Hollow fiber membrane model for gas separation: Process simulation, experimental validation and module characteristics study

Faizan Ahmad a,*, K.K. Lau b, S.S.M. Lock b, Sikander Rafiq c, Asad Ullah Khan c, Moonyong Lee a,*

a Process Systems Design and Control Laboratory, School of Chemical Engineering, Yeungnam University, Republic of Korea
b Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Sri Iskandar, 31750 Perak, Malaysia
c Department of Chemical Engineering, COMSATS Institute of Information Technology, Lahore, Pakistan

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Conceptual process simulations and optimization are essential in the design, operation and troubleshooting stages of a membrane-based gas separation system. Despite this, there are few mathematical models/tools associated with a hollow fiber membrane module available in a commercial process simulator. A mathematical model dealing with the hollow fiber module characteristics that can be included within a commercial process simulator is needed to examine the performance and economics of a gas separation system. In this study, a hollow fiber membrane model was incorporated in Aspen HYSYS as a user defined unit operation for the study of carbon dioxide separation from methane. The hollow fiber membrane model was validated experimentally. The study of a double stage membrane module with a permeate recycle, which was proposed to be the optimal configuration in previous studies, was extended to consider the effects of the module characteristics (such as the fiber length, radius of the fiber bundle, diameter of the fibers, and porosity) on the process performance and economics. The gas processing cost (GPC) increased with increasing fiber length and bundle radius, and decreased with increasing outer diameter of the fibers and porosity. At the same time, the separation efficiency (product quality) was also dependent on these module parameters. Therefore, the tradeoff for the hollow fiber membrane module characteristics needs to be determined based on the minimum GPC with respect to the desired product purity.

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INTRODUCTION

Membrane separation processes have been used successfully in the industrial separation of gases because of their many advantages, such as environmental friendly, favorable economics, ease of operation, and low maintenance, over conventional separation techniques [1–3]. In general, membrane separation units use spiral-wound, capillary-fiber and hollow-fiber modules because of the large membrane area packed in a small volume [4, 5].

The hollow-fiber membrane module, which has wide applications, consists of a large number of membrane fibers packed in module shell housing. Typically, the feed gas at higher pressure enters the shell side of the module at one end, and the more permeable components are withdrawn from the inside of the fibers through openings on the fiber tube sheet [6, 7].

In many areas of chemical process design and operation, the application of mathematical models for process synthesis, optimization and control studies has significant advantages [8]. Similarly, the mathematical modeling of membrane separation systems is an essential and integral aspect for better understanding the effects of various process parameters and flow patterns on the membrane performance [9]. When evaluating the performance of hollow fiber membrane modules for gas separation, mathematical modeling offers the advantages of cost effectiveness, safety and flexibility to extensive parametric studies compared to pilot plant testing.

