A mathematical method to study CO$_2$ -CH$_4$ separation in a hollow fibre module

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In this work a counter current hollow fibre module with feed entering to shell was studied in order to separate carbon dioxide from methane. New mathematical methods for prediction of specifications of permeate and retentate streams at various conditions were developed. The effects of operating and design variables on module efficiency for a mixture of CO$_2$ and CH$_4$ were studied. It was found that sweep pressure has inverse and direct effects on the CH$_4$ concentration in the retentate and permeate streams, respectively. The opposite effect was observed for CO$_2$.

Keywords: Hollow fibres, Membrane, CO$_2$ separation, Simulation

Membrane-based gas separation is an important unit operation for the separation of many gas mixtures in oil and petrochemical industries. Examples of these operations are separation of air into high-purity nitrogen and oxygen-rich air, removal of acid gases such as CO$_2$ and H$_2$S from natural gas and organic vapors removal from air

In the present article a model for simulation of hollow fibre membrane for carbon dioxide removal from syn-gas is presented. This gas is obtained from various resources including gas refineries in Iran. Permeance has been assumed to be variable along the membrane.

Theory

A hollow fibre module is considered in this work. This module is somehow similar to shell and tube heat exchangers. The cross section of a fibre is shown in Fig. 1. A typical hollow fibre module consists of 1000 fibres. Each fibre has the inside diameter of 0.5 mm and outside diameter of 0.7 mm. The pore size is 10 nm for gas separation.

![Fig. 1—The cross section of a fibre](image-url)
The tubular path (lumen) is a porous matrix covered by a selective layer. The feed can be introduced either into tubes or shell. The only difference is the direction of mass transfer. Assuming that the feed is introduced into the tubes, a part of the feed stream, passing through the tubes, gradually penetrates into the selective layer until reaches to the porous layer. A sweep flow, for instance nitrogen, is introduced into the other side to discharge the penetrated species from the module. Although for sweep mode, feed through shell side may generally be considered because of greater equivalent diameter, in the current study feed was considered passing through the tubes. This is for consistency with the available industrial plants in Iran.

The rate of mass transfer is directly proportional to the contact area between the feed and selective layer. The contact area for a tube and the total area for a number of tubes are calculated from the following equations:

\[ A = \pi d_o l \]  \hspace{1cm} \ldots (1)  
\[ A_t = \pi d_o n_t l \]  \hspace{1cm} \ldots (2)  

The total area is a function of the length, the outer diameter and number of fibres. Since the length and the diameter of the fibres are of much lower order in comparison with the number of the fibres, usually between 100000 and 500000, the total area is highly dependent on the number of fibres. In general, a larger ratio of area to volume can be obtained by means of hollow fibre modules.

Co-current and counter current are two types of stream arrangement for hollow fibre module. In co-current mode, the driving force and rate of mass transfer are reduced when passing along the fibre due to a reduction in concentration of the penetrated constituent. However in the counter current mode, except for the inlet and outlet sections, the mass transfer rate remains almost constant.

Since the feed stream can be introduced either into shell or tubes, based on the design, a number of states can be considered by a designer, each of which has its own simulation procedure. A counter current module with feed stream entering to shell was studied in this work.

To model the counter current hollow fibre module, the following assumptions were made:

(i) The fibres consist of a selective layer laminated on the top of a porous layer. The mass is totally transferred through the selective layer.
(ii) No axial mixing occurs when the bulk of gas passes, neither in shell nor in tubes.
(iii) The gas on the shell side of the hollow fibre and in the lumen is in plug flow.
(iv) The length of module is divided into \( N \) sections, in each of which part of the mass is transferred. The total mass transfer is equal to the summation of mass transfer rate in each section. The value of \( N \) can be obtained from the following Eq.:

\[ N = \frac{n_f 2 \pi R_f \left(1 - x_{F,j} + \Delta x_{\text{max}}\right) \left(Q_j\right) \left(P_{F,F,j}\right)}{F \Delta x_{\text{max}}} \]  \hspace{1cm} \ldots (3)  

where \( \Delta x_{\text{max}} \) is chosen based on the module specification and usually vary between 0.0005 and 0.1.

