Abstract. Gas separation using membrane is now an established unit operation in the chemical process industry. The performance of a single stage membrane permeator depends, among other things, on the feed and permeate flow pattern. In this paper, models for five different idealized flow patterns namely cocurrent flow, countercurrent flow, cross flow, perfect mixing and on-side mixing have been presented. A computer program written in Power Basic has also been developed. The models developed can be used for a binary mixture or multi-component gas feed system. A simple bisection method is used instead of the Newton iterative method originally suggested by Shindo et. al. [6] to solve the root finding-problem in order to ensure convergence. In this study countercurrent flow is found to be the most efficient flow pattern, giving the highest degree of separation and requiring the least membrane area.

1.0 INTRODUCTION
Since MONSANTO introduced its first commercial 'PRISM' gas separation system more than a decade ago, membrane technology has now entered territories that were previously dominated by more traditional separation methods such as cryogenic distillation, absorption and adsorption. Even in many cases where membranes have not yet completely replaced these technologies, hybrid systems based on membranes combined with one of these traditional techniques are being accepted as attractive options [1]. Compared to the more traditional separation methods, membranes have advantages such as low capital investment, ease of operation, low energy consumption, cost effectiveness and good weight and space efficiency [2].

Separation through membrane is achieved when different components in a gas mixture permeates with different rates through it under a driving force. The driving force for the gas permeation is the chemical potential gradient across the membrane surface, which is maintained by a partial pressure difference from the feed side to the permeate side of the membrane.

Although far back in 1868, Graham had already recognized the ability of membrane for separation of gases, its commercial application was hindered by the difficulties to obtain a membrane material having both the qualities of high permeability and high selectivity for commercial application. It is only when Loeb and Sourirajan in 1960 introduced a technique to prepare an asymmetrically structure membrane that the membrane technology began to make a breakthrough. The well known asymmetric membrane consists of two parts: the separation takes place in a very thin, nonporous, selective skin layer, while the remaining of the membrane consists of highly porous nonselective layer which acts as a support for the thin skin layer.
The performance of a membrane system depends not only on the polymeric material and morphology but also on the operating conditions, feed permeate flow pattern and configurations. The combination of membrane configurations and input-output port arrangement results in many possible feed and permeate flow patterns. Five different idealized flow pattern can be identified. These include: countercurrent flow, cocurrent flow, cross flow, one side mixing and perfect mixing.

A membrane system in either case is characterized by the following variables: feed compositions, intrinsic selectivity, pressure ratio, dimensionless area, retentate compositions, permeate compositions and stage cut. Mathematical modelling provides a useful way to study and predict the performance of a membrane system. The effect of different key parameters on the performance of the membrane system can be determined using parametric studies.

In the early days most models were developed for binary system. However the removal of carbon dioxide from natural gas, hydrogen recovery from ammonia synthesis, helium recovery from natural gas and removal of carbon dioxide from life support system involved a multicomponent separations.

Brubaker and Kammermeyer [3] studied ternary and quaternary systems with perfect mixing assumption. They observed that compositions of intermediate components in the permeated products can pass through a maximum value at a certain cut fraction. Stern et al. [4] developed an iterative calculation method for multicomponent mixture with perfect mixing. Pan and Habgood [5] presented a calculation method for a multicomponent mixture in the cross flow driving force adequately describes the permeation of any flow pattern in a permeator. Few researchers developed calculation method for multicomponent systems for five idealized flow patterns ([6], [7]). Sutrasno [8] developed a computer program for a multicomponent mixture, namely cross flow, cocurrent flow and on-side mixing using the approach suggested by Shindo et al. [6].

The objective of this study is to develop a computer programme based on the calculation methods suggested by Shindo et al. [6], that could be used for five idealized flow patterns. The program has been used to perform simulations on the effects of stage cut, pressure ratio, feed composition, flow patterns on module performance and membrane area requirements.

2.0 MODEL DEVELOPMENT

The models developed for the above mentioned five flow patterns are based on the following basic assumptions: (1) The ideal gas law is followed; (2) Operations is isothermal; (3) The rates of permeation obey Fick's law; (4) The permeabilities are independent of concentration and pressure; (5) The porous supporting layer of the membrane offers negligible resistance to gas flow; (6) The effective membrane thickness is uniform along the length of the permeator; (7) No concentration polatization; (8) Pressure drops of feed and permeate gas streams are negligible; (9) Fiber deformation under pressure is negligible.