Weller and Steiner developed the first mathematical model for membrane gas separation dealing with binary component gas mixtures using a non-porous membrane [10]. Pan presented a model for the practical representation of gas separation using a high flux, asymmetric hollow fiber membrane [11]. The
**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>membrane separation area (in.²)</td>
</tr>
<tr>
<td>( A_m )</td>
<td>cross section area of membrane module (in.²)</td>
</tr>
<tr>
<td>( A_f )</td>
<td>cross section area of fiber (in.²)</td>
</tr>
<tr>
<td>BPC</td>
<td>base plant cost (USD)</td>
</tr>
<tr>
<td>CC</td>
<td>installed compressor cost (USD)</td>
</tr>
<tr>
<td>CH₄LS</td>
<td>annual cost of methane loss in permeate (USD/year)</td>
</tr>
<tr>
<td>CMC</td>
<td>annual contract and material maintenance cost (USD/year)</td>
</tr>
<tr>
<td>CRC</td>
<td>annual capital related cost (USD/year)</td>
</tr>
<tr>
<td>DL</td>
<td>direct labor cost (USD/year)</td>
</tr>
<tr>
<td>d_i</td>
<td>inner diameter of fibers (in.)</td>
</tr>
<tr>
<td>d_o</td>
<td>outer diameter of fibers (in.)</td>
</tr>
<tr>
<td>d_m</td>
<td>diameter of membrane module (in.)</td>
</tr>
<tr>
<td>FC</td>
<td>fixed cost (USD)</td>
</tr>
<tr>
<td>GPC</td>
<td>gas processing cost (USD/MSCFD of natural gas product)</td>
</tr>
<tr>
<td>J</td>
<td>gas permeation flux through membrane (MMSCF/ft² day)</td>
</tr>
<tr>
<td>LOC</td>
<td>annual labor overhead cost (USD/year)</td>
</tr>
<tr>
<td>LTI</td>
<td>annual local tax and insurance cost (USD/year)</td>
</tr>
<tr>
<td>L</td>
<td>length of fibers (in.)</td>
</tr>
<tr>
<td>l</td>
<td>membrane life (years)</td>
</tr>
<tr>
<td>MC</td>
<td>total cost of membrane modules (USD)</td>
</tr>
<tr>
<td>MMBTU</td>
<td>10⁶ BTU</td>
</tr>
<tr>
<td>MSCFD</td>
<td>10⁶ ft³/day</td>
</tr>
<tr>
<td>MRC</td>
<td>annual membrane replacement cost (USD/year)</td>
</tr>
<tr>
<td>NGLS</td>
<td>annual loss of natural gas (MSCFD/year)</td>
</tr>
<tr>
<td>NHV</td>
<td>heating value of natural gas (1066.8 MMBTU/MMSCF)</td>
</tr>
<tr>
<td>NWP</td>
<td>wellhead price of crude natural gas (USD/MMBTU)</td>
</tr>
<tr>
<td>N_f</td>
<td>number of fibers/cross section area of fiber (in.⁻²)</td>
</tr>
<tr>
<td>n</td>
<td>number of fibers</td>
</tr>
<tr>
<td>n_1</td>
<td>number of fibers</td>
</tr>
<tr>
<td>n_2</td>
<td>number of fibers</td>
</tr>
<tr>
<td>n_3</td>
<td>number of fibers</td>
</tr>
<tr>
<td>n</td>
<td>index of membrane stage</td>
</tr>
<tr>
<td>OSF</td>
<td>on stream factor</td>
</tr>
<tr>
<td>P</td>
<td>project contingency (USD)</td>
</tr>
<tr>
<td>P_1</td>
<td>permeability of component A (barrer)</td>
</tr>
<tr>
<td>P_2</td>
<td>permeability of component B (barrer)</td>
</tr>
<tr>
<td>Q_f</td>
<td>feed flow rate (in.³(STP)/s)</td>
</tr>
<tr>
<td>Q_p</td>
<td>permeate flow rate (in.³(STP)/s)</td>
</tr>
<tr>
<td>Q_c</td>
<td>product/retentate flow rate (in.³(STP)/s)</td>
</tr>
<tr>
<td>R</td>
<td>radius of fiber bundle (in.)</td>
</tr>
<tr>
<td>R_g</td>
<td>Universal gas constant (psi R⁻¹ lb-mol⁻¹)</td>
</tr>
<tr>
<td>p_h</td>
<td>pressure on the high pressure side (psia)</td>
</tr>
<tr>
<td>p_l</td>
<td>pressure on the low pressure side (psia)</td>
</tr>
<tr>
<td>SC</td>
<td>start up cost (USD)</td>
</tr>
<tr>
<td>SCF</td>
<td>standard cubic feet (at standard temperature and pressure)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (°F)</td>
</tr>
<tr>
<td>TFI</td>
<td>total facilities investment (USD)</td>
</tr>
<tr>
<td>TPI</td>
<td>total plant investment (USD)</td>
</tr>
<tr>
<td>UC</td>
<td>annual utility cost (USD/year)</td>
</tr>
<tr>
<td>UCP</td>
<td>utility cost (USD/kWh)</td>
</tr>
<tr>
<td>u</td>
<td>index of finite element in radial direction</td>
</tr>
<tr>
<td>VOM</td>
<td>annual variable operating and maintenance cost (USD/year)</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu )</td>
<td>index of finite element in axial direction</td>
</tr>
<tr>
<td>( W_{cp} )</td>
<td>power requirement for compressors (hp)</td>
</tr>
<tr>
<td>( x_1 )</td>
<td>mole fraction of carbon dioxide on shell side</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>mole fraction of methane on shell side</td>
</tr>
<tr>
<td>( y_1 )</td>
<td>mole fraction of carbon dioxide on tube (permeate) side</td>
</tr>
<tr>
<td>( y_2 )</td>
<td>mole fraction of methane on tube (permeate) side</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>selectivity of the membrane</td>
</tr>
<tr>
<td>( \beta )</td>
<td>pressure ratio</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>porosity of the membrane (%)</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>packing density (%)</td>
</tr>
<tr>
<td>( \Delta Q )</td>
<td>molar permeation into an element (in.³(STP)/s)</td>
</tr>
<tr>
<td>( \Delta r )</td>
<td>radial increments</td>
</tr>
<tr>
<td>( \Delta z )</td>
<td>axial increments</td>
</tr>
<tr>
<td>( \delta )</td>
<td>membrane thickness (in.)</td>
</tr>
<tr>
<td>( \psi_{cp} )</td>
<td>compressor efficiency (%)</td>
</tr>
</tbody>
</table>

Assumption of constant permeate pressures is reasonable for a flat sheet and tubular membrane modules with small permeability values and cut fractions. On the other hand, modules employing hollow fibers cause significant pressure drops due to flow in the narrow channels [9]. Thorman et al. [12] incorporated the effects of a pressure drop in a study on the separation of binary mixtures employing silicone rubber capillaries. Antenson et al. [13] showed that the feed inside the fibers mode is better than the feed outside the type of operation. In all cases, the Hagen–Poiseuille equation is assumed to be applicable for estimating the pressure profiles.

Chern et al. [14] examined the case of a shell-side feed and countercurrent pattern and analyzed the effects of the process and design variables. The fiber dimensions were found to play a significant role, in affecting the permeate flow rate and purity. Thundyil and Koros presented a new approach [15] to solve the mass transfer problem posed by the permeation process in a hollow fiber membrane separator. In another type of model, Coker et al. [16] proposed an algebraic stage-wise method to solve the problems posed by hollow fiber separation.

