Mathematical Modeling of Gas Separation Process with Flat Carbon Membrane

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HIGHLIGHTS

- Mathematical modeling of gas separation process with carbon membrane.
- Considering flat configuration of carbon membrane.
- Surveying binary diffusion through the membrane.

GRAPHICAL ABSTRACT

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ABSTRACT

Carbon molecular sieve membranes (CMSMs) have been considered as very promising candidates for gas separation, in terms of separation properties as well as thermal and chemical stability. Due to the numerous advantages and wide applications of carbon membranes, their application for gas separation is of special importance. Because of the importance of carbon membranes and a large number of studies in the field of carbon membrane fabrication, in this study, mathematical modeling of the gas separation process in CMSMs has been investigated. Flat configuration is considered for the membrane, which has been applied for the separation process of CH₄ and C₂H₆. The Runge-Kutta method has been applied in order to solve the model. In the mentioned model, the sorption-diffusion mechanism has been considered as a dominant one for gas separation with CMSM. By comparing theoretical results with experimental ones for binary diffusion, good agreement was obtained. Finally, the effect of some parameters such as effective area of the module, module temperature, total feed pressure and feed flow rate on the purity of components in the retentate and permeate stream and recovery of fast components in the permeate stream have been investigated. Results demonstrated that increasing the effective area, membrane temperature and total feed pressure increased the recovery of the fast component in the permeate side, while the feed flow rate had an adverse effect.

1. Introduction

Conventional technologies for gas separation such as distillation, crystallization, absorption, adsorption, solvent extraction, or cryogenics have been optimized for decades [1,2]. In recent decades, higher energy costs, energy intensive methods and adverse impact on the environment have made the membrane processes competitive with other separation technologies. New studies have been focused on inorganic membranes [3] and among them, carbon membranes are promising candidates for gas separation because of their thermal and chemical stability and some unique advantages for many...
industrial applications [4-6]. Although the concept of carbon membrane for gas separation dated back to 1970, the interest to develop the carbon membrane grew since Koresh and Soffer [7,8] successfully prepared the crack-free molecular sieving hollow fiber carbon membrane by carbonizing cellulose hollow fiber.

Nowadays, new researchers are trying to prepare a carbon membrane, using different kinds of polymeric materials, which are resulting in different kinds of carbon membranes [9-14] and the different conditions of preparing the carbon membrane [15]. There is a considerable amount of published experimental data on the permeability of pure components through CMSMs [7,16-18], but there is little data on equilibrium adsorption, diffusion coefficient and multi-component transport [7]. Therefore, the large part of researches on the carbon membrane belongs to its preparation process [8,9,16-21]. There have also been reports on supported carbon membranes [22-25], composite carbon membranes [26-28] and mixed matrix membranes. Also, other reports include experimental data of pure component permeability and recently experimental data on adsorption equilibrium, diffusion coefficient [7,16,23] and multi-component transport [20,23,24,28].

According to the mentioned researches, it can be seen that the main portion of the studies have been experimental ones. However, it is noticeable that mathematical modeling also plays an important role in designing new equipment and processing optimization. Therefore, modeling of the gas separation process with carbon membranes in different configurations has great importance. This study has been focused on the modeling of the gas separation process with flat carbon membrane.

### 2. Model development

#### 2.1. Membrane fundamentals

Mass transfer in the membrane module consists of molecular diffusion (Equation (1)), bulk diffusion (Equation (2)) and permeation through the membrane.

$$ J_{i} = -D_{i} \frac{\partial C_{i}}{\partial x} $$  \hspace{1cm} (1)

$$ n_{i}^{\text{in}} = C_{i} u_{i} A $$  \hspace{1cm} (2)

where $D_{i}$ is diffusion coefficient of component $i$, $C_{i}$ is molar concentration of component $i$, $u_{i}$ is velocity of component $i$ and $A$ is the cross section of gas passage in retentate or permeate side of the membrane.

