Comparing Numerical Methods for Multicomponent Gas Separation by Single Permeation Unit

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ABSTRACT:
This paper is an effort of comparing numerical methods for the multicomponent membrane gas separation. As an example for membrane gas separation a detailed model of co-current flow process is considered. After the derivation of model, different numerical techniques for the solution of mathematical model are presented. Seven different numerical methods such as Bogacki–Shampine method, Dormand–Prince method, Adams-Bashforth-Moulton method, numerical differentiation formulas, modified Rosenbrock formula of order 2, Trapezoidal rule with free interpolant and Trapezoidal rule with backward difference formula of order 2 are used to solve ordinary differential equations. The methods, problems and comparison criteria are stated very carefully. Then the numerical methods are categorized on their stability basis. The recommended numerical method shows good agreement with the experimental and numerical values in the literature.

Keywords: numerical comparison, membrane gas separation, co-current flow

1. INTRODUCTION
Membrane gas separation occurs in chemical engineering in a large diversity. It plays an important role in many industrial production processes, like, e.g. hydrogen recovery, Air separation, natural gas dehydration, etc. A common characteristic of all those systems is that a gas mixture at a high pressure is fed to the feed side of the membrane, while the permeate gas at a lower pressure is removed from the permeate side of the membrane as shown in Figure 1. An appropriate modeling method to describe membrane gas separation in chemical engineering has been developed in the 1960s by the fundamental articles of [1, 2]. For a detailed overview on the modeling approach of membrane gas separation, the reader is referred to [3,4].

The application of the co-current flow based modeling approach to membrane gas separation leads in general to a complex mathematical model of coupled ordinary differential equations (ODEs). This ascends from the point that for a detail understanding of the main processes in a membrane gas separation, very comprehensive models on a microscopic level are required to explain multicomponent gas separation through a single permeation unit. It is clear that for correct analysis of this membrane gas separation flow processes, high computational effort is required. Most mathematical model
developed in the past were detailed models made up of ordinary differential equation, whose numerical values usually showed good agreement to experimental results [3-8].

For the study of main problems, for example the scale-up from laboratory to plant scale, it is essential to use mathematical models, whose numerical parameters are completely determined by the plant setup, its geometry and the used chemical system. But this demand also indicates the requirement for necessarily precise numerical methods in order to solve the resulting co-current flow process. On the one hand, adulterated modeling results due to numerical errors make the interpretation of the computed solutions and therefore the model validation unnecessarily difficult. On the other hand, the numerically analysis behavior should be determined only by the assumed physical principles and not by the chosen numerical method. If properties of the numerical method that affect the model results are not taken into consideration, this may even prohibit statements on the qualitative process behavior.

The scope within this article is to investigate the influence of different numerical methods on the dynamic and stationary behavior of a membrane gas separation model. The co-current flow process is considered in paper for the comparison of different numerical methods in single membrane gas separation unit. This process will be described by a detailed mathematical model containing mainly stage cut, membrane area permeation and rejection of component.

The article is prepared as follows: After a short description of the used co-current model and its derivation, different numerical methods for the numerical simulation of the model will be discussed. We limit our consideration to numerical methods for initial value problems related with systems of first order ordinary differential equations. The test problems and comparison criteria are chosen so that the results for a specific method will depend primarily on how well it can carry out relatively routine integration steps under a variety of accuracy requirement. The consequences of the application of the discussed numerical methods on the behavior of the modeled co-current flow will then be illustrated by numerical results. The relevance of an accurate numerical solution and the conclusions drawn from these investigations for the modeling and analysis of co-current flow process for membrane gas separation unit in general will be stated at the end of the article.
2. MODEL DERIVATION OF CO-CURRENT FLOW

The single permeation stage as presented in Figure 2 is divided into two parts by area A, membrane of constant permeabilities $K_i$, membrane thickness $\delta$ and width $W$. The feed $Q^f$ enters the unit and is finally divided into two streams [4]: $Q^p$ on the permeate side and $Q^o$ leaving on the reject side. These streams have mole fractions respectively $x_i^f$, $y_i^p$ and $x_i^o$. Hence

$$\sum_{i=1}^{n} x_i^f = 1 \quad (1)$$

$$\sum_{i=1}^{n} x_i^o = 1 \quad (2)$$

$$\sum_{i=1}^{n} y_i^p = 1 \quad (3)$$

It is supposed that the permeabilities are arranged in descending order, i.e.

$$K_1 > K_2 > \ldots > K_i > K_{i+1} > \ldots > K_n$$

The following assumptions have been made while carrying out the analysis:

1. The permeability of each component is the same as that of the pure species and is independent of pressure.
2. Assumed the steady state.
3. The membrane is of uniform thickness.
4. The total pressure is essentially constant on each side of the membrane.
5. There are no concentration gradients in perpendicular direction of the membrane.
6. Plug flow is assumed.