Zhao et al. [17] developed a mathematical model to describe a hollow fiber membrane separator for binary gases including water vapor under a low feed gas pressure and vacuum. Similarly, Lemanski and Lipscomb [18] conducted a theoretical and experimental study of the effects of the variable fiber properties on countercurrent hollow fiber gas separation module performance.

Khalilpour et al. [19] analyzed hollow fiber separation, and proposed a general finite difference method coupled with the Gauss–Seidel algorithm to solve the non-linear membrane differential algebraic equations. Recently, Sohrabi et al. developed a 2D model [20] to examine CO₂ transport through hollow fiber membranes. Furthermore, Ebadi Amooghin et al. [21] presented a new mathematical model to investigate the gas mixture permeation across a synthesized composite polymeric membrane.

In a membrane separation system, the membrane units are most likely to be part of a complex process flow sheet along with other unit operations. Therefore, it is advantageous to introduce the membrane unit into a commercial process simulator, which will provide a tool for simulating, designing and optimizing the overall process rather than an isolated membrane module.

Aspen product technology is favorable simulation software for modeling and simulating various membrane processes on an industrial scale because it provides a component-based framework...
that can be customized, updated and maintained easily to overcome changing user requirements [22–24]. A built-in model for a membrane separation system is not available in the standard version of Aspen HYSYS but it can be implemented along with its solution procedure using a Visual Basic (VB) or C++ subroutine.


A review of the literature [3,25–31] indicated that the study of hollow membrane model in a commercial process simulator that deals with the membrane module characteristics is limited. This scenario impedes the end-user to design and optimizes the hollow fiber membrane system using a commercial simulator.

Recently, we proposed a new method [32] to implement a cross flow model in Aspen HYSYS for CO2 capture from natural gas. This method was also used to examine the non-ideal effects of the process economics of gas separation systems [33]. On the other hand, the cross flow model was limited to examining the effects of the operating conditions and membrane selectivity on the gas processing cost [32]. A model that can include the depth of the module level and study its characteristics effects, such as fiber length, radii of fiber bundle, diameter of fiber, and porosity, on the process sensitivity and gas processing cost is needed.

In this study, an experimentally-validated hollow fiber membrane model was implemented in Aspen HYSYS as a user defined unit operation along with other available unit operations using the finite element method in the Visual Basic (VB) subroutine. This paper reports the results of a case study of CO2 removal from natural gas using a hollow fiber membrane to evaluate the performance and economics of a gas separation system. The membrane module characteristics, such as length of fiber, radii of the fiber and bundle, and porosity, were manipulated to yield different hollow fiber membrane performance data.

**Methodology**

**Mathematical method**

The solution diffusion model is the most widely accepted transport mechanism for gas separation through membranes. This consists of the following three steps: the sorption of feed gas molecules into the membrane interface followed by diffusion through the complete membrane thickness and finally desorption of the absorbed gas on the permeate side. The governing flux equation is given by Fick’s law of diffusion, where the driving force is the partial pressure difference over the membrane:

\[
J_i = \frac{P_i}{\delta} (p_i x_i - p_y y_i) \quad (1)
\]

where \( J_i \) is the flux of the gas component, \( p_i \) and \( p_y \) are the feed and permeate side pressures, respectively, \( x_i \) and \( y_i \) are the fractions of component \( i \) on the feed and permeate sides, respectively, and \( \delta \) is the membrane thickness.

For a binary gas mixture, the local permeation rate at any point in the stage over a differential membrane area, \( dA_m \), can be expressed as

\[
ydV = \frac{P_1}{\delta} (p_n x_n - p_y y) dA_m \quad (2)
\]

\[
(1 - y) dV = \frac{P_2}{\delta} (p_n (1 - x) - p_n (1 - y)) dA_m \quad (3)
\]

The following can be obtained by dividing Eq. (2) by Eq. (3):

\[
y = \frac{\alpha (x - (p_i/p_n)y)}{(1 - x) - (p_i/p_n)(1 - y)} \quad (4)
\]

where \( P_1 \) and \( P_2 \) are the permeabilities of the pure gas components (CO2 and CH4 in this work), \( x \) and \( y \) are the feed and permeate composition at any point along the membrane, \( \delta \) is the membrane thickness, and \( \alpha \) is the membrane selectivity [4]. The separation efficiency of two components \( i,j \) is a measured by the ratio of their permeability values known as selectivity. It is given by

\[
\alpha_{ij} = \frac{P_i}{P_j} \quad (5)
\]

Fig. 1 presents a schematic diagram of the hollow fiber membrane model. The bundle of fibers is sealed at one end while the other end of the fiber bundle is kept open to allow the flow of gases. The fiber bundle is housed as a tube in the middle of a shell. The feed gas is introduced in the system from the shell side that

![Fig. 1. Schematic diagram of the hollow fiber membrane separation.](Image)
flows radially inward perpendicular to the fibers toward the center. The permeate in the fibers flows axially to the permeate collector. As a result, the flow rates and compositions vary both axially and radially, making it a two-dimensional model.