2.1 Cocurrent Flow

The cocurrent flow pattern shown in Figure 1 was used to illustrate the development of a mathematical model.

The feed stream enters the permeator from the higher pressure side and the permeate stream exits the permeator from the low pressure side. The concentration of the more permeable component declines on the high pressure side, and the less permeable component enriches in the retentate stream. Therefore, the partial pressure difference of the more permeable component decreases along the high pressure side of the permeator and the opposite is true the less permeable component. For a surface element dA, the overall material balance is described by

\[-dF = dG\]  \hspace{1cm} (1)
COMPUTER MODELLING OF MULTICOMPONENT GAS SEPARATION

\[ dA \sum_{k=1}^{n} \frac{Q_k}{d} (P_f X_k - P_p Y_k) \]  

(2)

Where

- \( F \) - flowrate on the feed stream
- \( G \) - flowrate on the permeate stream parallel to the feed stream
- \( Q_k \) - permeabilities of component \( k \)
- \( d \) - thickness of the membrane
- \( P_f \) - pressure at the feed side
- \( P_p \) - pressure in the permeate side
- \( X_k \) - mole fractions of components \( k \) on the feed side
- \( Y_k \) - mole fractions of component \( k \) on the permeate side

The mass balance for any component \( i \) is,

\[ -d(X_i, F) = d(Y_i, G) \]  

(3)

\[ = dA \frac{Q_i}{d} (P_f X_i - P_p Y_i) \]  

(4)

Expanding the right hand side of equation (4), followed by substitution of equation (2) gives

\[ d_{x_i} = -\frac{dA}{F} \left[ \frac{Q_i}{d} (P_f X_i - P_p Y_i) - X_i \sum_{k=1}^{n} \frac{Q_k}{d} (P_f X_k - P_p Y_k) \right] \]  

(5)

Integration between the limits of inlet point to an arbitrary point gives

\[ G = F_f - F \]  

(6)

\[ Y_i = \frac{X_i F_f - X_i F}{F_f - F}; G = 0 \]  

(7)

where the subscript \( f \) refers to the inlet. Equation (7) does not apply for condition at the closed end of the permeator, where \( G = 0 \) at \( A = 0 \). In that case, the mole fraction \( Y \) is obtained by applying L'Hospital rule, and the ratio of two components is

\[ \frac{Y_i}{Y_i + 1} = \frac{Q_i (P_f X_i - P_p Y_i)}{Q_j (P_f X_j - P_p Y_j)} \]  

(8)

Rearrange equation (8)

\[ Y_i = \frac{X_j Q_j / Q_i}{P_p / P_f \left\{ (Q_j / Q_i) - 1 \right\} + (X_i / Y_i)} \]  

(9)

The mole fraction in summation for the feed and permeate streams respectively gives:

\[ \sum_{k=1}^{n} X_k = 1 \]  

(10)

\[ \sum_{k=1}^{n} Y_k = 1 \]  

(11)
Substituting equation (9) into equation (11) gives

\[ \sum_{k=1}^{n} \frac{X_k Q_k / Q_i}{P_p / P_f \left\{ (Q_k / Q_i) - 1 \right\}} + (X_i / Y_i) = 1 \]  

(12)

Mass balance around the entire permeator for component i gives

\[ X_{fi} = X_{ri} F + Y_{pi} (1 - F) \]  

(13)

The governing equations for computation are obtained by defining the following dimensionless parameters:

\[ \gamma = \frac{P_p}{P_f} \]  

(14)

The mass flow ratio in the feed and permeate side of the permeator are given in equations (15) and (16) respectively,

- Feed side mass flow ratio  
  \[ f = \frac{F}{F_f} \]  

(15)

- Permeate side mass flow ratio  
  \[ g = \frac{G}{F_f} \]  

(16)

- Dimensionless membrane area  
  \[ S = A Q_m P_h / F_f \]  

(17)

- Selectivity  
  \[ \alpha_i = \frac{Q_i}{Q_m} \]  

(18)

- Stage cut  
  \[ \theta = 1 - f_r \]  

(19)

Where \( Q_m \) is the permeability of the least permeable component and subscript r refers to the retentate stream.