In this modeling, the sorption-diffusion mechanism has been considered as a dominant one for gas separation with CMSM and has been defined from the Langmuir isotherm (Equation (3)):

$$ \theta_{i} = \frac{q_{i}}{q_{s}} = \frac{h_{i} p_{i}}{1 + h_{i} p_{i}} $$  \hspace{1cm} (3)

where $p_{i}$ is partial pressure of component $i$, $q_{i}$ is the concentration of component $I$ in the adsorbed phase, $q_{s}$ is its saturation capacity, $h_{i}$ is the affinity coefficient of component $I$ and $n_{i}$ is Langmuir constant of component $i$.

Binary or multicomponent diffusivities through CMSM are strongly concentration dependent and can be calculated by proposed relations of Yang et al. [23] (Equations (4) and (5)):

$$ D_{ij} = \frac{D_{0j}(1 - \theta_{i}) \theta_{j}}{[1 - \sum_{j=1}^{k} (1 - \theta_{j}) \theta_{j}]} $$  \hspace{1cm} (4)

$$ D_{ij} = D_{0j} \left[ \frac{1}{1 - \sum_{j=1}^{k} (1 - \theta_{j}) \theta_{j}} \right] $$  \hspace{1cm} (5)

where $D_{ij}$ is pure component diffusivity at zero coverage of component $i$, $\theta_{i}$ is surface coverage of component $i$ and $\lambda_{i}$ is interaction parameter of component $i$ and $j$. Component diffusivity at zero coverage can be described as a function of temperature (Equation (6)):

$$ D_{ij} = D_{0j} e^{-\frac{E_{ij}}{RT}} $$  \hspace{1cm} (6)

where is pre-exponential factor of component $i$, $E_{ij}$ is activation energy, $R$ is gas constant and $T$ is module temperature. In addition, $\lambda_{ij}$ (interaction of component $i$, sticking on adsorbed molecule $j$), can be calculated from Equation (7):

$$ \lambda_{ij} = e^{-(\varepsilon_{i} - \varepsilon_{j})/RT} $$  \hspace{1cm} (7)

where, $\varepsilon_{i}$ is activation energy for diffusion on the bare surface, which can be considered as heat of adsorption and $\varepsilon_{j}$ is activation energy for diffusion on adsorbed molecules (Equation (8)).

$$ \varepsilon_{ij} = (\varepsilon_{i} \varepsilon_{j})^{1/2} $$  \hspace{1cm} (8)

Therefore, for binary diffusion of components, flux can be written as Equation (9).

$$ J_{\text{app}} = -\frac{1}{\delta} \sum_{i=1}^{n} D_{i} (q_{\text{in}} - q_{\text{out}}) $$  \hspace{1cm} (9)

where, $\delta$ is the membrane thickness and $q_{i}$ is the average amount of binary diffusion coefficient, which can be determined from Equation (10):

$$ \frac{1}{q_{i}} = \frac{1}{q_{\text{in}}} + \frac{1}{q_{\text{out}}} $$  \hspace{1cm} (10)

### 2.2. Assumptions and model equations

A schematic diagram of a flat carbon membrane has been shown in Figure 1. According to this figure, feed enters the membrane module and based on the pressure difference between two sides of the membrane, the species penetrate through the membrane with different velocities. The species that can pass through the membrane are called permeate, while those being rejected by the membrane are called retentate.

Material balances have been carried out on the feed side and permeate side of the membrane module. Figure 2 shows a differential distance in the flat membrane and the mass balance that has been applied in it. It should be noted that in this modeling, the binary gas separation process is the required object.

The applied assumptions have been mentioned below:

1. Membrane layer is lumped.
2. Isothermal condition prevails in the module.
3. Process is steady-state.
4. Gas flow in the membrane module is co-current
5. Velocity in the module is constant.
6. The length of the module is too long in comparison with other directions.
7. $y$ direction of the system is considered solid.
8. Molecular diffusion is negligible in comparison with bulk diffusion in $x$ direction.
9. Ideal gas behavior is considered.
10. Gas is incompressible.
11. Carrier gas does not permeate through the membrane.

