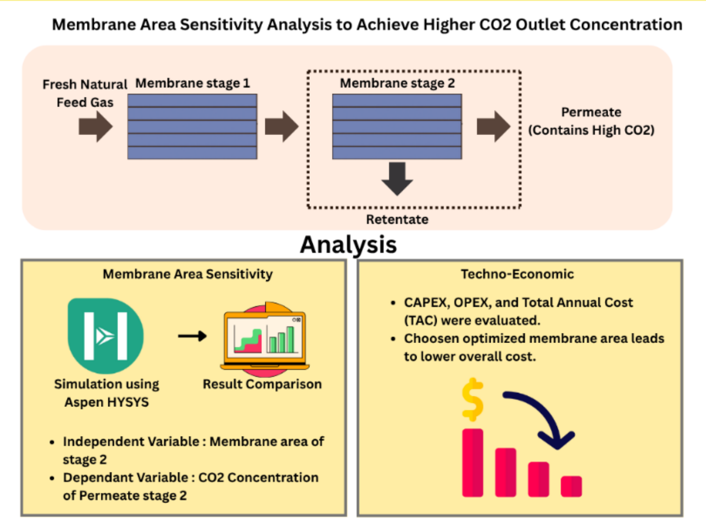
***Abstract*—** The CO_2 separation from natural gas using membrane technology offers several benefits such as low energy requirement, simple flow process, and no phase change. Moreover, its process only requires sufficient area suitable for remote and offshore facilities. This research will focus on how to improve CO_2 concentration in the membrane stage 2 output or permeate stage 2. It will discuss techno-economic and modify 2-stage membrane technology to achieve higher carbon dioxide concentration from natural gas by evaluating several membranes using ASPEN HYSYS. From the simulation results, it was found that reduced membrane area had the effect of increasing the carbon dioxide concentration in permeate stage 2 but decreasing the gas flow rate. Lowering the membrane area can increase the concentration of CO_2 at permeate stage 2 from 82.47 to 84.7 - 96 % mol of CO_2. Based on the evaluation of several membrane areas, a membrane area of 2.5 m^2 was chosen because it can produce 91.78% mol CO_2 in permeate stage 2. From the economic analysis, total annual cost could reduce up to USD 1,426,296.



***Keywords*—** Aspen Hysys, Carbon Dioxide, Membrane, Permeate, Separation

I. Introduction

Separation with membrane technology offers several benefits, namely low energy requirements, simple process flow schemes, and no phase changes. In addition, the process only requires a small area and is suitable for remote areas. Polymeric membrane separation works by the solution-diffusion method and is commonly used to separate CO_2 in natural gas, usually using cellulose acetate (CA) as a polymer. One of the leading CA membrane manufacturers is UOP Separex and Cynara.[1]

Membranes for carbon dioxide separation have been applied to natural gas sweetening where the concentrations of CO_2 and H_2S contained in high-pressure natural gas should be lowered to the levels of meeting the gas pipeline specifications (CO_2 < 2% and H_2S < 4 ppm). [2] [3]

Hundreds of plants have been built to separate carbon dioxide from natural gas. Some with a small capacity, the process is only 1-10 MMSCFD of natural gas, but currently many large plants with a capacity of 50-100 MMSCFD have been built. Many plants use cellulose-acetate membrane either in the form of hollow fiber (Cynara) or spiral wound module (GMS and Separex). [4]

The membrane can be thought of as a permselective barrier that exists between the two homogeneous phases. Transport through the membrane occurs when a thrusting force is applied to the components in the feed. In most membrane processes, the driving force is a difference in pressure or a difference in concentration (or activity)

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across the membrane. [5] The classification of membrane processes based on thrusting force is presented in table 1.

