Mathematical Modeling of CO₂/CH₄ Separation by Hollow Fiber Membrane Module Using Finite Difference Method

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Abstract: Removal of CO_2 in landfill gas recovery processes and fractured wells as well as its application in enhanced oil recovery and its environmental aspects are of interest. Also separation of CO_2 from CH_4 in Ethylene Oxide plant is an environmental policy of Marun Petrochemical Company. In the present work, a shell-fed hollow fiber module was modeled mathematically for CO_2 separation from CH_4 . Finite difference method was used for solving the equations. Comparison between co-current and counter-current flow patterns showed that for all conditions, counter current pattern had better efficiency for CO_2/CH_4 separation. Influence of operating parameters such as feed pressure, permeate pressure, feed flow rate, fiber length and CO_2 concentration of feed on separation efficiency of CO_2/CH_4 mixture was investigated. Also the effect of feed and permeate pressures on required membrane area showed that the membrane area increases by increasing permeate pressure and decreases by increasing feed pressure. The modeling offers valuable data about feasibility study and economical evaluation of a gas separation unit operation as a helpful unit in the industry.

Keywords: Hollow fiber, modeling, CO₂/CH₄, operating parameter, membrane area.

1. INTRODUCTION

The focus of much of the new awareness has turned towards examining greenhouse gas emissions and their impact on global climate [1]. Carbon dioxide which is emitted from fossil fuels, natural and refinery off-gases and many other sources is representing about 80% of greenhouse gases [2-5]. From the global environmental perspective, it is important to separate CO₂ from gas mixtures to avert the threat of global warming; thereby attaining the carbon emission reduction targets set out by the Kyoto Agreement [2] therefore, recovery of carbon dioxide from large emission sources is a formidable technological and scientific challenge which has received considerable attention for several years [1]. Currently, commercially available CO₂ separation technologies, including pressure swing adsorption, amine absorption, and cryogenic separation are highly energy intensive [6, 7], but membrane technologies are becoming more frequently used for separation of wide varying gas mixtures in different industries because of the economic competitiveness of the existing separation technologies and the present challenges of aggressive environments [8,9]. The application of membrane technology for CO₂ removal from CH₄ for upgrading the natural gas, landfill gas and enhanced oil recovery emerged in the 1980s after several major

membranes are the most advantageous form of membranes used in the gas separation processes. They can be produced by any method employed for the manufacture of chemical fibers [15]. Hollow fibers are the cheapest on a per square meter basis with the highest membrane area to module volume ratio. They do not require any support, whether the feed flows inside or outside of the fiber tubes [16]. A hollow fiber module contains a large number of membrane fibers housed in a shell; its arrangement is similar to countercurrent shell and tube heat exchangers. Feed can be introduced on either the fiber or shell side, but commonly, pressurized feed gas is fed to the shell side and the components permeate at different rates to the fiber bore. Permeate is usually withdrawn in a cocurrent or counter-current manner, with the latter being generally more effective [17]. In co-current manner, the driving force and mass transfer rate are reduced due to concentration reduction of penetrated constituent but in counter-current mode, except of inlet and outlet sections, mass transfer rate remains constant [18]. In order to improve the performance of membrane gas separation process, optimization (operating and

breakthroughs [10-12]. One of the principal revolutions was the preparation of high flux asymmetric Loeb-