Mass balance for component \( i \) in the feed side is as follows:

\[
\frac{dp_{\text{in}_i}}{dx} = \frac{RT}{Q_p} w_{J_{\text{in}_i}}
\]

By considering the above assumptions and substituting Equations (1), (2) and (9) in Equation (14), Equation (15) will be obtained:

\[
\frac{dp_{\text{in}_i}}{dx} = \frac{RT}{Q_p} w_{J_{\text{in}_i}}
\]

Boundary conditions are as follows:

\[
x = 0 \quad P_{\text{in}_1} = P_f
\]

\[
 x = L \quad P_{\text{in}2} = P_i
\]

In order to obtain the pressure distribution along the membrane module, Equations (15) and (16) must be solved together. It can be seen that the equations obtained from the modeling of the flat carbon membrane are nonlinear ordinary differential equations (ODE) and a kind of initial value problem. Thus, in order to solve the equations, the Forth Runge-Kutta method has been applied.

3.3. Mole fraction distributions in the length of the membrane module

3.4. Validation of the model

In 1994, Chen and Yang [23] prepared a flat CMSM. They measured steady-state diffusion fluxes of single-component and binary mixtures of CH\(_4\)/C\(_2\)H\(_6\) through the membrane. Then, in order to verify the validation of their results, they compared the results with the theory of permeation flux. So continuing Chen and Yang’s work, in this study, modeling of the membrane module has been done and the obtained results of permeation flux have been compared with the experimental flux of Chen and Yang [23] for two temperatures of 323 K and 353 K. This comparison is reported as the percentage of absolute error in Tables 1 and 2. It should be noted that feed stream includes methane, ethane and Helium as carrier gas, in which case only methane and ethane permeate through the carbon membrane. In turn, it has been called binary diffusion.

![Table 1: Binary diffusion of CH\(_4\)/C\(_2\)H\(_6\) through CMSM at 323 K](image)

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed mole fraction</th>
<th>Model flux of binary diffusion (10(^{-6}) mol m(^{-2}) s(^{-1}))</th>
<th>Experimental flux of binary diffusion [23] (10(^{-6}) mol m(^{-2}) s(^{-1}))</th>
<th>Percentage of absolute error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>0.203</td>
<td>4.80 (\pm) 1.62</td>
<td>3.65 (\pm) 1.73</td>
<td>14.00 (\pm) 0.00</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>0.086</td>
<td>1.30 (\pm) 1.30</td>
<td>1.10 (\pm) 1.23</td>
<td>9.00 (\pm) 2.40</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.395</td>
<td>12.70 (\pm) 1.28</td>
<td>12.80 (\pm) 1.32</td>
<td>0.78 (\pm) 3.00</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>0.009</td>
<td>18.10 (\pm) 1.02</td>
<td>16.60 (\pm) 0.94</td>
<td>9.70 (\pm) 8.80</td>
</tr>
</tbody>
</table>

According to the present model, transport characteristics of the carbon membrane have been illustrated in Table 3. In addition, the characteristics of the flat carbon membrane used in the current study have been mentioned in Table 4.

Single-component equilibrium and diffusivity parameters on the carbon molecular sieve, which are mentioned in the Appendix, have been determined according to Chen and Yang [23]. Tables 1 and 2 show that the error between the experimental results and modeling ones are between 0.78 to 14 percent. It can be seen that the lower error is related to the diffusion at 323K with the mentioned mole fractions: methane 0.395, ethane 0.089 and the other portion refers to the carrier gas. Therefore, these conditions have been applied in the following study of the flat carbon membrane.

![Table 2: Binary diffusion of CH\(_4\)/C\(_2\)H\(_6\) through CMSM at 353K](image)

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed mole fraction</th>
<th>Model flux of binary diffusion (10(^{-6}) mol m(^{-2}) s(^{-1}))</th>
<th>Experimental flux of binary diffusion [23] (10(^{-6}) mol m(^{-2}) s(^{-1}))</th>
<th>Percentage of absolute error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>0.221</td>
<td>0.0105 (\pm) 1.35</td>
<td>0.93 (\pm) 1.74</td>
<td>2 (\pm) 3</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>0.477</td>
<td>16.60 (\pm) 1.8</td>
<td>14.00 (\pm) 1.90</td>
<td>14 (\pm) 9</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.252</td>
<td>0.395 (\pm) 1.69</td>
<td>0.36 (\pm) 7.95</td>
<td>13 (\pm) 13</td>
</tr>
</tbody>
</table>

3.2. Mole fraction distributions in the length of the membrane module

To the best of our knowledge, the fast component tends to permeate through the membrane, while the slow one tends to remain in the retentate side. In this binary system, methane is the fast component and ethane is the slow one. So, although Figure 3 shows that mole fraction of the components decrease in the retentate side and increase in the permeate side along the module, the increase of methane in the permeate side is much more than ethane and the increase of ethane in the retentate side is higher. Therefore, as it was expected, the permeate side of the module becomes rich from methane and the retentate side of the module becomes rich from ethane.