Based on chemical phenomenon, the absorption using alkanolamines is probably the most extended process for acid gas removal. However, membrane technologies are considered as an alternative in specific cases for their better performance, cleanness, energy requirements, operating costs and location flexibility. Membrane system able to reduce energy requirements and emission up to 5% and 4% in respect to absorption process. [6]

Despite the advances made in recent years, a significant gap remains between laboratory scale studies and real-world industrial applications. Most efforts have focused on developing new membranes to enhance process efficiency. However, limited work has been done to optimize existing membrane configurations for practical use or to conduct comprehensive techno-economic assessments under industrial conditions, such as high pressures, mixed gas compositions, and long-term operation. These aspects will be addressed in this paper. [7]

In the separation process using membrane technology, the feed will be separated in the flow to the membrane, namely permeate, and the fraction of the feed that does not penetrate the membrane, namely retentate. [5]

Gas permeation is a technique for fractionating a mixture of gases using a non-porous polymer membrane that has selective permeability to the gas according to the dissolution-diffusion mechanism. The process of separation of membrane gases is driven by the pressure difference along the membrane.

Commercial membrane separation processes usually operate with a feed-to-permeate pressure ratio (θ) in the range of 5–15. This limited pressure ratio means that the optimum membrane may not be the one with the highest selectivity; rather, a membrane with lower selectivity, but tailored to the pressure ratio, may result in a more economical process. In other words, when a process is pressure ratio limited, the useful selectivity is also limited. The balance between pressure ratio and selectivity is often ignored by membrane developers. [8]

TABLE 1.
CLASSIFICATION OF MEMBRANE PROCESSES BASED ON DRIVING FORCE [5]

Pressure Difference	Concentration (activity) Difference	Temperature Difference	Electrical Potential Difference
Microfiltration	Pervaporation	Thermo-osmosis	Electrodialysis
Ultrafiltration	Gas Separation	Membrane Distillation	Electro-osmosis
Nanofiltration	Vapour Permeation		Membrane electrolysis
Reverse Osmosis	Dialysis		
Piezodialysis	Diffusion Dialysis		
	Carrier-mediated transport		

The membrane can be either flat sheets or hollow fibers. In general, hollow fibers are preferred because they can achieve a higher effective membrane area in each module volume. [5] The gas separation process using membrane technology is described in Figure 1.

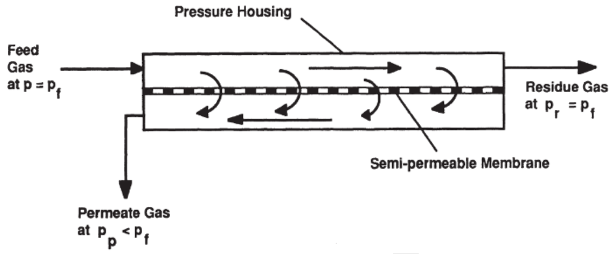

Figure 1. Schematic Diagram for Gas Separation using Membrane [5]

As known, membrane performance is mainly characterized by two parameters [9] permeance and selectivity. Although membranes with extremely high perm selectivity are available for different processes, the feasibility of membrane process depends on not only the membrane selectivity and permeance, but also the operating conditions (including operating pressure and number of stages). [10]

Aim to achieve a high purity CO_2 permeate and reduce CH_4 losses, reference [11] assessed multiple stage membrane designs for separation of CH_4 and CO_2. Single stage, 2 stage and 3 stage arrangements are considered in the study with several configuration which are with and without recycle line. 2 stage membranes with the second stage retentate as recycle proved the best separation strategy. [11]

A technical and economic analysis of gas sweetening processes for natural gas with amine absorption and membrane technology has been conducted in reference [3]. Amine absorption is still considered a state-of-the-art technology for gas sweetening but membranes have shown a great potential in this area, if the flux and selectivity for CO_2 is high enough. The simulation results show that CO_2 purity of achieved gas streams is for instance lower when using membrane process, while higher CO_2 purity of gas in amine process is paid by high total capital investment and a potentially more harmful environment process. [3]