(v) Deformation of fibres which may happen under high pressure is neglected.
(vi) All fibres have uniform outer and inner diameter and the thickness of the selective layer is also considered to be constant.
(vii) The module operates at steady state.

Since the module was considered as one unit consisting of \( N \) sections, the mass transfer occurring in each section is of cross flow type as shown in Fig. 2.

Fig. 2—Schematic of modeling
The contact area for a section is calculated from the following equation:

\[ \Delta A_k = \frac{2\pi R \ln f}{N} \quad \ldots (4) \]

The partial molar flow rate for each section can be calculated using the following equations for tube and shell sides:

\[ v_{j,k} = y_{j,k}V_k \quad \ldots (5) \]

\[ l_{j,k} = x_{j,k}L_k \quad \ldots (6) \]

The total molar flow rates are calculated from:

\[ V_k = \sum_{j=1}^{\infty} v_{j,k} \quad \ldots (7) \]

\[ L_k = \sum_{j=1}^{\infty} l_{j,k} \quad \ldots (8) \]

Since a part of existing components in mixture passing through the shell will be transferred to the tube side, the mass balance and mass transfer rate equation can be written as:

\[ m_{j,k} = l_{j,k+1} - l_k \quad \ldots (9) \]

\[ m_{j,k} = Q_k \Delta A_k (P_{j,k+1} y_{j,k+1} - P_{j,k} y_{j,k}) \quad \ldots (10) \]

where \( Q_k \) stands for each component’s permeance, defined as permeability divided by the thickness of membrane active layer.

As pressure gradient is the driving force of mass transfer in gas separation processes, the total pressure of inlet streams entering to each section should be considered in mass transfer equation. In previous studies \( Q_k \) has been considered as a constant parameter for all sections and all stages. However as a novel approach in this work, its value in each section is calculated from the following Eq.9:

\[
P_{j,k+1} - P_{j,k} = \frac{128\mu_{\text{mix}}}{\pi d_h^4} \frac{lQ}{N} \left[ \frac{1}{\pi n_j d_i^4} \frac{1}{Q_k} \left( \frac{D_m^2 - n_j d_o^2}{n_j d_o} \right) \right] \ldots (11)\]

The mixture viscosity can be determined by Wilke method11 which is described in the following equations:

\[ \mu_{\text{mix}} = \sum_{i=1}^{n} \frac{p_i \mu_i}{\sum_{j=1}^{n} p_j \Phi_{ij}} \quad \ldots (20) \]
\[
\varphi_j = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j}\right)^{-\frac{1}{2}} \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{-\frac{1}{2}} \left(\frac{M_i}{M_j}\right)^{-\frac{1}{4}}\right]^2
\] ... (21)

Since the total input pressure is known, the output pressure for shell and tube sections can be calculated from the following equations:

\[
P_{V,k} = P_{V,k-1} - 128\mu_{\text{mix}} \frac{l}{N} Q_k \frac{1}{\pi n_j d_i^4}
\] ... (22)

\[
P_{L,k} = P_{L,k+1} - 128\mu_{\text{mix}} \frac{l}{N} Q_k \frac{1}{\pi \left(D_o^2 - n_j d_i^2\right)}
\] ... (23)

To determine the temperature changes of streams passing through the shell and tube sides, Joule-Thomson coefficient was used. This thermodynamic property is expressed in terms of PVT relations:

\[
\mu = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V\right]
\] ... (24)

Virial equation of state was used to calculate the volume and the deviation of volume against temperature at constant pressure. The mixture heat capacity was determined from the following mixing rule:

\[
C_p = \sum_i C_{p,j} x_i
\] ... (25)

The heat capacities of pure CO\(_2\) and CH\(_4\) are defined in Table 1.