![Figure 3](image)
3.3. Effect of membrane area on separation performance

Figures 4 and 5 show the effect of the membrane area on the separation performance along the membrane length. Results of modeling suggest that although increasing the effective area of the membrane decreases the mole fraction of both components in the retentate side, the decrease of methane is more than ethane, so the retentate side of the membrane becomes rich from ethane. Similarly, an increase of methane in the permeate side is more than ethane, so the permeate side of the module becomes rich from methane. As it can be seen, increasing the membrane area benefits the separation and increases the methane recovery in the permeate side of the module (Figure 6). According to these figures, it is noticeable that increasing the effective area from 0.15 to 0.25 m² is more effective than increasing the area from 0.25 to 0.35 m². This subject is also obvious in the amount of methane recovery in the permeate side. Therefore, it should be noted that the effective area has an optimum point, since after this point it is not affordable.

3.4. Effect of feed pressure on separation performance

By increasing the feed pressure, the driving force of permeation through the membrane increases. Thus, it is anticipated that increasing the feed pressure benefits the separation. Figure 7 shows that by increasing the feed pressure, the methane purity in the permeate side and ethane purity in the retentate side increases. Furthermore, in Figure 8 it can be seen that increasing the feed pressure increases the amount of methane recovery in the permeate side of the module. The other observation of Figure 7 is that increasing the feed pressure from 66.7 to 106.7 kPa leads to more ethane purity in the retentate side, in comparison with feed pressure in the range of 40–66.7 kPa. As a result, in the range of 66.7 to 106.7 kPa of feed pressure, better separation has been obtained.

3.5. Effect of feed flow rate on separation performance

It is important to bear in mind that the existence of a driving force leads to the separation process. Hence, the more the gas residence time in the module, the more separation will be achieved. Thus, by increasing the feed flow rate, gas velocity increases and retention time decreases. As a result, increasing the feed flow rate does not benefit the separation. As it was expected, Figure 9 shows that increasing the feed flow rate increases the purity of both components in the permeate side, but decreases the amount of methane recovery in the permeate side (Figure 10).

3.6. Effect of temperature on separation performance

By and large, by elevating the temperature, gas adsorption decreases. However, diffusion through the membrane rises, in which case, diffusion of methane is more than ethane (Figure 11), due to its higher interaction parameter and lower diffusion activation energy. The mentioned results can be derived respectively from Equations (6) and (7). This leads to the condition in which the permeation flux of methane and ethane increases; however, the elaboration amount of methane is more than ethane. As a result, the permeate side of the membrane becomes rich from methane and retentate becomes rich from ethane (Figure 11) and recovery of methane burgeons (Figure 12).

4. Conclusion

Inorganic carbon membranes are good candidates for the gas separation process due to their high thermal and chemical stability. Therefore, in this study, modeling of the gas separation process with the flat carbon membrane was applied and compared with experimental data. In this modeling, the separation of \( \text{CH}_3/\text{C}_2\text{H}_6 \) has been investigated. By comparing the modeling
results with the experimental ones, good agreement was obtained and the amount of error was between 0 -14%.

Furthermore, after investigating some parameters, the following results were obtained:

- Increasing the feed pressure increases the recovery of the fast component and increases its purity in the permeate stream.
- Increasing the feed flow rate decreases the recovery of the fast component and increases its purity in the permeate stream.
- Increasing the effective area of the membrane increases the recovery and purity of the fast component in the permeate stream.
- Increasing the temperature of the module increases the recovery and purity of the fast component in the permeate stream.