Reference [12] performed comparative analysis between membrane system, absorption with amines and a hybrid system (membranes and amines) for CO_2 separation from natural gas. In the case of membrane systems, a single stage and 2 stage arrangements were considered. The result showed that 2 stage membranes could reduce 28% total membrane area of single membrane with the same output. [12]

Seven different membrane process configurations have been examined by computer simulations. The 'base-case' studies considered a 35 MMSCFD (million standard cubic feet per day) feed stream of natural gas at 800 psia with CO_2 concentrations in the range of 5 to 40 mole%. The operating variables for each of the process configurations were optimized on the basis of new process variables in order to determine the lowest cost of CO_2 removal from natural gas. It was concluded that, for the base-case operating conditions, the separation cost for the removal of CO_2 from natural gas is lowest for a three-stage configuration. [13]

Reference [14] performed techno-economic of CO_2/CH_4 separation using multi stage membranes. The aim of this study is to simulate and optimize the separation of CO_2 and CH_4 from different sources using a simple multistage process, considering up to three stages. Simulation of the multistage membrane separation of CO_2/CH_4 demonstrated that a three-stage separation process scheme based on membrane units, with the selected biopolymer-based MMMs, can achieve the targets imposed on product quality, yielding high-quality CO_2 and CH_4. In the most demanding scenario, which imposed 95% purity and recovery of the CO_2 product stream from the permeate line, CH_4 recovery values higher than 97% in the retentate line could be achieved. [14]

A systematic design strategy for spiral-wound gas separation systems is studied using a recently proposed algebraic permeator model. [15] Nonlinear programming (NLP) is used to determine operating conditions which satisfy the separation requirements while minimizing the annual process cost. The design method is applied to the separation of CO_2/CH_4 mixtures in natural gas treatment and enhanced oil recovery applications. It is shown that a two-stage configuration with permeate recycle and a three-stage configuration with residue recycle are suitable for natural gas treatment, while a three-stage configuration with both permeate and residue recycle is appropriate for enhanced oil recovery. [16]

2 stages membrane simulation performed in reference [12] and achieve 84.75% for CO_2 concentration at Membrane stage 2 permeate. Generally, the CO_2 used for EOR should have a purity of around 90-98%. [17] CO_2 separation from natural gas by membrane technology is a well-known and implemented industrial process. There are quite a few membrane plants installed around the world, but these membranes do not have optimum performance with respect to CO_2 purity in the product, therefore require fairly large membrane areas.[3] Several researches mostly compare between absorption and membrane system, adding process stages in membrane system, and binary mixture. The objective in this research is to improve CO_2 fraction mole in 2 stage membrane system specifically in the permeate side of membrane stage 2 without add more process stages. Using ASPEN Hysys, we perform study to observe the effect of stage 2 membrane area variables on the CO_2 concentration of permeate stage 2. The study will continue by calculating CAPEX (capital expenditure), OPEX (operating expenditure) and TAC (total annual cost) to evaluate from economical aspect.

II. METHOD

The transport of gases through a dense polymer membrane is defined in the following Equation 1 as below. [18]

$$J_i = \frac{D_i K_i (p_{i_o} - p_{i_l})}{l} \quad (1)$$

Where J_i is the flux volume of component i, l is the thickness of the membrane, p_{i_o} is the partial pressure of component i on the feed, p_{i_l} is the partial pressure of component i on the permeate. The diffusion coefficient D_i is an indication of the mobility of molecules in the membrane material, and the gas absorption coefficient K_i is an indication of the number of molecules dissolved in the membrane material. $D_i K_i$ product can be written as P_i, i.e. membrane permeability. Membrane permeability is a parameter to measure the ability of membranes to absorb gases. [18]

Peng-Robinson fluid package is used in the simulation since it's commonly used for hydrocarbon mixture and suitable for CO_2 separation simulation. Membrane unit extension v3.0a is added to Aspen HYSYS for modelling the membrane. With this extension, we have additional unit operation for membranes.