We can write overall mass balance as

$$Q^f = Q^p + Q^o \quad (4)$$

Figure 2. Co-current flow.
Also, we can write component balance as

$$Q'_i x'_i = Q^p y_i^p + Q^0 x_i^0$$

(5)

The stage cut is defined as

$$\Phi = \frac{Q^p}{Q'} = \frac{Q'_i - Q^0}{Q'}$$

(6)

Figure 1 shows the schematic representation of co-current flow. The flow direction of gas streams is parallel and in same direction on both sides of the membrane. This paper deliberates the case for any number of components in a gas mixture. Following equations can be got by taking the differential area element dA [4].

$$Q' = q^h + q'^i$$

(7)

$$Q'_i x'_i = q^h x_i + q'^i y_i$$

(8)

$$dq^h = -dq'^i$$

(9)

$$d(q^h x_i) = -y_i dq'^i$$

(10)

$$y_i dq'^i = \left[ \frac{dA}{\delta} \right] K_i (P_h x_i - P_i y_i)$$

(11)

$$\frac{d(q^h x_i)}{dA} = -\frac{K_i}{\delta} (P_h x_i - P_i y_i)$$

(12)

also

$$\frac{d(q^h x_i)}{dA} = q^h \frac{dx_i}{dA} + x_i \frac{dq^h}{dA}$$

(13)

The following equations can be obtained by summing over the components from Equation (12)

$$\frac{dq^h}{dA} = -\sum_{i=1}^{n} \left[ \frac{K_i}{\delta} (P_h x_i - P_i y_i) \right]$$

(14)

The following equation is obtained for $x_i$ by using Equations (12), (13), and (14).

$$\frac{dx_i}{dA} = \left[ x_i \sum_{j=1}^{n} \frac{K_j}{\delta} (P_h x_j - P_i y_j) \right] - \frac{K_i}{\delta} (P_h x_i - P_i y_i)$$

(15)
By using Equations (7) and (8) we got

\[ y_i = \frac{Q_f - x_i^f - q^h x_i}{Q_f - q^h}, Q_f \neq q^h \]

When \( Q_f = q^h \) then \( q^f = 0 \), and the condition \( y_i = f(x_1, x_2, x_3, ..., x_n, i = f(x_i), i) \) is satisfied and may be used for determining \( y_i \)'s. Thus

\[ y_i = \begin{cases} \frac{Q_f - x_i^f - q^h x_i}{Q_f - q^h}, & Q_f \neq q^h \\ f(x_1, x_2, x_3, ..., x_n, i = f(x_i), i, Q_f = q^h) \end{cases} \]

Equations (14) and (15) along with relation (16) form a set of \((n + 1)\) coupled differential equations. The initial conditions for the differential equations are

\[ x_i \big|_{A=0} = x_i^f \quad \text{&} \quad q^h \big|_{A=0} = Q_f \]

For the case of known area these equations can be integrated from \( A=0 \) to \( A=\text{area} \). For known \( \Phi \) the integration carried out until the required flow rates are gotten. Once \( x_i^0 \)'s are identified, \( y_i^p \) can be calculate from equation (5).

Introducing the dimensionless quantities[4]

\[ \Pr = \frac{P_i}{P_h} \]

\[ \gamma_i = \frac{K_i}{K_i} \]

\[ \bar{q}^h = \frac{q^h}{Q_f} \]

\[ \bar{A} = \frac{AK_1P_h}{\partial Q_f} \]

where \( \gamma_i \) is the ideal separation factor of the \( i^{th} \) component with respect to the most permeable component, \( \bar{q}^h \) is the dimensionless flow rate, and \( \bar{A} \) is the dimensionless area. Governing equations in terms of these dimensionless variables become

\[ \frac{d\bar{q}^h}{d\bar{A}} = -\sum_{i=1}^{n} \left[ \gamma_i (x_i - \Pr y_i) \right] \]
3. NUMERICAL METHODS

Except for some special and quite simple cases, co-current flow models in common cannot be solved analytically. Thus, it is significant to think about appropriate numerical methods in order to simulate, at least the qualitative behavior, in an acceptable way. In order to find the important conditions for such a numerical method, the main phenomena of membrane gas separation processes have to be briefly summarized. The results of membrane gas separation process are generally determined by the feed flow rate, pressure gradient, membrane thickness, permeabilities, permeate and reject values, often dominate the whole processes. Therefore, it is important to numerically approximate permeate and reject values as accurate as possible, in order to avoid in accurate flow rate values at the feed side that would lead to errors in permeate and reject values, and ultimately to errors in the analysis of the entire process.