Sourirajan membranes with selective layer thicknesses

of less than 0.1µm [13]. In the last 40 years, the

asymmetric single-layer hollow fiber membrane is

always a favorable configuration in the membrane

based gas separation systems owing to their large

surface area over unit volume, self mechanical support,

good flexibility and easy scale [14]. Hollow-fiber

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design) and analysis of the process should be accomplished. Modeling and simulation are tools to achieve these objectives [19]. An appropriate modeling, offers important information about design, optimization, and the economics of membrane units. The issue of mathematical modeling of membrane gas separators was first addressed by Weller& Steiner [20]. In recent years, simulation of membrane gas separation has attracted increasing more attention and many researchers have studied modeling of hollow fiber membrane for gas separation. Boucif et al. [21, 22] derived an algebraic model for binary mixtures, this model was obtained from differential mass balance equations and these equations were highly non-linear. They offered numerical solution of boundary value problems encountered in hollow fiber binary gas permeators having co-current or countercurrent permeate flow with and without axial pressure drop inside the fiber bore. Chern et al. [23] developed a model for simulating the performance of an isothermal countercurrent hollow-fiber gas separator for binary mixture. The model equations were solved numerically as a boundary-value problem. Permeate pressure buildup has been considered explicitly and concentration dependence of the permeabilities are taken into account by using the dual-mode sorption and transport models. Rautenbach & Dahm [24] presented an analytical solution for binary mixtures in the counter current module. They considered constant permeate pressure along the permeate side. Krovvidi et al. [25] derived two models with different assumptions for binary mixtures in co-current and counter current module. They assumed a linear (OLM model) or quadratic (DFM model) relationship between the feed composition and the permeate composition along the membrane. The DFM model is implicit model and more accurate than OLM model (explicit model). Kovalli et al. [26] presented a linear approximation model (LAM) to solve the multi-component countercurrent gas permeator transport equations considering pressure variation inside the fibers. The models provided very effective and guick solution to the nonlinear coupled differential equations using the assumption of the linearity of feed and permeate side compositions. This assumption leads to algebraic analytical expressions for the prediction of membrane area and pressure ratios. Coker et al. [27, 28] presented a model for a multi-component gas mixture in an isothermal and nonisothermal hollow-fiber gas separation contactor that permits rapid solution of the governing differential mass and pressure distribution using a computational scheme that does not rely on conventional shooting

techniques for numerical integration. The model was developed for countercurrent, co-current and cross flow patterns with and without permeates purging. Kaldis et al. [29] presented a model for multi-component gas mixture; the equations were solved by orthogonal collocation to approximate differential equations, and to solve the resulting system of non-linear algebraic equations by the Brown method. Zaho et al. [30] simulated a binary gas separation permeator for countercurrent hollow fiber membrane modules. A differential mathematical model and an efficient numerical solution procedure based on orthogonal collocation and Quasi-Newton method was developed.Peer et al. [31] presented a mathematical model for simulation of gas separation in hollow fiber membrane modules with all flow patterns (cross-flow, counter-current and co-current). This model can be used for calculation of membrane performance or its required surface area for a specific separation. Madaeni et al. [32] modeled a counter-current module for a binary mixture. They considered as the membrane as a unit consisting of many sections and derived equations from mass balance.

Separation of CO_2/CH_4 is the second most investigated gas pair for membrane processes. Most of the industrial processes to separate CO_2 from CH_4 are high-pressure applications with total feed pressures up to 100 bars. Depending on the fraction of CO_2 in these feeds, the resulting CO_2 partial pressures are approximately 10-50 bars [18, 33].

In this paper, separation of CO_2/CH_4 by membrane was modeled mathematically in a hollow fiber module. Effect of operating parameters such as feed pressure; permeate pressure, feed flow rate, fiber length and CO_2 concentration of feed on separation efficiency of CO_2/CH_4 mixtures of Ethylene Oxide plant of Marun Petrochemical Company was investigated. This modeling gives valuable information about feasible study optimum process and design condition and economical calculation for this separation and can be modified for separation of other gases from binary gas mixtures.

2. MODELING

2.1. Model Assumptions

The following assumptions were used for simplification of the model [31, 32]:

1- Module operates at steady state and isothermal conditions.

- 2- Ideal gas behavior is considered.
- 3- Mass is only transferred through selective layer and permeation mechanism is solution-diffusion.
- 4- Pressure drop in feed side is negligible.
- 5- Gas flow in both sides is plug flow.
- Membrane permeability is independent of pressure and feed composition.
- 7- No axial mixing occurs due to gases flow.
- 8- All fibers have uniform outer and inner diameter and selective layer thickness is considered constant.
- 9- Fibers deformation under high pressure condition is neglected.

