Analysis of Mass Transfer During Natural Gas Purification Process in a Vertical Tube

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ABSTRACT

The effects of axial and radial velocities on mass transfer during the purification of natural gas in a vertical pipe are studied numerically. The natural gas flowing inside a vertical channel and monoethanolamine (MEA) flowing as a film along the inner wall of the channel is taken together for the purification process. The direction of laminar flow of both fluids is gravity direction. The environment is assumed as isothermal. Comparisons are performed for the interface (wall) between the film and the gas in the presence and absence of axial mass flow. Grams’ finite difference formulation are used to solve governing equations and solved by using Grams’ package code. It is found that the interface axial velocity effect on mass transfer can be neglected for low Reynolds numbers.

Keywords: Natural gas, Purification, Mass transfer, Reynolds number

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>molar concentration, mol/cm³</td>
</tr>
<tr>
<td>Da</td>
<td>Damköhler number</td>
</tr>
<tr>
<td>Dij,B</td>
<td>polynary diffusion coefficient, cm²/s</td>
</tr>
<tr>
<td>Dij</td>
<td>binary diffusion coefficient, cm²/s</td>
</tr>
<tr>
<td>d</td>
<td>pipe diameter</td>
</tr>
<tr>
<td>H</td>
<td>Henry Law constant</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate constant, 1/s</td>
</tr>
<tr>
<td>mi</td>
<td>diffusion mass flux, g/(cm²s)</td>
</tr>
<tr>
<td>M</td>
<td>mass flux, g/(cm²s)</td>
</tr>
<tr>
<td>mi_tr</td>
<td>chemical transformation, g/(cm³)</td>
</tr>
</tbody>
</table>

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\[ \dot{n}_{re} \] reaction rate, mol/(cm^3·s)

\[ P \] pressure (atm)

\[ R \] pipe radius

\[ R_s \] specific gas constant, joule/(gK)

\[ \overline{R} \] universal gas constant, joule/(molK)

\[ Re \] Reynolds number

\[ Sc \] Schmidt number

\[ S \] area, cm^2

\[ T \] temperature, K

\[ u \] axial velocity, cm/s

\[ v \] radial velocity, cm/s

\[ V \] volume, cm^3

\[ y \] weight fraction (wt) (%)

\[ x \] axial coordinate

**Greek symbols**

\[ \alpha \] loading (mol of CO_2/mol of amine)

\[ \mu \] molecular weight, g/mol

\[ \sigma_{ij} \] Lennard-Jones parameters

\[ \Omega_{ij} \] Lennard-Jones parameters

\[ \rho \] density, g/cm^3

\[ \eta \] dynamic viscosity, g/(cm·s)

\[ \sigma \] weight factor

\[ \delta \] film thickness, cm

**Subscripts**

0 value at the inlet

c wall

D diffusion

i component

max maximum

t total

**Superscripts**

* dimensionless

1. INTRODUCTION

Natural gas is one of the important fuels for heating, water heating, cooling and automotive fuels. Nowadays, it plays a critical role on energy supply. It is essential to purify the natural gas from its undesired gases although natural gas yielding a considerably reduced emission is the cleanest fuel among fossil fuels. Numerous researches have been conducted on solubility of carbon dioxide and hydrogen sulphur in alkanolamine aqueous solution.