The assumptions for the suggested model are as follows:

1. The model holds only for a binary gas mixture. Although it is an ideal assumption, it is a first step in understanding realistic modeling and simulation of many important separations [11,15,29,34–36], such as CO2–methane separation in the current work.

2. The shell side pressure variations were negligible due to constant bulk flow in an axial direction, whereas the permeate side pressure drop was determined using the Hagen–Poiseuille equation [11,15,26,29,36].

3. The permeabilities of the mixed gas were same as those of the pure components [15].

4. The system operates under isothermal conditions [3,11,15,26,29,36].

One of the approaches used to solve this two dimensional model is the ‘succession of states’ or finite element method. The main advantage of the finite element method over a solution of differential equations is that it is easy to incorporate non ideal effects in the former method, such as the permeate pressure drop in the fiber and tube sheet, Joule Thompson (JT) effect, and pressure and temperature dependence of membrane permeability. The method divides the membrane area into a number of elements with a constant driving force and specified inlet conditions, and calculates the mass transfer to obtain the outlet conditions [15].

The hollow fiber membrane module is characterized mainly by [15,37,38]:

(a) Dimensions of the fibers bundle, such as the fiber length, \( L \), and radius of fiber bundle, \( R \).

(b) Inner and outer diameter of the fibers, \( d_i \) and \( do \).

(c) Measure the packing density and porosity.

The packing density of the hollow fiber membrane module is defined as the fraction of the cross section area of all fibers over the cross section area of the module [38]:

\[
\text{packing density} = n_f A_f / A_m = n_f do / A_m
\]  

where \( n_f \) is the number of fibers, \( A_f \) is the cross section area of the fibers, and \( A_m \) is the cross section area of the module. Furthermore; number of fibers/cross sectional area of the fiber (\( N_f \)), porosity of the fiber bundle (\( \epsilon \)), and membrane area/bundle volume (\( A/V \)) are connected as follows [15]:

\[
N_f = \frac{1 - \epsilon}{\pi/4 d_i^2}
\]  

\[
\frac{A}{V} = \frac{(1 - \epsilon) A}{d_o}
\]  

The model divides the fiber bundle (tube side) into a predetermined number of elements. The elements can be divided into four types depending upon their radial and axial location in the fiber bundle of the module, as shown in Fig. 2. The calculation proceeds from the Type I to Type III elements until the end of the bundle and then start again from the Type II elements through the succession of Type IV elements. The number of elements in the radial direction (index \( u' \)) is \( N \), whereas the number of elements in the axial direction (index \( v' \)) is \( M \) [15].

Fig. 3 shows the element \((u, v)\) over which mass transport occurs. The finite element is assumed to exist at a radius, \( r \), from the center of the bundle with radius of \( D_r \) and length of \( D_z \). The membrane separation area of each finite element is determined by its volume \((2\pi r \Delta r \Delta z)\), and the specific area of the membrane bundle (membrane bundle area/unit volume of membrane bundle) is as follows:

\[
A = 2\pi \Delta r (\Delta z)(1 - \epsilon)/d_o
\]  

For a binary system, the permeate composition, \( y_1 \) (faster permeating component), in the first and second types (Type I and
Type II) of the finite elements is given in terms of the mole fraction of the shell side, \( x_1 \) (faster permeating component), as follows [15]

\[
y_1 = \frac{((\alpha - 1)\beta x_1 + 1) + \beta - ((\alpha - 1)(\beta x_1 + 1) + \beta)^2 - 4\alpha \beta x_1 (\alpha - 1)^{0.5})}{2(\alpha - 1)}
\]  

(10)

where \( \alpha \) is the selectivity of the membrane and \( \beta \) is the pressure ratio of higher pressure side to lower pressure side. The flow rate into the finite element of the permeate side is given by the following equation:

\[
\Delta Q = \left( \frac{P_1}{\beta} \right) (p_h x_1(u - 1, j) - p_y y_1(u, j)) + \left( \frac{P_2}{\beta} \right) (p_h x_2(u - 1, j) - p_y y_2(u, j)) A
\]

(11)

where \( x_2 = 1 - x_1 \) and \( y_2 = 1 - y_1 \) (binary component gas mixture).

Similarly, the shell side flow rate, \( Q_s(u, 1) \), and permeate side flow rates, \( Q_s(u, 1) \) contacting the next element are given by

\[
Q_s(u, 1) = Q_s(u - 1, 1) - \Delta Q
\]

(12)

\[
Q_T(u, 1) = \Delta Q
\]

(13)

The shell side composition, \( x_1(u, 1) \), of respective element is given by

\[
x_1(u, 1) = \frac{Q_s(u - 1, 1) x_1(u - 1, 1)}{Q_s(u, 1)}
\]

(14)

For elements in contact with the feed (Type I), the suffixes \( (u - 1, 1) \) are replaced with the feed conditions, such as \( Q_s \) and \( x_1 \). These elements will not have any preceding elements in the radial direction.