Equations (14 - 19) are used in equations (2, 4-7, 9-13) to arrive at the following governing equations in terms of dimensionless variables:

\[ \frac{df}{dS} = - \sum_{k=1}^{n} \alpha_i (X_k - \gamma Y_k) \]  

(20)

\[ \frac{dX_i}{dS} = \frac{1}{f} \left[ \alpha_i (X_i - \gamma Y_i) - X_i \frac{df}{dS} \right] (i = 1, ..., n - 1) \]  

(21)

\[ X_n = 1 - \sum_{k=1}^{n-1} X_k \]  

(22)

\[ X_i = X_1 (1 - \theta) + Y_{pi} \theta (i = 1, ... n) \]  

(23)

\[ g = 1 - f \]  

(24)

\[ Y_i = \frac{X_i - fX_i}{1 - f}, g \neq 0 (i = 1, ..., n - 1) \]  

(25)
The solution for a multicomponent gas separation problem in the cocurrent flow pattern is an initial value problem and can be obtained by solving equations (20-28) sequentially and iteratively with initial conditions \( X_i = X_{fi} \), \( f = f_i \) from \( S = 0 \) until \( S = S \). The solution starts with the calculation of the least permeable component in the permeate by equation (26), which is a root finding problem (in the case \( Y_i \)). The Newton's iterative procedures suggested by Shindo et al. [6] was found to diverge at \( Y_i \) close to 0 and 1. A simple bisection method is employed here to ensure convergence. The remaining permeate concentration in the close end of the permeator (\( g = 0 \)) can be calculated using equations (27 - 28) which are simple algebraic equations. To calculate \( X_i \), two couple ordinary differential equations (19 - 20) need to be solved. A simple Euler method is employed and found satisfactory. For \( Y_i \) in the remaining path of the permeator (when \( g = 0 \) = 0) equation (24) is used.

### 2.2 Countercurrent Flow

For countercurrent flow pattern (Figure 2), the derivation of the governing equation is similar to the one for cocurrent flow except that the permeate flow parallel to the feed stream, \( g \), always has a negative value. The system of equations (20 - 28) is still valid, except that equations (24 - 25) are replaced by equations (30-31) by integrating from an arbitrary point to the outlet

\[
g = f - (1 - q) \quad (30)
\]

\[
Y = \frac{X_i F - X_{oi} (1 - \theta)}{f - (1 - \theta)} ; \quad g \neq 0 \quad (31)
\]

The solution procedure is similar to the cocurrent flow except that the integration is carried out backward. Numerical integration of the system of equations is obtained iteratively backward from \( S = S \) to \( S = 0 \) with an initial guess of \( X_{fi} \) (i = 1, ..., n - 1) and \( q \) until \( X_{iS} \) and \( f \) at \( S = 0 \) are sufficiently close to \( X_{fi} \) (i = 1, ..., n - 1) and \( f \) respectively.

### 2.3 Cross Flow

The model assumes that the gas on the high pressure side of the permeator flows parallel to the membrane with plug flow, while the permeate on the low pressure side flows perpendicular to the membrane without mixing with each other. Since the permeate stream is in the direction perpendicular to the feed stream, there is no parallel flow to the feed stream on the permeate side, so \( g = 0 \) over the entire membrane surface area. Equations (20 - 22, 26 - 28) are solved iteratively with initial condition \( X_{iS} = X_{fiS} \) from \( S = 0 \) until \( S = S \). The mole fractions of the permeate at the outlet can be calculated by equation (29).
2.4 One-side Mixing
For one-side mixing model as shown in Figure 4, the gas stream at the high pressure side is assumed to be in plug flow, while the gas stream on the low pressure side is maintained perfectly mixed which means the mole fraction of permeated gas is uniform at all points along the membrane. Thus the system of equations is reduced to equation (20 - 23). The calculation procedure starts with guessing the value of $Y_{iS}$ ($i = 1, \ldots, n - 1$) and integrating from $S = 0$ to $S = S$ until the values of q satisfy equation (29).

2.5 Perfect Mixing
The model of perfect mixing is shown in Figure 5. The model assumes that the rate of mixing on the high pressure side of the permeator is so rapid, as compared with the flow rate, that the gas stream has the same composition as the unpermeated streams at all points along the membrane. The same assumption is made for the low pressure side. For perfect mixing

$$\frac{Y_{pi}}{Y_{pj}} = \frac{Q_i (X_i - \gamma Y_{pi})}{Q_j (X_j - \gamma Y_{pj})}$$  \hspace{1cm} (32)

Eliminating $X_n$ and $X_p$ using equation (23) and rearranging for $Y_{pj}$ gives

$$Y_{pj} = \frac{X_n \alpha_j}{(\gamma + \theta - \gamma \theta) \left\{ (\alpha_j - 1) + (X_n / Y_{pj}) \right\}}$$  \hspace{1cm} (33)