There are some studies in literature on this subject. Among these, Jou et al. [1] assessed the solubility of CO_2 in a solution containing 30% monoethanolamine (MEA) at eight different temperatures ranging from 0 to 150 °C and at CO_2 partial pressures ranging from 0.001 to 20.000 kPa. Similarly, Li and Shen [2] examined the solubility of hydrogen sulphur (H_2S) in N-methyldiethanolamine (MDEA) and monoethanolamine aqueous solutions at H_2S partial pressures ranging from 1 to 450 kPa and at temperatures 40, 60, 80 and 100 °C. The higher the H_2S partial pressure, the higher the loading capacity of H_2S in solution is observed. As for the temperature effect, the lower the temperature, the higher the H_2S loading is obtained. Faiz and Al-Marzouqi [3] studied the simultaneous absorption of CO_2 and H_2S from natural gas...
using aqueous potassium carbonate solutions as the absorbent solvent while utilizing hollow fiber membrane contactors. Their results showed that lower concentrations of carbonate solutions resulted in higher absorption rates, while the presence of high bicarbonate concentrations in the solution was the main incentive for the enhanced reversible reactions and thus, lower absorption rates were achieved. Dong et al. [4] used a commercially available polyimide material Matrimid® as the benchmark polymer material in fabrication of hollow fibers for natural gas purification. High CO₂/CH₄ separation factors (ranging up to 67) are achieved which are among the highest reported for purely polymeric hollow fibers without post-treatments and exceeded the commonly reported bulk values of Matrimid®.

Yeh and Bai [5] used ammonia (NH₃) and monoethanolamine (MEA) solvents to clean the greenhouse gas emissions. Pagella and De Faveri [6] established a new process to reduce hydrogen sulphur (H₂S) from the gas streams. Lin and Shyu [7] examined the CO₂ absorption by amines in a packed column experimentally using the primary monoethanolamine (MEA) and third N-methyl-2-pyrrolidone (NMP) in gas purifying. There have been also few theoretical studies to investigate the purification process in detail. Yigit [8] described a model of absorption process in the lithium bromide. Negny et al [9] developed a new numerical model to determine the amount of hydrodynamic effects on heat and mass transfer during the absorption for the laminar film on an alternating wall column. Hughes and Bott [10] have devised a model demonstrating the geometry of the fluids running downwards inside and outside vertical tubes. Negny et al. [11] have examined numerically the heat and mass characteristics and the flow model for film stream on an alternating vertical column. Öztop and Akpinar [12] made a typical application to see the effects of velocities on mass transfer for convective drying of some products. They used finite volume method to predict time dependent moisture distribution in products at different inlet flow temperature. Results show good agreement between numerical and experimental values. Finally, the numerical technique and computer code are capable of modeling moisture distribution inside the rectangular moist products. Other related studies can be found in Refs. [17-19].

The main objective of this work is to understand the effects of axial and radial velocities on mass transfer during the purification of natural gas absorbed by monoethanolamine (MEA). The above literature clearly shows that theoretical studies on purification process of natural gas absorbed by monoethanolamine (MEA) are limited and much less is known of how axial and radial velocity affects mass transfer in the purification process of natural gas. Thus, the study will help to scientific researchers and designers.

2. CONFIGURATION

The physical model is plotted in Fig. 1 with coordinates. In this figure, the natural gas flowing inside a vertical channel and monoethanolamine (MEA) flowing as a film along the inner wall of the channel is taken together for the purification process.

![Fig. 1. Schematic representation of system.](image-url)
3. EQUATIONS

Flow, continuity, mass transfer, ideal gas, gas absorption and film stream equations were used to analyze the purification process of natural gas. The equations of the system were expressed with dimensionless magnitudes comprising of Sherwood number (Sh), Schmidt number (Sc) and Damköhler number (Da) constituting the diffusion coefficients that determine the process. Polynary diffusion coefficients were calculated for continuous (barycentric) systems. The modified Stefan-Maxwell equation has been used as the basic equation when calculating the diffusion coefficients. After subsequently linearization of nonlinear terms in the partial derivative equation system obtained in a dimensionless manner, the solution has been achieved by Grams' finite differences method.