Modeling is possibly the most important part of a numerical study. Indeed, a numerical study is as good as the numerical model. On the basis of criteria mentioned in [9] the following, Bogacki–Shampine (BS) method [10, 11], Dormand–Prince (DP) method [12-14], Adams-Bashforth-Moulton (ABM) method [15], numerical differentiation formulas (NDF) [16, 17], modified Rosenbrock formula of order 2 (MRF2) [18, 19], Trapezoidal rule with free interpolant (TRFI) [17] and Trapezoidal rule with backward difference formula of order 2 (TR-BDF2) [20, 21] are selected. These methods are used to solve and compare the coupled ordinary differential equations of co-current flow in a single permeation unit.

3.1 Syntax of Numerical Methods

The model was solved using MATLAB R2008b on a PC with core i5 CPU of 2.3 GHz and 4 GB of RAM. The syntax for all the methods used in MATLAB is as follow.

\[ [T,Y] = solver(odefun,tspan,y0) \]

Where \( T \) is column vector of time points, \( Y \) is solution array. Every row in \( Y \) relates to the solution at a time returned in the corresponding row of \( T \), \( solver \) is one of above mentioned methods.
seven numerical methods. *Odefun* is a function handle that evaluates the right side of the differential equations, *tspan* is a vector stating the interval of integration, \([t_0,t_f]\). The solver executes the initial conditions at *tspan*(1), and integrates from *tspan*(1) to *tspan*(end). To get solutions at particular times (all decreasing or all increasing), use *tspan* = \([t_0,t_1,...,t_f]\) and *y0* is a vector of initial conditions.

### 3.2 Solution Algorithm

The solution algorithm for membrane gas separation with co-current flow is

1. **Input:** Feed composition \(x_{i}^{0}\), permeabilities of \(i^{th}\) component (\(K_i\)), membrane thickness (\(\delta\)), feed flow rate (\(Q_f\)), feed pressure (\(P_h\)) and permeate pressure (\(P_t\)).
2. Calculate pressure ratio (\(Pr\)) and permeabilities ratio (\(\gamma_i\)) using equation (17) and (18) respectively.
3. Calculate \(y_i^{(initial)}\) using equation (25) by calling any above mentioned solver until the equation (3) is satisfied. Use \(x_i = x_i^{0}\) and \(P = P_h\).
4. Calculate \(\frac{dQ}{dA}\) and \(\frac{dy_i}{dA}\) by using equation (21) and (22) respectively with the help of boundary condition given in equation (23) and (24). After each step update the value of \(y_i\) with the new values of \(x_i\). Proceed solving based on update values until \(A = 1\).
5. Calculate permeate flow rate (\(Q_p\)) and stage cut (\(\Phi\)) from equation (4) and (6) respectively.
6. Finally calculate the mole fraction of \(i^{th}\) component in permeate by using equation (16).

### 4. RESULTS AND DISCUSSION

The process conditions for the separation of a four component mixture are given in Table 2 and Table 3. The model of co-current flow is solved by various numerical methods.
by using step size of 0.1 and tolerance level of $10^{-9}$. Figures (3)-(6) show the reject and permeate mole fraction of hydrogen, nitrogen, oxygen and methane respectively obtained using above mentioned numerical methods. Since the flow rate acts as a driving force to permeate the gas mixture through the membrane. So, with the increase in membrane area, the reject flow decreases and its tendency of permeation decreases.

Table 2. Operating Parameters for Separation of Multicomponent Mixture, Taken from Walawender and Stern [2].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P^h$</td>
<td>380 cm Hg</td>
</tr>
<tr>
<td>$P^l$</td>
<td>50 cm Hg</td>
</tr>
<tr>
<td>$d$</td>
<td>2.54 mm</td>
</tr>
<tr>
<td>$Q^f$</td>
<td>106 cm³/s</td>
</tr>
</tbody>
</table>

Table 3. Operating Parameters for Separation of a Multicomponent Mixture, Permeabilities Taken from Plate et al [22].