For Type III and Type IV elements, the shell and tube flow rates and compositions are known and mass transport is measured by solving the following equations [15]:

\[
\Delta Q = \left[ \left( \frac{P_1}{\beta} \right) (p_h x_1(u - 1, v) - p_y y_1(u, v)) \right] A + \left[ \left( \frac{P_2}{\beta} \right) (p_h x_2(u - 1, v) - p_y y_2(u, v)) \right] A
\]

(15)

\[
\Delta Q_1 = \left[ \left( \frac{P_1}{\beta} \right) (p_h x_1(u - 1, v) - p_y y_1(u, v)) \right] A
\]

(16)

\[
Q_s(u, v) = Q_s(u - 1, v) - \Delta Q
\]

(17)

\[
Q_T(u, v) = Q_T(u - 1, v) + \Delta Q
\]

(18)

\[
x_1(u, v) = \frac{Q_s(u - 1, v) x_1(u - 1, v) - \Delta Q_1}{Q_s(u, v)}
\]

(19)

\[
y_1(u, v) = \frac{Q_T(u - 1, v) y_1(u - 1, v) + \Delta Q_1}{Q_T(u, v)}
\]

(20)

where \( \Delta Q_1 \) is the permeation rate of component 1 in the element, and \( \Delta Q \) is the total permeation rate in the element. For elements in contact with the feed (Type III), the suffixes \( (u - 1, v) \) are replaced with the feed conditions, such as \( Q_s \) and \( x_1 \).

The viscosity of the gas mixture was calculated using Wilke’s method, whereas the viscosity of the pure components and their temperature dependence were determined using Lucas’ method [39]. The expressions based on these methods are given in Appendix.

Mass transport across the membrane for each element can be computed by solving Eqs. (10)–(20). The calculation proceeds from the epoxy sealed end of the hollow fiber tubes to the tube-sheet end of these fibers.

**Simulation and design aspects**

In this study, hollow fiber membrane model (Fig. 1) was interfaced with the process simulation program (Aspen HYSYS) to calculate permeate and retentate flow rates and compositions, allowing complex process simulations.

The hollow fiber membrane extension in Aspen HYSYS consists of two independent components. An ActiveX Server dynamic link library (DLL) and an extension definition file (EDF). The ActiveX Server DLL contains the actual code for the extension. Visual Basic (VB) provides the easiest development environment to create a unit operation extension [22]. Therefore, it is applied to create an extension for the hollow fiber membrane model within Aspen HYSYS in the present study. The EDF file works as the interface view within Aspen HYSYS and is the point for variable declaration and storage. The file is created through the Extension View Editor that is included in the Aspen HYSYS package [22,32].

The permeate and product compositions, flow rates, and membrane area required for separation are calculated by solving Eqs. (9)–(19) using VB code as a subroutine in ASPEN HYSYS. These parameters, along with the methane loss, stage cut and compressor power, define the gas processing cost (GPC) for the membrane system.

The compressor power is given by the expression [40]:

\[
W_{cp}(hp) = R_g T \sum_{n=1}^{2} Q_{p,n} \ln \left( \frac{p_h}{P_{in}} \right) \times 1.341
\]

(21)

where \( Q_p \) is the permeate flow rate, \( n \) is the index of membrane stage, \( T \) is the temperature and \( R_g \) is the ideal gas constant.

Table 1 lists the procedure to calculate the gas processing cost (GPC). This includes the capital related cost (CRC), the variable operating and maintenance cost (VOM), and the cost of CH₂ lost in the permeate stream (CH₄LS) [17,29,41]. The GPC must be a minimum subject to the operating conditions, material and energy balances, and individual permeator mathematical model [36]. It should also be noted that retentate is considered as product in the current study.

One of the approaches to the design of a membrane separation process is to select a small number of design configurations and optimize the operating conditions of each configuration. The final optimal design is chosen to be the system with the most favorable economics [15,42–44]. A previous study [32] reported that a double stage with a permeate recycle system (shown in Fig. 4) gives the optimal design configuration due to the minimum process gas cost involved with it. This study will be conducted further into the depth of the module level and its characteristics effect, such as fiber length, radii of the fiber bundle, diameter of fiber, and porosity, on the process sensitivity and gas processing cost for the abovementioned best design configuration.

**Simulation conditions**

The composition, flow rates, pressures and temperature of crude natural gas depend mainly on the source. Therefore, the feed conditions distinctive for a medium sized natural gas treatment plant to remove the acid gases were selected. As a result, the feed flow rate of crude natural gas was maintained at 1.3 MMSCF whereas the feed pressure and permeate pressures were maintained at 1000 psia and 20 psia respectively. Unless specified otherwise, the simulations were run at a fiber length of 100 cm (39.37 in.) and a fiber bundle radius of 10 cm (3.94 in.).
The hollow fiber module was composed of fibers with an outer diameter of 0.040 cm (0.016 in.) and a porosity of 50% unless specified otherwise [15]. The porosity was varied from 45% to 60% to avoid higher or lower packing densities. A lower packing density may cause flow channeling outside the hollow fibers, whereas a higher packing density can lead to a decrease in flow space for shell-side feeding, which may cause an unexpected higher pressure drop [38].