2.2. Model Equations

The permeation of gases through polymeric membrane occurs by a combination of kinetic and equilibrium controlled phenomena [17]. Diffusion of gases from selective layer can be described by Fick's first law as equation (1):

$$J_i = -D_i^* \frac{dC_i}{dl} \tag{1}$$

Where D_i^* is the concentration dependent diffusion coefficient of component i in the membrane and dc_i/dl is the concentration gradient in the permeation direction inside the membrane. Integrating Equation (1) under the assumption of constant diffusivity and connecting the concentrations at the gas/membrane and membrane/gas interfaces by Henry's law to the bulk gases properties results in Equation (2)

$$J_i = Q_i (P_F x_i - P_P y_i) \tag{2}$$

Where P_F and P_P are feed and permeate pressure side of membrane respectively, and Q_i is the permeance. Under the present assumptions, the permeability does not vary with composition and operating conditions is therefore constant.

Figure **1** shows schematic of counter current gas permeation in a hollow fiber.

The material balance for component i in a hollowfiber module is presented as Equation (3)

$$\pm d[Lx_i] = d[Vy_i] = Q_i dA(P_F x_i - P_P y_i)$$
(3)

For hollow fiber:

$$dA = N_F \pi D_{IM} dz \tag{4}$$

The Hagen-Poiseuille relation [34] was used to calculate pressure drop for permeate side as Equation (5)

$$\frac{dP_P}{dz} = -\frac{128\mu Q}{N_F \pi D_i^4} \tag{5}$$

Due to gas ideal behavior:

$$Q = \frac{T V R_g}{P_P}$$
(6)

By introducing the dimensionless variables as:

$$z^{*} = \frac{z}{l_{E}}; L^{*} = \frac{L}{F_{0}}; V^{*} = \frac{V}{F_{0}}; \gamma = \frac{P_{P}}{P_{F}}; \alpha_{i} = \frac{Q_{i}}{Q_{n}}$$
(7)

$$K_{1} = \frac{\pi D_{LM} l_{E} N_{F} P_{F} P_{n}^{G}}{F_{0}}$$
(8)



Figure 1: Schematic of a counter current permeation into a hollow fiber membrane.



Figure 2: a, b- Co-current and countercurrent pattern in hollow fiber modules, respectively.

$$K_{2} = \frac{128\mu T R_{g} l_{E} F_{0}}{N_{F} \pi D_{i}^{4} P_{F}^{2}}$$
(9)

By introducing of these variables in to Equations 3 and 5, governing equations for co-current and countercurrent shell-fed hollow fiber module was obtained. Figure **2a**, **b** present co-current and countercurrent pattern in hollow fiber modules, respectively.

Tables **1**, **2** present the governing differential equations for co-current and counter-current shell-fed hollow fiber module for the present system, respectively.

Table 1: Governing Equations for Co-Current Shell-Fed Hollow Fiber Module for a Two Component System [35]

$\frac{dx}{dz^*} = -K_1 \frac{\alpha(1-x)(x-\gamma y) - x[(1-x) - \gamma(1-y)]}{(1-V^*)}$	(10)
$\frac{dy}{dz^{*}} = K_{1} \frac{[\alpha(1-y)(x-\gamma y) - y[(1-x) - \gamma(1-y)]}{V^{*}}$	(11)
$\frac{dV^*}{dz^*} = K_1[\alpha(x - \gamma y) + (1 - x) - \gamma(1 - y)]$	(12)
$\frac{d\gamma}{dz^*} = -K_2 \frac{V^*}{\gamma}$	(13)
Boundary conditions: at	
$z^* = 0$ $V^* = 0$, $x = x_F$ and $y = \varphi(x, \gamma)$	(14)
at $z^* = 1$ $\gamma = \omega(\gamma_0, V^*)$	(15)