The output temperature of each section can be obtained using the Joule-Thomson coefficient, pressure drop in tube and shell sides and the input temperature:

\[
T_k = T_{k-1} - \mu \left(P_{V,k-1} - P_{V,k}\right)
\] ... (26)

\[
T_k = T_{k+1} - \mu \left(P_{L,k+1} - P_{L,k}\right)
\] ... (27)

Table 1—Heat capacities of pure CO\(_2\) and CH\(_4\)

<table>
<thead>
<tr>
<th>Component</th>
<th>Heat Capacity (J/mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>(C_{P,CO_2} = 33.523 + 0.022143T - 3.8694e^{-6}T^2)</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>(C_{P,CH_4} = 25.35964 + 0.01686781T + 7.13121e^{-5}T^2 - 4.083709e^{-8}T^3)</td>
</tr>
</tbody>
</table>

The input temperature of the first section of the tube side and the \(n^{th}\) section of the shell side are assumed as the sweep and feed temperatures, respectively.

The following algorithm has been implemented in order to solve the equations.

1- Calculate \(N\) from Eq. (3).
2- Calculate \(\Delta A\) from Eq. (4).
3- Guess an initial value for \(m_{j,k}\).
4- Calculate the partial molar flow for components in each section from Eqs (9) and (13).
5- Calculate the total molar flow of each section from Eqs (7) and (8).
6- Calculate the mole fraction of components in each section from Eqs (14) and (15).
7- Calculate the mixture viscosity for each section based on Wilke method.
8- Calculate the passing volume of fluid in each section from Virial EOS.
9- Calculate the pressure drop for each section from Eqs (18) and (19).
10- Calculate the outlet pressure of each section from Eqs (22) and (23).
11- Calculate \(C_p\)s from Table 1.
12- Calculate the Joule-Thomson coefficient in each section.
13- Calculate the outlet temperature of each section from Eqs (26) and (27).
14- Calculate the permeability of components from Eq. (11).
15- Calculate the mass transfer rates from Eq. (10).
16- Calculate the partial molar flow for components in each section from Eqs (9) and (13).
17- Calculate the total molar flow of each section from Eqs (7) and (8).
18- Calculate the mole fraction of components in each section from Eqs (14) and (15).
19- Check the convergence criterion of Eq. (16). If it is not satisfied go back to step 7.

Results and Discussion

The model was employed for characterization of a mixture of CO\(_2\) and CH\(_4\) entering the hollow fibre module. The CO\(_2\) and CH\(_4\) concentrations in permeate and retentate streams depend on the operating and design variables. Feed flow rate, feed and sweep pressures were denoted to the operating variables. Surface area which is a function of module length, number and diameter of fibres, was considered as the
design variable (Table 2). Although the sweep flow rate has an important effect on decreasing the CO$_2$ concentration in the retentate stream, the CO$_2$ mole fraction in permeate stream was significantly decreased; therefore, the variation of sweep flow rate was not studied in this work.

Figure 3 represents the variation of CO$_2$ concentration in the retentate stream with the feed pressure. The CO$_2$ mole fraction is slightly decreased by increasing the feed pressure. Increasing the feed pressure i.e. increasing the driving force enhances the permeability. This is due to higher solubility of the gas in the dense skin layer of the membrane. The similar effect has been reported by other researchers.$^{13,14}$ Both phenomena (increasing driving force and permeability) result in more passage of CO$_2$ through the membrane i.e. less CO$_2$ in the retentate side. It should be mentioned that gas solubility, permeability, mass transfer potential and rates directly depend on the feed pressure at constant sweep pressure.

Although CH$_4$ passes through the membrane, its apparent concentration is slightly increased (Fig. 4). The absolute concentration of CH$_4$ is decreased but this is less than the decline in CO$_2$ concentration. Therefore it seems that the concentration of CH$_4$ is increased. In general in a gas separation membrane process, the changes in the permeate flows depends on the changes in the fluxes of the components.

Figures 5 and 6 represent the variation of molar flow rates of retentate and permeate streams with the feed pressure. This trend is similar to the general knowledge in this field i.e. molar flow rate of retentate is decreased and molar flow rate of permeate is increased by increasing the feed pressure.

![Fig. 3 — Variation of CO$_2$ mole fraction in retentate stream versus feed pressure](image)

![Fig. 4 — Variation of CH$_4$ mole fraction in retentate stream versus feed pressure](image)

Table 2 — Default values to study the effect of operation and design variables.