3.1. Diffusion Theory (Ternary Diffusion)

The system was analyzed based on barycentric system, which is continuous and hydrodynamically active. In this case, the diffusion mass flux \( m_i \) and mass flux \( M_i \) are determined phenomenologically as follows:

\[
\dot{m}_i = \rho \sum_{j=1}^{N} D_{ij,B} \frac{dy_j}{dr} \quad (1), \quad \dot{M}_i = \dot{m}_i + y_i \dot{M}_i \quad (2)
\]

where \( D_{ij,B} \) are polynary diffusion coefficients for barycentric systems \((I = A, B, C)\). The general statement for ternary diffusion coefficients is [13]:

\[
D_{ij} = \left[ (y_j + y_k)\mu_i (\mu_k + y_i (\mu_j - \mu_k) \right] D_i D_k + y_i \mu_j (\mu_k + y_k (\mu_i - \mu_k)) D j D k + + y_i y_k \mu_i (\mu_j - \mu_k) D j k D j k \right] / D
\]

where coefficient D is defined as

\[
D = y_i \mu_i \mu_k \overline{D}_{jk} + y_j \mu_j \mu_k \overline{D}_{ik} + y_k \mu_i \mu_j \overline{D}_{ij}
\]

(4)

Dimensionless diffusion coefficients \( D^{*}_{AB,B} \), \( D^{*}_{AC,B} \), \( D^{*}_{BC,B} \), \( D^{*}_{CA,B} \), \( D^{*}_{CB,B} \) are obtained considering polynary diffusion coefficients -

\[
D_{AB,B}, D_{AC,B}, D_{BC,B}, D_{CA,B}, \text{and } D_{CB,B}
\]

and equations \( \mu_B^* = \mu_B / \mu_A, \mu_C^* = \mu_C / \mu_A, \)

\[
D_{ij,B}^* = \frac{D_{ij,B}}{D_{AC}}, \quad D_{ij}^* = \frac{D_{ij}}{D_{AC}}
\]

A sample formulation for dimensionless polynary diffusion coefficient, \( D^{*}_{AB,B} \), is given as follows:

\[
D_{ij,B}^* = \left( (y_a + y_c)(\mu_i^* + y_i (\mu_a - \mu_i^*) \right] \overline{D}_{AB} + y_a \mu_i^* (\mu_a + + y_c (1 - \mu_i^*) \right] D_{AB} \overline{D}_{BC} + y_a y_c \mu_i^* (\mu_a - 1) \overline{D}_{BC} \right] / D
\]

(5)

Where \( \overline{D}_{AB} \) and \( \overline{D}_{BC} \) are dimensionless binary diffusion coefficients and \( D' \) is defined as

\[
D' = y_a \mu_i \mu_c \overline{D}_{BC} + y_a \mu_c \overline{D}_{AB} + y_c \mu_B \overline{D}_{ABC}
\]

(6)

It is possible to calculate the dimensional binary diffusion coefficient for low-density (diluted) gases from the kinetic theory of gases. Based on the theory of Chapman-Enskog [14], binary diffusion coefficient is calculated as:

\[
\overline{D}_{ij} = 1.8583 \times 10^{-2} \left[ \frac{1}{T} \left( \frac{1}{\mu_i} + \frac{1}{\mu_j} \right) \right] \frac{P_0 \sigma_i^2 \Omega_{ij}}{\rho T}
\]

(7)

The binary diffusion coefficient depends proportionally on temperature and inversely proportional to molar masses and pressure. This means that \( \overline{D}_{ij} \) will increase with an increase in temperature, and decrease with an increase in molar masses and pressures. Both the dimensional and dimensionless binary diffusion coefficients calculated are presented in Table 1. The reaction rate definition for the \( i \)’th component can be written based on the ideal gas equation as follows:

\[
\dot{n}_{i} = k_i c_i = k c x_i \quad (i = A, C \text{ components})
\]

(8)

In Eq.(8), \( x_i \) defines the ratio of the mole number of \( i \) component to total mole number and it is called as mole percentage. By substituting

\[
P_i = \rho_i R_i T = H_i x_i,
\]
If there is no mass transfer in the axial direction, the mass flow, \( \dot{M}_{ic} \), on the wall is equal to the chemical transformation \( \dot{m}_u \cdot \dot{M}_{ic} = 0 \) for component B (CH\(_4\)) which is the passive gas on the wall. Thus, \( \dot{m}_D \) can be rewritten as [13]:

\[
\dot{m}_D = \frac{k_c R T \delta y_i - \rho y_i v_c}{H_i} \tag{10}
\]