Substituting of equation (33) into equation (11) gives

$$\sum_{k=1}^{n} \frac{X_{nk} \alpha_k}{(\gamma + \theta - \gamma \theta) \left\{ (\alpha_k - 1) + (X_n / Y_{pj}) \right\}}$$  \hspace{1cm} (34)

Equation (34) is implicit in $Y_{pi}$ and can solved conveniently by Newton's iterative procedure. The value of $Y_{pi}$ for the other component can be obtained using equation (33). The mass balance for the overall membrane surface area is.

$$\theta = S \sum_{k=1}^{n} \alpha_k (X_{nk} - \gamma Y_{pk})$$  \hspace{1cm} (35)

The solution procedure for perfect mixing involves guessing a value of $\theta$, calculating $Y_{pi}$'s by equations (33 - 34) and $X_{nk}$ by equations (32) until equation (35) is satisfied.

3.0 COMPUTATION RESULTS AND DISCUSSION
As mentioned earlier a membrane permeator is characterized by the variables: $X_{fi}$, $\alpha_{is}$, $g$, $S$, $X_{ni}$ and $Y_{pi}$'s and $\theta$. Usually for a particular system, the feed compositions ($X_{fi}$), selectivities ($\alpha_{is}$) and pressure ratio ($\gamma$) are given. With the remaining variables, many situations can be considered. We will treat only the two most commonly encountered problems.

Type 1 problem: To find $X_{ni}$, $Y_{pi}$'s and $\theta$ for given $X_{fi}$, $\alpha_{is}$, $\gamma$ and $S$
Type 2 problem: To find $X_{ni}$, $Y_{pi}$'s and $S$ for given $X_{fi}$, $\alpha_{is}$, $\gamma$ and $\theta$
The calculation methods presented above are used for Type 1 problem. The system of equation required for the calculation of Type 2 problem can be obtained by rearranging those used for Type 1 problem. The calculation method for Type 2 problem are shown in Appendix A.

The separation of a three component mixtures: \( \text{NH}_3, \text{H}_2 \) and \( \text{N}_2 \) by permeation through a polyethylene membrane was used for this computation. The permeability data used are shown in Table 1. The computation conditions and results are shown in Table 2 and 3.

Computations were performed for all the five flow patterns. Simple Euler method was found to solve the ordinary differential equations satisfactorily. Equations (26, 34) were solved using simple bisection method to ensure convergence. A trial-error procedure was required for countercurrent flow, perfect mixing and one-side mixing. Modified Box method as described by McCandless [9] is used for this purpose. The computer program was written in Power Basic Ver 2.10 and the simulations were run on an IBM PC-386.

4.0 CONCLUSION

The computer program written in Power Basic Version 2.10 has been successfully developed and used to solve mathematical models for separation of multi-component gas mixture in a membrane permeator under different flow patterns namely cocurrent, countercurrent, cross flow, one side mixing and perfect mixing. A three component gas mixture which consists of \( \text{NH}_3, \text{H}_2 \) and \( \text{N}_2 \) was used to test and verify the models with good result especially for the countercurrent flow pattern. The models can also be extended further to incorporate the effect of pressure build-up on the performance of permeator in a hollow fiber configuration.

5.0 ACKNOWLEDGMENT

The authors wish to acknowledge the Membrane Research Unit (MRU) and Petronas Research and Scientific Services (PRSS) for their contributions in making this study possible. Other parties which are directly or indirectly involved are also thanked.

6.0 APPENDIX A

Dividing equation (21) by equation (20) gives

\[
\frac{dX_i}{df} = \frac{\alpha_i (X_i - \gamma Y_i)}{f (- \frac{df}{dS})}; (i = 1, \ldots, n - 1)
\]  

(A-1)

\[
\frac{dS}{df} = \frac{-1}{\sum_{k=1}^{n} \alpha_k (X_k - \gamma Y_k)}
\]  

(A-2)

For cocurrent flow, countercurrent flow, crossflow and one-side mixing, the solution procedures are the same as Type 1 problem except that equations (A-1) and (A-2) are used instead of equations (20 - 21). For perfect mixing, the values of \( Y_i \)s and \( X_i \)s can be directly calculated by equations (29, 33 - 34).