<table>
<thead>
<tr>
<th>Component Specification</th>
<th>Feed Stream Properties</th>
<th>Module Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component Name</td>
<td>Molar Flow</td>
<td>Pressure</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.138</td>
<td>69.8</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.200</td>
<td>1015.5</td>
</tr>
<tr>
<td></td>
<td>1.55 x 10$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

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![Image of Hollow Fiber Module](image)
The variation of the dependent variables with the sweep pressure at constant feed pressure is shown in Figs 7-10. Sweep pressure has inverse and direct effects on the CH$_4$ concentration in the retentate and permeates streams, respectively. For CO$_2$ it shows opposite effect. Although absolute values of permeated gases increase with pressure, but the relative value of CO$_2$ concentration decreases.

The variation of CH$_4$ and CO$_2$ concentrations in retentate and permeate versus feed flow are depicted in Figs 11-14. By increasing the feed flow, CH$_4$ passes through the membrane more easily resulting in a reduction in the mole fraction of CH$_4$ in the retentate.
The higher feed flow provides more CO$_2$ in the vicinity of the membrane. However due to lack of CO$_2$ permeation through the membrane, higher mole fraction of CO$_2$ in the retentate is established (Fig. 12). Although the absolute value of CH$_4$ in the permeate is increased by increasing the feed flow, its mole fraction decreases (Fig. 13). An opposite behaviour is obtained for CO$_2$ (Fig. 14).

**Conclusions**

A counter current hollow fibre module with a variable permeance along the membrane was modeled for separation of carbon dioxide from methane. The developed model is able to predict the specifications of permeate and retentate streams at various conditions. It was found that sweep pressure has inverse and direct effects on the CH$_4$ concentration in the retentate and permeates streams, respectively. The opposite effect was observed for CO$_2$.

**Nomenclature**

- $A$: contact area for one tube, [m$^2$]
- $A_t$: total area for a number of tubes, [m$^2$]
- $b_j$: hole affinity constant for component (j), [atm$^{-1}$]
- $C_{pi}$: specific heat in constant pressure for component (i), [J/(g mol$^o$C)]
- $D_i$: diffusion coefficient component i, [m$^2$/s]
- $D_m$: diameter of module, [m]
- $d_h$: hydrolic diameter, [m]
- $d_o$: outer diameter of fibre in module, [m]
- $F$: total feed flow rate, [kmol/s]
- $F_i$: relative diffusion coefficient Longmuir to Henry position, [-]
- $K$: Henry law constant, [-]
- $L$: active length of fibre in module, [m]
- $L_k$: total retentate (shell side) flow rate in stage k, [kmol/s]
- $I_k$: flow rate component j in stage k (shell side), [kmol/s]
- $M$: molecular weight, [g/mol]
- $N$: number of sections, [-]
- $n_f$: number of fibres, [-]
- $P_i$: partial pressure component (i), [Pa]
- $P_F$: Feed pressure, [Pa]
- $P_{L_k}$: pressure in shell side at stage k, [Pa]
- $P_{V_k}$: pressure in tube side at stage k, [Pa]
- $Q_i$: each component’s permeance, [kmol/(m$^2$.Pa.s)]
- $Q_k$: flow rate in stage k, [kmol/s]
- $R_o$: outer radius of fibre, [m]
- $S_i$: solubility coefficient component i, [kmol/(m$^2$.Pa)]
- $T_k$: temperature in stage k, [°K]
- $V_k$: total permeate (tube side) flow rate in stage k, [kmol/s]
\( X_{Fj} \): mole fraction component \( j \) in feed, [-]
\( x_{kj} \): mole fraction component \( j \) at stage \( k \) (in shell side), [-]
\( y_{kj} \): mole fraction component \( j \) at stage \( k \) (in tube side), [-]
\( \Delta A_k \): area available for mass transfer in stage \( k \), [m²]
\( \Delta X_{max} \): maximum change in mole fraction of each component, [-]
\( \delta \): active membrane layer thickness, [m]
\( \partial T \): deviation of temperature, [°K]
\( \partial V \): deviation of volume, [m³]
\( \mu_j \): viscosity of component \( j \) in feed, permeate, retentate stream, [g/(cm.s)]
\( \mu_{mix} \): viscosity of mix components in feed, permeate, retentate stream, [g/(cm.s)]
\( p_j \): density of component \( j \), [g/cm³]

References