Where,

\[
v_c = \frac{k_c R T \delta}{H_A} y_A + \frac{k_c R T \delta}{H_C} y_c \tag{11}
\]

The dimensionless diffusion mass flux can be obtained using the following equations:

\[
\dot{m}_D^* = \dot{m}_D \frac{R}{\rho_0 D_{AC}} \tag{12}
\]

\[
v^* = 2 \frac{d}{D_{AC}} v \tag{13}
\]

Then, the Damköhler number (Da) which is an important parameter in the analysis of catalytic gas reactions defines the ratio of the reaction rate to diffusion rate. The first Damköhler number (Da1) for “A” component and the second Damköhler number (Da2) for “C” component are formulated as shown in Eq(15) and Eq(16) respectively:

\[
Da_1 = \frac{k_c R T}{D_{AC} H_A} \delta \tag{15}
\]

\[
Da_2 = \frac{k_c R T}{D_{AC} H_C} \delta \tag{16}
\]

The dimensionless parameter, \( v^*_c \), can be calculated by taking into account

\[
v^*_c = 4 Da_1 y_A + 4 Da_2 y_C \tag{17}
\]

the wall (namely film) interface mass transfer equations for A and C components have been shown as follows:

\[
\begin{align*}
\frac{\partial}{\partial r} \left( r y_A \frac{\partial y_A}{\partial r} \right)_c + \frac{1}{4} y_A v^*_c = 0 \\
\frac{\partial}{\partial r} \left( r y_C \frac{\partial y_C}{\partial r} \right)_c + \frac{1}{4} y_C v^*_c = 0
\end{align*}
\tag{18}
\]

Similarly, if mass transfer occurs in the axial direction on the wall due to the interface velocity, the following equation can be expressed:

\[
V \dot{m}_u + \rho_i u_c S = (\dot{m}_D + \rho_j v_c) S = \dot{M}_{ic} \tag{20}
\]

Then, the dimensionless diffusion mass flux, \( \dot{m}_D^* \), can be re-derived as:

\[
\dot{m}_D^* = Da_i \rho_j y_i - \frac{1}{4} \rho_j y_i v_c + \frac{1}{2} \rho_i u_c y_i \quad \text{ReSc} \tag{21}
\]

With the combination of Eqs. (20) and (21) by replacing i with A and C components in Eq. (20), the radial velocity on the wall is obtained as [13]

\[
v^*_c = 4 Da_1 y_A + 4 Da_2 y_C + 2 \text{ReSc} v^*_c \tag{22}
\]

The axial velocity for the wall used in the equations above can be defined by Navier-Stokes equation subjected to Prandtl simplification as described by Kaufmann [15] including constant, laminar and compressible flow. Considering Navier-Stokes equations, the following equation can be defined as
\[
\frac{\rho u}{\partial x} + \rho v \frac{\partial u}{\partial t} = - \frac{dP}{dx} + \eta_k \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) \right] \quad (23)
\]

Assuming fully developed flow conditions and \( \rho v \frac{\partial u}{\partial t} = 0 \), integration of \( \rho u \frac{\partial u}{\partial x} \) accounting boundary values (\( r = 0, u = u_{\text{max}} \) and \( r = R, u = u_c \)) results in:

\[
u = u_c + 2u_0 \left( 1 - \left( \frac{r}{R} \right)^2 \right) \quad (24)
\]

\[r^* = \frac{r}{R} \text{ and } u^* = u/u_0 \text{ if the equation is written in dimensionless form,}
\]

At \( r^* = 1 \), \( u^* = u_c^* \)

At \( r^* = 0 \) \( u_{\text{max}}^* = u_c^* + 2 \)