Natural gas contains different amounts of CO2 ranging from sweet (CO2-free) gas in Siberia to very high CO2 content of 90% in the Platong and Erawa fields in Thailand [45]. The natural gas field in the Greater Sarawak Basin (Indonesia), with estimated 46 trillion cubic feet recoverable reserves, remains undeveloped due to high CO2 contents of 71% [45,46]. In Malaysia, 13 trillion cubic feet natural gas reserves are undeveloped due to high CO2 content that varies from 28% to 87% [46,47]. Therefore, three cases have been investigated including lower concentration feed (10% CO2), medium concentration feed (40%) and higher CO2 concentration feed (70% CO2).

The simulations were run for a membrane material of polyimide, which exhibits a CO2 permeance of 50 GPU and a CO2/CH4 selectivity of 30 according to the published data [15]. The temperature of the feed stream was maintained at 104 °F (40 °C) before being introduced into the membrane using a cooler.

### Experimental method

Mathematical models must be supported and validated by experimental data. Therefore, the proposed model was verified by a comparison of the simulated and experimental results. The experimental setup consisted of a hollow fiber membrane module and a gas separation testing unit, where the module is installed, to evaluate the performance of the membrane.

### Module manufacture

The early designs of hollow fiber modules were derived from the patents of Dow [48] and DuPont [49]. In design from Dow, modules were formed by potting the ends of the individual fibers or a fiber tow in the form of a plug. Finally, the plugs were placed in the holes (arranged in a regular array) of two opposite metal plates. In the DuPont design, loops of fibers were formed by winding the individual fibers or fiber tows around a rotating wheel. Tubesheets were formed by placing a mold over the end of the fiber that possessed connections to introduce a tubesheet forming material, such as epoxy resin [50].

Hollow fiber modules might have different configurations to meet the needs of the different applications. The present work used shell-side feeding hollow fiber module, as shown in Fig. 1. In this configuration, two tube sheets hold the fiber ends in place and separate the retentate from the permeate flow. One is a plug-sealed
tube sheet, in which the openings of the fiber ends are blocked by the epoxy resin; the other is an open-end tube sheet, in which the bores of the hollow fibers are exposed [38].

The hollow fibers used for the experimental work are commercial (Alpha Membrane Hi-Tech Pte. Ltd, Singapore). The material of the membrane used is polyimide with a permeance of 10 GPU for CO₂ and 0.25 GPU for CH₄ at 50 °C. The fibers have an outer diameter of 400 μm (0.016 in.) and an inner diameter of 180 μm (0.007 in.). The required number of fibers and the fiber length were calculated based on the diameter of the hollow fibers and the length of the module assuming a 40–50% packing density. For the test in the current study, the fibers were cut into approximately 28 cm lengths. Five different cases, 5, 15, 20, 30 and 50 fibers in the bundle, were investigated.

Using the same procedure for bundle preparation, as explained in the literature [38,51], the fibers were cut to the desired length while defective fibers were removed. The remaining fibers were placed in parallel order as a fiber bundle. A piece of barrier film (Parafilm M®) was taken, stretched and wrapped on one end of the fiber bundle. The end of the fiber bundle became denser due to shrinkage of the film. The wrapped side was cut with a sharp razor blade to yield a smooth end.

Shells made from stainless steel (SS 316) with an outer diameter of 1/2 in. (1.27 cm) and 1 in. (2.54 cm) were used. With the help of string, the fiber bundle was housed in the shell. The void space between the fibers and the internal wall of the shell was potted, i.e., filled with epoxy glue (Loctite® E-30CL Hysol® adhesive). The purpose was to separate the permeate stream from the retentate stream. Unlike the open side, the other side of the fibers was sealed completely by the epoxy glue to form a dead end. The glue hardened in several minutes but reached its maximum strength in 24 h. The openings of the fibers were inspected carefully to ensure that all were properly embedded in the glue.

**Separation testing unit**

A hollow fiber membrane module was installed in the experimental set up, as shown in Fig. 5. The testing unit consisted mainly of gas cylinders, mass flow controllers, compressor, and infrared analyzer. Natural gas (with impurities) and pure methane can be used alternatively in the set up. In addition, nitrogen was used to purge the separation system. In the current study, pure methane and CO₂ were used to evaluate the performance of the separation system.

Mass flow controllers (Sierra Smart Trak 2), which can control up to 100 standard liters per minute (3.53 ft³/min) were used. They were calibrated according to each type of gas. The compressor (DMC-3/200) had a capacity of 3 N m³/h (105.94 ft³/h) and could compress the gases up to an outlet pressure of 100 bar.

Thermocouples and pressure gauges were installed before and after the permeation test cell to monitor the temperature and pressure drop across the membrane module. A back pressure regulator was fixed after the membrane module to generate the trans-membrane pressures needed to separate the gases. Coriolis flow meters were used to measure the mass flow rates of the feed and retentate streams. In addition, a bubble flow meter was used to measure the flow rate of the permeate stream. This is a simple but highly accurate way of measuring the flow rates, and involves the measurement of time for the movement of bubbles of a soap film up the glass tubes between the marks with a known volume.

An infrared gas analyzer was used to measure the composition of the feed, permeate and retentate streams. They were connected...
to a data acquisition system to record the gas concentrations of the streams at different times. The whole system except the feed cylinders, compressor and analyzer was placed in an oven to maintain the temperature of the system and isolate it from external effects.