2.3. Solution Method

For both flow patterns, the model equations are represented by a set of coupled nonlinear boundary

value problem differential equations. Finite difference method was used [36]. Shooting method was employed for co-current pattern but for counter current flow, the resulting set of equations for y_i can be represented in matrix notation as Equation (22)

Table 2: Governing Differential Equations for Counter-
Current Shell-Fed Hollow Fiber Module for a
Two Component System [35]

$$\frac{dx}{dz^*} = K_1 \frac{\alpha(1-x)(x-\gamma y) - x[(1-x) - \gamma(1-y)]}{(1-V^*)}$$
(16)

$$\frac{dx}{dz^*} = K_1 \frac{[\alpha(1-x)(x-\gamma y) - y[(1-x) - \gamma(1-y)]}{V^*}$$
(17)

$$\frac{dV^*}{dz^*} = \frac{dL^*}{dz^*} = K_1[\alpha(x - \gamma y) + (1 - x) - \gamma(1 - y)]$$
(18)

$$\frac{d\gamma}{dz^*} = -K_2 \frac{V^*}{\gamma} \tag{19}$$

Boundary conditions: at $z^* = 0$ $V^* = 0$ and $y = \varphi(x, \gamma)$ (20) at $z^* = 1$ $L^* = 1$, $x = x_F$ and $\gamma = \omega(\gamma_0, V^*)$ (21)

$$A_i y_i = b_i \tag{22}$$

Where, A_i is the matrix of constants and the boundary conditions were appeared as boundary elements in b_i matrix. The matrix expression was written for each of the dependent variables involved in the set of differential equations. The solution of the matrix equations was started with an estimate of all the dependent variables at all the grid points. The successive iterations were proceeded till convergence achieved. Figure **3a**, **b** show flowchart of equations



Figure 3: a, b- Flowchart of equations solution for co-current and counter-current flow pattern, respectively.

solution for co-current and counter-current flow pattern, respectively.

3. RESULTS AND DISCUSSIONS

The mathematical model was applied for CO_2/CH_4 separation in a shell-fed hollow fiber module with cocurrent and counter-current flow patterns. The selected material for the membrane is a polyimide and the experimental values for the permeabilities are taken from Nagel *et al.* [37]. Operating conditions and module parameters have been presented in Table **3**.

The concentrations of each component in permeate and retentate streams depend on design and operating conditions. Feed flow rate, feed temperature, feed and permeate pressure have been denoted to the operating condition and membrane area was considered as the design target. Feed enters in shell and permeate flows

Parameter	Value	Unit
т	308	К
P _F	35*10 ⁵	Ра
P _P	101325	Ра
Q _{CO2}	3.207*10 ⁻¹³	mol/(Pa.s.m ²)
Q _{CH4}	0.133*10 ⁻¹³	mol/(Pa.s.m ²)
Fo	50	mol/s
Ι _Ε	2	m
N _F	3*10 ⁵	-
Di	125*10 ⁻¹⁰	m
Do	250*10 ⁻¹⁰	m

 Table 3: Basic Operating Conditions and Modeling Parameters for the Present Study

in fibers. In fibers; CO₂ diffuses faster than CH₄ in order

to higher permeability, therefore along the module CO2



Figure 4: a- CO_2 concentration profile along the module for a (50%-50%) mixture at 35 bars and 308 K. **b**- CH_4 concentration profile along the module for a (50%-50%) mixture at 35 bars and 308 K.

concentration in shell side falls and CH_4 concentration increase gradually. Figures **4a**, **4b** show the concentration profile along the module.