Above equations made dimensionless in the case with and without consideration of mass transfer due to the interface (wall) axial velocity, are solved separately with finite differences and adapted to the packaged program given by Gram [16]. The values calculated are shown in Table 2. These data and the equations obtained for Re = 0 and Re = 2 are adapted to the computer software and the results are illustrated in Figure 2 to 5. Where A, B and C stands for CO\(_2\), CH\(_4\) and H\(_2\)S, respectively.

\[\mu_i^* = \frac{\mu_i}{\mu_A} \text{; dimensionless molar mass for i component, } \eta_i^* = \frac{\eta_i}{\eta_A} \text{; dimensionless dynamic viscosity for i component.} \]

\[
\frac{U \frac{\partial u}{\partial x}}{\frac{\partial u}{\partial t}} = \left[ \sigma U_{i,j+1} + (1 - \sigma)U_{i,j} \left( u_{i,j+1} - u_{i,j} \right) \right] / \Delta x^* \quad (29)
\]

\[
\frac{\partial u}{\partial t} = \left[ \sigma(u_{i+1,j+1} - u_{i-1,j+1}) + (1 - \sigma)(u_{i+1,j} - u_{i-1,j}) \right] / 2\Delta r^* \quad (30)
\]

\[
\frac{\partial \left( \frac{F \frac{\partial u}{\partial t}}{\partial t} \right)}{\partial r} = \frac{1}{\Delta r^*} \left[ \sigma \left( F'_{i+1/2,j+1}(u_{i+1,j+1} - u_{i,j+1}) - F'_{i-1/2,j+1}(u_{i,j+1} - u_{i-1,j+1}) \right) \right] +
\]
where $U$ and $F$ are symbols for variables. Subscripts $i$ and $j$ in Equations above are used for the variables in radial and axial directions. Forward direction for the first order derivative using 4 points is defined as

$$\frac{\partial y}{\partial h} = \frac{1}{6\Delta h} \left( -2y_4 + 9y_3 - 18y_2 + 11y_1 \right)$$

Where, $h = r^*$. Concentration gradients on the wall can be computed as

$$\left( \frac{\partial y_i}{\partial r^*} \right)_{r^*=1} = \frac{1}{6\Delta r} \left( -2y_{i,39} + 9y_{i,38} - 18y_{i,40} + 11y_{i,41} \right)$$

The radial velocities are obtained by numerical integration using Trapezoidal rule and Simpson’s rules.

$$v^* = \frac{1}{r \rho^*} \int r^* \frac{\partial}{\partial x^*} \left( r^* \rho^* u^* \right) dr^*$$

The equation systems obtained for $U^*$, $Y_A^*$, and $Y_C^*$ are solved iteratively by Gauss elimination technique. With the iterative solution, the linearization magnitudes of $U'$ and $F'$ take the values computed at the previous iteration step. For values obtained at every iteration step, the relative error limit is assigned as

$$\left| \frac{U - U'}{U} \right| \leq 10^{-4}$$

The implicit method is used in the numerical solution of the problem. The weight factor is taken $\sigma = 0.75$ in the computations due to the stability of the problem. The vertical tube inlet temperature is assumed to be 50°C for the calculations.

### 4. RESULTS AND DISCUSSION

A numerical study has been performed to analyze the purification of natural gas absorption via monoethanolamine (MEA). Effects of Damköhler number, Reynolds number and different reactant were tested.

Solubility of Carbon Dioxide ($CO_2$) in aqueous mixtures of monoethanolamine (MEA) with methyldeethanolamine (MDEA) has been measured at 40, 60, 80 and 100°C and at partial pressures of carbon dioxide between 1 and 200 kPa. The solubility of carbon dioxide ($CO_2$) in aqueous solutions is reported as functions of partial pressures of carbon dioxide at the temperatures studied. In this study, solubilities of $CO_2$ in 15.3 wt %MEA aqueous solution at 40 °C have been measured and the results are presented in Figure 2. The solubility data obtained in this study are generally in good agreement with the data reported by other investigators in Figure 3. The higher the $CO_2$ partial pressures, the higher the $CO_2$ loading obtained in the alkanolamine aqueous solutions. Generally, the solubility of $CO_2$ with temperature; the higher temperature of the system, the lower the $CO_2$ solubility observed [14].
Fig. 2. Solubility of CO$_2$ in 15.3 wt % MEA aqueous solution at 40°C.