Results and discussion

Model validation and error analysis

The suggested hollow fiber membrane model was validated experimentally by assessing CO2 removal from natural gas using a membrane separation process. The CO2 concentration in the feed gas was varied from 20% to 70% at a constant feed pressure of 10 bar. The temperature of the feed gas was 303 K (545.4°F). The material of the membrane used was polyimide (matrimid) with a CO2 permeance of 10 GPU and a CH4 permeance of 0.25 GPU. Therefore, the selectivity of the membrane used was 40. Furthermore, the feed gas flow rate was maintained at 10 standard liters per minute (0.353 ft3/min) for the simplest design configuration of a single stage membrane system without a recycle stream. Fig. 6(a) shows the experimental and simulated results of a stage cut as a function of CO2 contents in the feed.

The number of fibers in the module was varied from 5 to 50 to determine its effect on stage cut, as shown in Fig. 6(b), and compared it with the simulations performed under the same conditions. The suggested model was in agreement with the experimental results with a maximum error of <10%. The error might be because non-ideal effects, such as the pressure and temperature effects on the membrane permeance, and the Joule Thompson effect, were not considered in the suggested model.

The model is further compared to experimental data published by Pan [11] as shown in Fig. 6(c). The data is based on the experiments performed on sour natural gas. Feed conditions used are 48.5% CO2, 27.9% CH4, 16.26% C2H6 and 7.34% C3H8. The membrane material is cellulose acetate with permeance values of 40.05 for CO2, 1.11 for CH4, 0.31 for C2H6 and 0.06 for C3H8 [6]. Thus, it can be assumed that most of heavy hydrocarbons (such as C2H6 and C3H8) pass to the product without permeating though the membrane. The simulations are performed in Aspen HYSYS on the basis of 48.5% CO2 and 27.9% of CH4 in the feed with membrane permeance values of 40.05 and 1.11 respectively while allowing other components to pass across the module without permeation. The temperature and pressure values of the gas are 10°C (50°F) and 35.28 bars, respectively, while the permeate pressure is 9.28 bar. The selectivity is assumed to be 25. The same process conditions are maintained for the simulated model and compared with the experimental data. Fig. 6(c) shows that the suggested model gives good approximation to the experimental data with maximum percentage error <3%.

The succession of states approach is based on the assumed dependence of mass transfer across a single element on the inlet conditions of that particular cell. Therefore, the asymptotic value obtained from a differential cell should be attained with a decrease in the size of the finite element [15]. To estimate the accuracy, the simulations were run for a different number of finite element divisions (25–500 elements on either axis). The results are compared in Fig. 7. The stage cut decreased slightly with increasing number of elements. The size of the cell decreased with increasing number of elements, resulting in a change in the inlet conditions for that cell. The stage cut remained relatively constant for 300 elements and above (with a difference of <0.01%) showing the simulation error within the acceptable limits. The number of elements were set to 500 on either axis (250,000 elements overall) for the parametric and economic study.

Fig. 6. Experimental validation of the hollow fiber flow model. (a) Effect of the CO2 content in the feed on stage cut. (b) Effect of the number of fibers on the stage cut. (c) Effect of stage cut on permeate CO2 mole fraction using data by Pan [11].

Parametric and economic analysis

To analyze the separation efficiency and processing cost of the CO2 removal process from natural gas, different membrane module characteristics, such as the fiber length, radius of the fiber bundle, outer diameter of fiber, and porosity, were varied to determine their effects on methane loss, stage cut, compressor power, and GPC.
Methane loss
Methane (CH₄) loss can be described as the percentage of methane lost in the permeate stream to the methane present in the feed stream. The loss increases with increasing membrane separation-area and vice versa [15].

Figs. 8 and 9 show the effects of the fiber length and radius of the fiber bundle, respectively, on CH₄ loss for different CO₂ concentration feed. The CH₄ loss increased with increasing fiber length and radius of the fiber bundle. An increase in fiber length and the radius of the fiber bundle basically enhances the membrane separation area. As a result, there will be higher permeation through the membrane, leading to higher methane loss.

Figs. 10 and 11 show the effects of the outer diameter of the fibers and porosity on the level of methane loss. The level of methane loss decreased in both cases but the extent of the decrease was more pronounced with a decrease in the outer diameter of fibers than the porosity of the membrane module. This is because the increase in outer diameter or porosity of the fiber at a constant fiber length and radius of the fiber bundle results in a decrease in membrane area. The decrease in membrane area leads to lower permeation and less methane loss.

Higher feed concentrations (40% CO₂ and 70% CO₂) lead to higher methane loss compared to lower feed concentrations (10% CO₂).

Stage cut and product/residue CO₂ composition
Stage cut is the ratio of the permeate flow rate to the feed flow rate for any membrane module. Figs. 12–15 show the effects of the fiber length, radius of the fiber bundle, outer diameter, and porosity on the stage cut respectively. Owing to the increase in membrane area, an increase in the fiber length and radius of fiber bundle improves the stage cut. On the other hand, an increase in the outer diameter and porosity has an opposite effect on the stage cut by decreasing it slightly.