3.1. Effect of Feed Pressure

Figure **5a** represents the influence of feed pressure on CO_2 concentration profile in retentate stream with for co-current and counter- current flow patterns. CO_2 concentration decreases by increasing feed pressure for both flow patterns but CO_2 concentration rate for cocurrent is slightly higher than counter-current. At higher feed pressure; the driving force for mass transfer increases and, therefore, the CO_2 purity of the permeate is enhanced. Increasing feed pressure results in more CO_2 passage through membrane and therefore less CO_2 in retentate stream.

By increasing feed pressure, CH₄ passage through membrane is also increased but less than CO₂,



Figure 5: a- CO₂ concentration profile in retentate stream with feed pressure in co-current and counter- current flow patterns for a (50%-50%) mixture at 308 K.

b- CH₄ concentration profile in retentate stream with feed pressure in co-current and counter- current flow patterns for a (50%-50%) mixture at 308 K.



Figure 6: a- Influence of feed flow rate on CO₂ concentrations in retentate for co-current and counter-current flow patterns for a (50%-50%) mixture at 35 bars and 308 K.

b- Influence of feed flow rate on CH_4 concentrations in retentate for co-current and counter-current flow patterns for a (50%-50%) mixture at 35 bars and 308 K.

therefore CH_4 concentration in retentate will be increased (Figure **5b**).

3.2. Effect of Feed Flow Rate

The influence of feed flow rate on CO_2 and CH_4 permeation for co-current and counter-current flow patterns have been shown in Figures **6a** and **6b**.

By increasing feed flow, the fraction of CO₂ removed from the feed decreases, consistent with the

shorter contact time of the high-pressure residue gas with the active membrane area at higher feed flow rates, therefore the concentration of CO_2 in retentate will be increased.

3.3. Effect of Permeate Pressure

Permeate pressure is a key parameter for membrane unit design. The CH_4 and CO_2 concentration profile in retentate for co-current and



Figure 7: a- CO_2 concentration profile in retentate for co-current and counter-current flow patterns as a function of permeate pressure for a (50%-50%) mixture at 35 bars and 308 K.

b- CH₄ concentration profile in retentate for co-current and counter-current flow patterns as a function of permeate pressure for a (50%-50%) mixture at 35 bars and 308 K.



Figure 8: a- Influence of CO₂ concentration in feed on CO₂ concentrations in retentate for co-current and counter-current flow patterns at 35 bars and 308 K.

b- Influence of CO₂ concentration in feed on CH₄ concentrations in retentate for co-current and counter-current flow patterns at 35 bars and 308 K.

counter-current flow patterns as a function of permeate pressure have been depicted in Figures **7a** and **7b**.

The results showed the permeate pressure has considerable effect on CO_2 concentration in the retentate due to driving force reduction for both flow patterns, but the co-current pattern is more sensitive than counter-current. By increasing pressure, CO_2 passage through the membrane will be decreased.

Opposite behavior was observed for CH_4 concentration profiles in retentate stream for co-current and countercurrent patterns.

3.4. Effect of CO₂ Concentration in Feed

The most important parameter in membrane process design is concentration of impurities in feed. Required membrane area and the number of modules



Figure 9: a- Effect of fiber's length on CO_2 concentration profiles in retentate stream for co current and counter current flow patterns for a (50%-50%) mixture at 35 bars and 308 K.

b- Effect of fiber's length on CH₄ concentration profiles in retentate stream for co current and counter current flow patterns for a (50%-50%) mixture at 35 bars and 308 K.

depend on the impurities in feed. In CO_2/CH_4 separation, as feed CO_2 concentration increases, the amount of gas that can be diffused decreases because more CO_2 must be removed from the feed gas with a fixed amount of membrane area. Figures **8a**, **8b** represent the influence of CO_2 concentration in feed on CO_2 and CH_4 concentrations in retentate for both co-current and counter-current patterns, respectively.

3.5. Effect of Fiber's Length

By increasing fiber's length, membrane area raises. This arrangement will prepare higher membrane area and leads to higher permeation of gases. More permeation of CO_2 makes higher concentration of CO_2 compared with CH_4 in permeate stream, therefore by increasing fiber's length while the number of fibers are constant, CO_2 concentration in permeate stream will be raised. Figures **9a** and **9b** indicate the effect of fiber's length on CO_2 and CH_4 concentration profiles in retentate stream for co-current and counter- current flow patterns, respectively.