\[ e_r \]  Activation energy for diffusion on adsorbed molecules
\[ e_o \]  Activation energy for diffusion on bare surface (J.mol\(^{-1}\))
\[ D_i \]  Diffusion coefficient of component i (mol.m\(^{-2}\).s\(^{-1}\))
\[ J_i \]  Permeation flux of component i through the membrane (mol.m\(^{-2}\).s\(^{-1}\))
\[ L \]  Module length (m)
\[ n_i^p \]  Langmuir constant for component i (mol.s\(^{-1}\))
\[ n_i \]  Pre exponential factor of component i (mol.m\(^{-2}\).s\(^{-1}\))
\[ q_i \]  Adsorbed amount of component i (mol.Kg\(^{-1}\))
\[ q_i^* \]  Saturated adsorbed amount of component i (mol.Kg\(^{-1}\))
\[ Q \]  Volumetric flow rate of stream j (m\(^3\).s\(^{-1}\))
\[ R \]  Gas constant (J.mol\(^{-1}\).K\(^{-1}\))
\[ T \]  Module temperature (K)
\[ u_i \]  Velocity of component i (m.s\(^{-1}\))
\[ w \]  Module width (m)
\[ X_i \]  Adsorbed phase mole fraction at equilibrium of component i
\[ y \]  Mole fraction

**Subscript**

A, B component A, B
cf carrier gas in feed stream
eff effective area of the membrane
f feed stream
i,j components i and j
if component i in feed stream
in side of the membrane that is in contact with the retentate stream
ip component i in permeate stream
ir component i in retentate stream
out side of the membrane that is in contact with the permeate stream
p permeate stream
r retentate stream
s total saturated adsorbed amount
t total
x, y, z coordinate axes

**Greek symbol**

\[ \delta \]  membrane thickness (m)
\[ \lambda_i \]  interaction parameter
\[ \theta_i \]  surface coverage of component i

Nomenclature

- **A** Cross sectional area (m\(^2\))
- **b**
- **C** Langmuir constant of component i (bar\(^{-1}\))
- **D_i** Molar concentration of component i (mol.m\(^{-3}\))
- **D_i** Diffusion coefficient of component i (mol.m\(^{-2}\).s\(^{-1}\))
- **D_i** Pure component diffusivity at zero coverage of component i (mol.m\(^{-2}\).s\(^{-1}\))
- **D_i** Pre exponential factor of component i (mol.m\(^{-2}\).s\(^{-1}\))
- **D_i** Binary diffusion coefficient (mol.m\(^{-2}\).s\(^{-1}\))
- **D_i** The average amount of binary diffusion coefficient (mol.m\(^{-2}\).s\(^{-1}\))
- **E_i** Diffusion activation energy (J.mol\(^{-1}\))

**References**

Table A1
Single-component equilibrium and diffusivity parameters on carbon molecular sieve membrane.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>( \bar{f} ) (kJ)</th>
<th>( q_s ) (mol kg(^{-1}))</th>
<th>( b ) (bar(^{-1}))</th>
<th>( n )</th>
<th>( \lambda )</th>
<th>( D^* \times 10^{20} ) (m(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>297</td>
<td>1.145</td>
<td>0.368</td>
<td>1.24</td>
<td>0.956</td>
<td>1.695</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1.021</td>
<td>0.238</td>
<td>1.21</td>
<td>0.993</td>
<td>2.429</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>0.797</td>
<td>0.316</td>
<td>1.22</td>
<td>0.280</td>
<td>3.438</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>297</td>
<td>2.072</td>
<td>15.001</td>
<td>0.84</td>
<td>0</td>
<td>0.146</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>1.821</td>
<td>3.975</td>
<td>1.03</td>
<td>0</td>
<td>0.388</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>1.549</td>
<td>3.705</td>
<td>0.90</td>
<td>0</td>
<td>0.315</td>
</tr>
</tbody>
</table>

Table A2
Energetic parameters and pre-exponential factor for diffusivity in carbon molecular sieve membrane.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>( \bar{f} ) (kJ)</th>
<th>( q_s ) (mol kg(^{-1}))</th>
<th>( b ) (bar(^{-1}))</th>
<th>( n )</th>
<th>( \lambda )</th>
<th>( D^* \times 10^{20} ) (m(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>10.502</td>
<td>7.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>12.426</td>
<td>0.21</td>
<td></td>
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</tbody>
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