These results can be explained by the fact that these module characteristics cause a change in the membrane separation area. The increase in membrane area improves the amount of CO₂ permeating through the membrane, leading to a higher stage cut [15,35] and vice versa.

Compressor power
The effect of the membrane module characteristics on the compressor power requirement was investigated for the proposed
design configuration. Figs. 16–19 show that the compressor power requirement increases with increasing fiber length and radius of the fiber bundle, whereas it decreases with increasing outer diameter of the fiber and porosity. In fact, these module characteristics change the membrane separation area, which causes a change in the stage cut, as explained in section ‘Stage cut and product/residue CO₂ composition’. By keeping the feed flow rate constant, a change in stage cut would mean a change in the permeate flow rate. Eq. (20) shows that compressor power depends on the permeate flow rate along with the feed and permeate pressures. Therefore, a change in permeate flow rate results in a change in compressor power requirement.

A change in the compressor power requirement is more pronounced at smaller fiber lengths and radii of the fiber bundle. Similarly, there is significant change in the power requirements with a change in the outer diameter of the fiber. On the other hand, a change in porosity causes a slight change in power requirements. This is due to the characteristics of the specific feed and operating conditions for the investigation.
Comparison study of separation efficiency and gas processing cost

Separation efficiency can be calculated as the ratio of the percentage of methane in the product to the methane in the feed. The variations in the fiber length, radius of the fiber bundle, fiber diameter and porosity were examined based on the desired separation efficiency and gas processing cost (GPC) for different CO₂ concentrations in the feed.

Figs. 20–22 show change in fiber length (membrane area) for different CO₂ feed concentrations based on the desired separation efficiency and GPC. Larger fiber lengths yield a higher GPC because the GPC depends mainly on membrane module cost (MC), compressor cost (CC) and annual cost of CH₄ lost in the permeate (CH₄LS). The above mentioned costs increase with increasing fiber length, as shown in previous sections, resulting in an increase in GPC.

The GPC was a minimum (0.018 USD/MSCFD of product) for a fiber length of 50 cm in the case of 10% CO₂ in the feed gas but at the same time, achieved a separation efficiency of 95.9%, as shown in Fig. 18. To increase the separation efficiency, larger fiber lengths are needed, which leads to an increase in GPC, because a higher membrane area would lead to an increase in the amount of methane in residue/product, resulting in higher separation efficiency.

In the cases of 40% and 70% CO₂ in the feed, the GPC was 0.026 and 0.032 USD/MSCFD of product with an achieved separation efficiency of 80.6% and 71.5%, respectively, as shown in Figs. 19 and 20. The increase in CO₂ concentration in the feed leads to a higher GPC due to the higher methane loss and compressor power requirements. To meet the higher demand for separation efficiency, a higher membrane area will be needed, which also results in an increase in GPC. Therefore, the module characteristics, such as the fiber length, can be optimized based on the minimum GPC, keeping the required separation efficiency in consideration.

Conclusions

A cross flow model for hollow fiber membrane separation was included in the process simulation (Aspen HYSYS) as a user defined unit operation along with the other available unit operations to investigate the membrane separation system for CO₂ removal from natural gas. The simulated model was validated experimentally and with a comparison with published data. The simulation showed good agreement with the experimental and published results. The design sensitivity was investigated by changing the membrane module characteristics, such as the fiber length, radius of the fiber bundle, diameter of the fibers, and porosity, for the proposed design configuration. The level of methane loss, stage cut and compressor power increased with increasing fiber length or radius of fiber bundle. On the other hand, an increase in the outer diameter of the fiber or porosity decreases the methane loss, stage cut and compressor power. The GPC increased with increasing membrane area (fiber length) but the separation efficiency was also dependent on membrane area. Therefore, the membrane module characteristics need to be optimized based on the minimum GPC with respect to the required separation efficiency.

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Wilke’s method

Wilke derived expressions for the viscosity of an n-component system which are as follows

$$\eta_{mix} = \sum_{i=1}^{n} \eta_i \left[ 1 + \sum_{j \neq i}^{n} \Phi_{ij} X_j \right]^{-1} \tag{22}$$

and

$$\Phi_{ij} = \frac{1}{2\sqrt{2}} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{\eta_i}{\eta_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/2} \right]^2 \tag{23}$$

where $\eta$ and $X$ represent the coefficient of viscosity and mole fraction respectively. $M$ is the molecular weight and the subscripts refer toward the molecular species.$^{[39,52]}$

Lucas’ method

An empirical relation for reduced viscosity of pure gas at low temperatures was proposed by Lucas that included polar and quantum correction factors, $F_p$ and $F_q$ respectively.$^{[39,53]}$. The equation in terms of $T_R$ is given by

$$\eta = 0.807T_R^{-0.618} - 0.357\exp(-0.449T_R) + 0.34\exp(-4.058T_R) + 0.018/F_pF_q \tag{24}$$

where

$$\xi = \frac{T_R^{1/6}}{M^{1/2}P_c^{1/3}} \tag{25}$$

$T_c$ and $P_c$ represent for critical temperature and pressure whereas $M$ refer to molecular weight of pure gas.

References