The dimensionless membrane area, \( S \) is given by

\[
S = \frac{\theta}{\sum_{k=1}^{n} \alpha_k (X_k - \gamma Y_{pk})}
\]  

(A-3)
REFERENCES


NOMENCLATURE
A  membrane area (m²)
F  Flow rate on the feed stream (mol/s)
f  dimensionless flow rate on the feed stream
G  Flow rate on the permeate stream parallel to the feed stream
g  dimensionless flow rate on the permeate stream parallel to the feed stream
n  number components
P  pressure (Pa)
Q  permeability (mol/s.m.Pa)
S  dimensionless membrane area
X  mole fraction of the gas component in the feed stream
Y  mole fraction of the gas component in the permeate stream

GREEK
γ  pressure ratio, Pp/Pf
θ  stage cut
α  selectivity, ration of permeability over the least permeable component

SUBSCRIPT
i, j, k  component indication
f  inlet
p  permeate
r  retentate
Figure 1 Schematic diagram of a single stage permeator with cocurrent flow

Figure 2 Schematic diagram of a single stage permeator with countercurrent flow

Figure 3 Schematic diagram of a single stage permeator with cross flow
Figure 4 Schematic diagram of a single stage permeator with one-side mixing

Figure 5 Schematic diagram of single stage permeator with perfect mixing
Table 1 Permeability of gasses through a polyethylene membrane at 50°C

<table>
<thead>
<tr>
<th>No</th>
<th>Gas</th>
<th>Q (mol/s.mPa)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH₃</td>
<td>36.9 × 10⁻¹⁵</td>
<td>15.311</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>11.7 × 10⁻¹⁵</td>
<td>4.858</td>
</tr>
<tr>
<td>3</td>
<td>N₂*</td>
<td>2.41 × 10⁻¹⁵</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Note* - Base Component

Table 2 Computation results for Type 1 problem

<table>
<thead>
<tr>
<th>Permeate</th>
<th>Mole Fraction, Y&lt;sub&gt;p&lt;/sub&gt;</th>
<th>NH₃</th>
<th>H₂</th>
<th>N₂</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Countercurrent flow</td>
<td>0.7371</td>
<td>0.2009</td>
<td>0.0630</td>
<td>0.3742</td>
<td></td>
</tr>
<tr>
<td>Cross flow</td>
<td>0.7340</td>
<td>0.2036</td>
<td>0.0624</td>
<td>0.3726</td>
<td></td>
</tr>
<tr>
<td>One-side Mixing</td>
<td>0.7325</td>
<td>0.2046</td>
<td>0.0629</td>
<td>0.3718</td>
<td></td>
</tr>
<tr>
<td>Cocurrent flow</td>
<td>0.7302</td>
<td>0.2068</td>
<td>0.0630</td>
<td>0.3702</td>
<td></td>
</tr>
<tr>
<td>Perfect Mixing</td>
<td>0.6986</td>
<td>0.2230</td>
<td>0.0784</td>
<td>0.3365</td>
<td></td>
</tr>
</tbody>
</table>

System parameters: pressure ratio, γ = 0.13; dimensionless area, S = 1.0, permeabilities, Q as shown in Table 1. Feed composition: NH₃ = 0.45, H₂ = 0.25, N₂ = 0.30

Table 3 Computation results for Type 2 problem

<table>
<thead>
<tr>
<th>Permeate</th>
<th>Mole Fraction, Y&lt;sub&gt;p&lt;/sub&gt;</th>
<th>NH₃</th>
<th>H₂</th>
<th>N₂</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Countercurrent flow</td>
<td>0.7058</td>
<td>0.2202</td>
<td>0.074</td>
<td>1.4616</td>
<td></td>
</tr>
<tr>
<td>Cross flow</td>
<td>0.7006</td>
<td>0.2241</td>
<td>0.0752</td>
<td>1.4759</td>
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<tr>
<td>One-side Mixing</td>
<td>0.6961</td>
<td>0.2273</td>
<td>0.0766</td>
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<tr>
<td>Cocurrent flow</td>
<td>0.624</td>
<td>0.2304</td>
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<tr>
<td>Perfect Mixing</td>
<td>0.6395</td>
<td>0.2494</td>
<td>0.0116</td>
<td>1.7509</td>
<td></td>
</tr>
</tbody>
</table>

System parameters: pressure ratio, γ = 0.13; stage cut, θ = 1.5, permeabilities, Q as shown in Table 1. Feed composition: NH₃ = 0.45, H₂ = 0, N₂ = 0.30