The research began with a study of the literature around CO_2 separation, specifically membrane technology. Furthermore, data collection was carried out to support the creation of Aspen HYSYS simulation for membrane technology. HYSYS simulation will be created to evaluate CO_2 separation technology using membranes. Authors will prepare simulation of Aspen HYSYS for membrane technology based on previous research by reference [12]. Some references to create membrane models on Aspen HYSYS refer to reference [19] and reference [20]. Based on data from reference [12], CO_2 concentration from fresh feed gas is 22.66%. Gas composition and condition data of fresh feed gas is presented in Table 2 and 3.

TABLE 2.
GAS COMPOSITION OF FRESH FEED GAS [12]

Feed Composition, mole fraction	
CH_4	0.7608
C_2H_6	0.0055
C_3H_8	0.0028
iC_4H_{10}	0.0000
nC_4H_{10}	0.0021
nC_5H_{12}	0.0000
nC_5H_{10}	0.0022
CO_2	0.2266

TABLE 3.
CONDITION OF FRESH FEED GAS [12]

Parameter	
Temperature, degC	30
Pressure, kPa	6895
Gas Flow, MMSCFD	35

As per reference [12], membrane-1 and membrane-2 are having different configuration in terms of membrane area and permeability. Membrane-2 equipped with smaller membrane area than membrane-1. In terms of permeability, membrane-1 is lower than membrane-2. Membrane data is presented in table 4.

TABLE 4.
MEMBRANE DATA IN UNIT EXTENSION [12]

Membrane-1	
Total Unit	50
Membrane Area/Unit	40 m^2
Membrane Permeability to CO_2	0.4 barrer
Membrane-2	
Total Unit	50
Membrane Area/Unit	6 m^2
Membrane Permeability to CO_2	2 barrer

Data from table 4 will be used in the membrane unit extension and will be adjusted according to the cases in the study. Membrane area of stage 2 as the independent variables will be adjusted to observe the effect in CO_2 concentration of permeate stage 2 as dependant variables. Cases in this study are presented in table 5.

TABLE 5.
MEMBRANE AREA SENSITIVITY ANALYSIS

Case	Membrane Area per unit, m^2
Base Case	6
1	5
2	4
3	2.5
4	1.5
5	1

The study will conduct simulation of membrane process with smaller membrane area in stage 2 and observed the impact on CO_2 concentration of permeate stage 2. Several boundaries of this research will be stated as below:

1. Focus on permeate side of membranes
2. Carbon tax and incentives is not considered

III. RESULTS AND DISCUSSION

Base case simulations have been made with schematic as described in Figure 2. The base case configuration produces CO_2 concentrations of 45.71 % (permeate-1) and 82.47% (permeate-2).

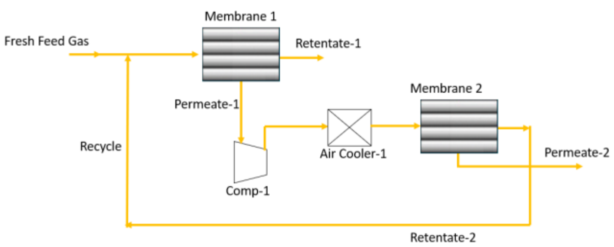

Figure 2. Flow Diagram of Membrane Separation (Base Case)

Validation is carried out by comparison with the results based on reference [12] presented in table 6 and 7. Relative error is calculated to measure the error between journal data and simulation result. Relative error is calculated by below equation 2.

$$RE\ (\%) = Absolute\left(\frac{Existing\ Data - Simulation\ Data}{Existing\ Data}\right) \times 100 \quad (2)$$

TABLE 6.
*REFERENCE [12] RESULT VS SIMULATION OUTPUT FOR CO_2 CONCENTRATION IN MEMBRANE STAGE 1

	*Permeate-1	Permeate-1	Relative Error, %
CO_2 Molar Fraction, %	44.95	45.71	1.69

TABLE 7.
REFERENCE [12] RESULT VS SIMULATION OUTPUT FOR CO_2 CONCENTRATION IN MEMBRANE STAGE 2

	*Permeate-2	Permeate-2	Relative Error, %
CO_2 Molar Fraction, %	84.75	82.47	2.69

To achieve higher CO_2 concentration in permeate-2, performed sensitivity analysis on membrane areas value on Membrane-2 to understand the effect on CO_2 concentration of permeate-2. Sensitivity summary presented in table 8.