3.6. Effect of Feed and Permeate Pressures on Membrane Area

Membrane area is considered as the most important design variable for economical evaluation. Increasing membrane area can raise capital cost; therefore optimum condition should be determined. Pressure changing of feed and permeate change the membrane area for a special permeate purity. Figure **10** indicates the influence of permeate and feed pressures on



Figure 10: Influence of permeate and feed pressures on membrane area for 98% purity of methane in permeate stream in counter current flow pattern at 308 K.

membrane area for 98% purity of methane in permeate stream in a counter current flow pattern. Results show the required membrane area is raised by increasing permeate pressure and declined by increasing feed pressure. Also it is obvious that required membrane area increases sharply for low pressure feeds and high pressure permeates.

4. CONCLUSION

A shell-fed co-current and counter-current hollow fiber module was modeled mathematically for CO₂ separation from CH₄ in Ethylene Oxide plant of Marun Petrochemical Company as an environmental policy. This model is valid to predict specifications of retentate and permeate streams at various conditions. Comparison of co-current and counter-current flow patterns showed such as the other unit operations, the counter current pattern had better efficiency for CO_2/CH_4 separation for all conditions. It was found that feed flow rate, feed pressure and module fiber length had direct effect and permeate pressure had adverse effect on CH₄ purity in the retentate for both flow patterns. Also required membrane area increased by increasing permeates pressure and decreased by increasing feed pressure. Because of having no data about fixed properties of used membrane and changing membrane behavior with temperature, study of these parameters on separation factor were impossible. Application of a membrane with much information about membrane properties and performance is suggested. Modeling of CO₂ separation from ternary and multi-component gas mixture and comparison of finite difference method with other solving methods such as orthogonal collocation are future directions of this work.

5. NOMENCLATURES

- A = membrane area, $[m^2]$
- A_i = see equation 22, [-]
- b_i = see equation 22, [-]
- C_i = concentration of component i, [mol/m³]
- D_i^{-} = diffusion coefficient for component i, $[m^2/s]$
- D_i = inner diameter of fiber, [m]
- $D_{LM} = \log \text{ mean diameter of fiber, [m]}$
- D_o = outer diameter of fiber, [m]

- F_0 = feed flow rate, [mol/s]
- J_i = diffusion of component i, [mol/ (m².s)]
- K_1 = constant see equation 8, [-]
- K_2 = constant see equation 9, [-]
- L = dimensionless form of retentate flow rate, [-]
- L = retentae flow rate, [mol/s]
- I_E = effective length of fiber in module, [m]
- N_F = number of fibers, [-]
- P_F = feed pressure, [Pa]
- P_n^G = Permeability of component n, [mol/ (m.Pa.s)]
- P_{P} = permeate pressure, [Pa]
- Q = Volumetric flow rate in permeate side, [m³/s]
- Q_i = Permeance of component i, [mol/ (m².Pa.s)]
- $R_g = Universal gas constant, [Pa.m³/ (mol.K)]$
- T = Temperature, [K]
- V = dimensionless form of permeate flow rate, [-]
- V = permeate flow rate, [mol/s]
- x _ mole fraction of fast gas in shell side, [-]
- x_F = mole fraction in feed,[-]
- y = mole fraction of fast gas in tube side, [-]
- z = dimensionless form of diffusion direction,[-]
- z = diffusion direction,[m]

Greek Letters

- α_i = selectivity for component i, [-]
- γ = permeate pressure to feed pressure ratio, [-]
- μ = gas mixture viscosity, [Pa/s]
- ω = see equation 15, 21, [-]

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Received on 18-07-2012

Accepted on 24-08-2012

Published on 04-10-2012

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