Fig. 3. Solubility of CO$_2$ in 30 wt % MEA aqueous solution at 40-100°C
Table 1. Dimensional and dimensionless binary diffusion coefficients for substance pairs.

<table>
<thead>
<tr>
<th>Substance pairs</th>
<th>CO$_2$-CH$_4$(B)</th>
<th>CH$_4$(B)-H$_2$S(C)</th>
<th>CO$_2$(A)-H$_2$S(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overline{D}_{ij}$  (cm$^2$ s$^{-1}$)</td>
<td>0.194</td>
<td>0.2</td>
<td>0.1373</td>
</tr>
<tr>
<td>$\overline{D}_{ij}^*$</td>
<td>1.413</td>
<td>1.4566</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2. Physical properties of the components in the gas mixture.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$y_i$</th>
<th>$\mu_i$ (g/mol)</th>
<th>$\mu_i^*$</th>
<th>$\eta_i$ (g/cm.s)</th>
<th>$\eta_i^*$</th>
<th>$\rho_i$ (g/cm$^3$)</th>
<th>Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.2</td>
<td>44.01</td>
<td>1</td>
<td>16.211x10$^{-5}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.7</td>
<td>16.04</td>
<td>0.3644</td>
<td>11.954x10$^{-5}$</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.1</td>
<td>34.09</td>
<td>0.7745</td>
<td>13.776x10$^{-5}$</td>
<td>0.85</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO$_2^+$</td>
<td>CH$_4^+$</td>
<td>19.562</td>
<td>(1)</td>
<td>12.6795x10$^{-5}$</td>
<td>0.7381x10$^{-3}$</td>
<td>(0)</td>
<td>1.251</td>
</tr>
<tr>
<td>H$_2$S</td>
<td></td>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this study, the results of numerical solution of purification of natural gas absorbed by monoethanolamine (MEA) are presented in Figure 4 through 5. The primary cause of molecular diffusion is the concentration gradients. Hence, the concentration area change must be known in order to examine the diffusion area. The change of the concentration profiles of A and C components at various $x^*$ values are shown in Figure 4. The transformation increased with the elevation of $X^*$ and $r^*$ values, but because of that $Y_A$ and $Y_C$ values decreased (Re = 0). The variation of the concentration profiles of A, C components at various $X^*$ values as to the radial coordinate in Fig. 5 (a) and (b) drawn when Re exists in the obtained equations.
Fig. 4. The radial change of different reactants concentration at various values of dimensionless axial coordinate

\[ x^* = \frac{r}{d} \frac{1}{Re Sc} \], in the case of Da = 15 (Re = 0), a) A (CO₂), b) C(H₂S)
Fig. 5. The radial change of different reactants concentration at various values of dimensionless axial coordinate

$$x^* = \frac{x}{\frac{1}{d \text{ Re Sc}}}$$, in the case of Da = 15 (Re = 2), a) A (CO\(_2\)), b) C(H\(_2\)S)
5. CONCLUSIONS
In this study, the process during the purification of natural gas is investigated. It is observed that the effect of interface axial flow velocity between natural gas and MEA can be neglected in mass transfer calculations. The effect of interface axial flow velocity is also negligible for Re = 0 and very small Re numbers, since the concentration change is resulted in A and C components as expected in the used Gram’s packaged software. If the figures of both cases are compared, it can be seen that the correct results are obtained by taking the very low Reynolds number value into account in the interface axial direction. It is an important result that all calculations can be made for the case in Re = 0.

REFERENCES