Based on simulation result summarized in table 8, CO_2 concentration on permeate-2 is increasing when membrane area is decreased. Case 3, 4 and 5 are preferable since CO_2 concentration is higher than 90% for EOR purpose. The evaluation continues for the molar flow for each case in permeate-2, which presented in table 9. From this evaluation, we will lose more flow if we choose smaller membrane area although the concentration will increase.

TABLE 8.
MEMBRANE AREA SENSITIVITY ANALYSIS

Case	Membrane Area per unit, m^2	Permeate-2 CO_2 mole fraction, %
Base Case	6	82.2554
1	5	84.7524
2	4	87.4324
3	2.5	91.7866
4	1.5	94.7149
5	1	96.0175

TABLE 9.
PERMEATE-2 AND RETENTATE-2 MOLAR FLOW COMPARISON

Cases	Permeate-2, MMSCFD	Retentate-2, MMSCFD
Base Case	2.803	2.517
3	2.232	3.320
4	1.783	4.108
5	1.382	4.828

An economic analysis is carried out to support the results of the technical evaluation and become a consideration in choosing the case to be used. CAPEX (Capital Expenditure) and OPEX (Operational Expenditure) comparison presented in Figure 3 and 4.

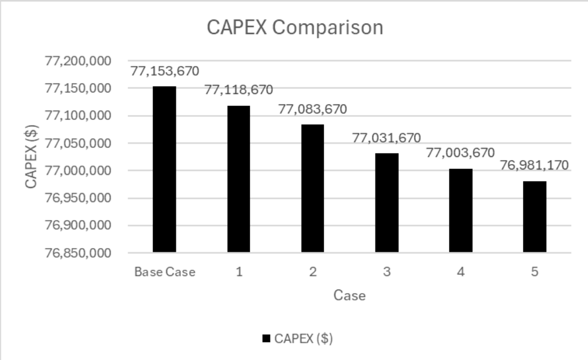

Figure 3. Economic Analysis of CAPEX

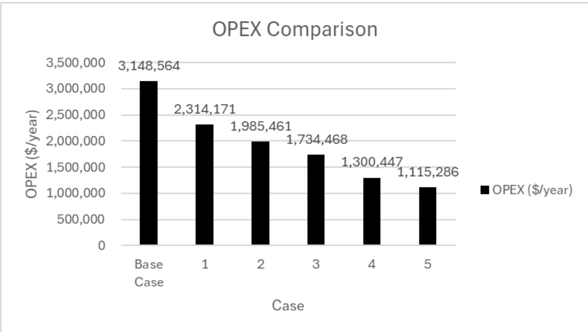

Figure 4. Economic Analysis of OPEX

Total annual cost is amount of cost spent over certain of period for operation or asset. In this research, we calculate total annual cost for 10 years of operation and the result presented in Figure 5. [5]

[6]

Figure 5. Total Annual Cost

[9]

IV. CONCLUSION

Systematic design has been proposed for gas separation using membrane process. Proposed model was validated with journal data, where the simulated data resulted minimum error value. Membrane area sensitivity has been performed and proved that reduced membrane area will increase permeate concentration (CO_2). Based on simulation result and economic analysis, chosen case 3 with membrane area 2.5 m^2 since it could increase CO_2 concentration up to 91.78%. Permeate-2 flowrate only decreased 0.6 MMSCFD compared with base case. Choosing case 3 will reduce our total annual cost (TAC) up to USD 1,426,296. [10]

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