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole fraction at inlet</th>
<th>Permeability $\times 10^{-7}$ (cm³·cm/cm²·s·cmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.23</td>
<td>0.11</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.40</td>
<td>0.044</td>
</tr>
<tr>
<td>Methane</td>
<td>0.27</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Figure 3. Mole fraction of Hydrogen for different numerical methods.
The reject side acts as a source from which the components are passing through the membrane. So, the permeation level decreases with gradual decrease in reject. For a value of stage cut from 0 to 0.05, the composition in reject is 0.09. This is the higher value recorded at the reject side for any other value of stage cut. So, the value in the permeate side is also higher in that stage cut value. Further increase in stage cut from 0.05 to 0.6, the reject level decreases. In other words the source from which the gases have been...
permeated is decreasing which results in the continuous decrease in permeate compositions. A similar behavior can be observed in the case of nitrogen.

Oxygen and methane are the least permeable components in this case. Their graph shows different variation in comparison with the hydrogen and nitrogen. Here the permeate streams going to be increased while the rejected streams are increasing. Since these are the least permeable components so the membrane does not allow them to be passed out. With the continuous permeation hydrogen and nitrogen, space produces at the reject side or the reject flow rate is becoming enriched with the least permeable components. At the permeate side, the streams going to be increased slightly, and they can act as minor fractions in the permeate side.

In Figures 3-6 all model shows stable behavior except numerical differentiation formulas (NDF) in reject streams while the numerical behavior of all methods is permeate streams is summarized in Table 4. The three numerical methods Dormand–Prince method, Adams-Bashforth-Moulton method and modified Rosenbrock formula of order 2 show stable behavior in all components while other numerical models have inconsistent numerical behavior. Table 5 shows CPU time elapsed by different numerical methods to solve the co-current flow model for membrane gas separation. Adams-Bashforth-Moulton (ABM) method used least time of 0.247755 seconds to solve the model while numerical differentiation formulas take 0.622862 seconds to show the slowest behavior.

Adams-Bashforth-Moulton (ABM) is observed most stable and efficient method for the separation of gases through membrane using co-current flow model. To validate the model the results obtained by using ABM model are compared with experimental results and simulation results reported by other researchers. For comparison of the ABM model results with multicomponent gas mixture experimental data, experimental results by Kaldis et al. were used [23].

Figure 6. Mole fraction of Methane for different numerical methods.
Table 4. Numerical Behaviour of different method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Problem Type</th>
<th>Hydrogen</th>
<th>Nitrogen</th>
<th>Oxygen</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bogacki–Shampine</td>
<td>Nonstiff</td>
<td>Stable</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Unstable</td>
</tr>
<tr>
<td>Dormand–Prince</td>
<td>Nonstiff</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>Adams-Bashforth-Moulton</td>
<td>Nonstiff</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>Numerical differentiation formulas</td>
<td>Stiff</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Unstable</td>
</tr>
<tr>
<td>Modified Rosenbrock formula of order 2</td>
<td>Stiff</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>Trapezoidal rule with free interpolant</td>
<td>Moderately Stiff</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Stable</td>
</tr>
<tr>
<td>TR-BDF2</td>
<td>Stiff</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Stable</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

Table 5. Time elapsed by different numerical methods.

<table>
<thead>
<tr>
<th>Numerical method</th>
<th>Time elapsed (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bogacki–Shampine</td>
<td>0.258900</td>
</tr>
<tr>
<td>Dormand–Prince</td>
<td>0.304146</td>
</tr>
<tr>
<td>Adams-Bashforth-Moulton</td>
<td>0.247755</td>
</tr>
<tr>
<td>Numerical differentiation formulas</td>
<td>0.622862</td>
</tr>
<tr>
<td>Modified Rosenbrock formula of order 2</td>
<td>0.502016</td>
</tr>
<tr>
<td>Trapezoidal rule with free interpolant</td>
<td>0.622284</td>
</tr>
<tr>
<td>TR-BDF2</td>
<td>0.477841</td>
</tr>
</tbody>
</table>

A hollow fiber polyimide membrane module with an effective membrane area of 10 cm² was used for separation of a multicomponent gas mixture containing H₂, CH₄, C₂H₆, and CO₂. Actually, membrane separation of a gas oil desulfurization refinery stream was investigated. However, because of handling problems and safety consideration, H₂S was used instead of CO₂ in the experiments. It must be stated that in the PI membranes the permeabilities of CO₂ and H₂S are relatively the same. Operating parameters and permeabilities of different components of the feed are given in reference Table 6 and Table 7 respectively.

In the experiments, the feed flow was varied from 5 to 30 Nl hr⁻¹, feed pressure was constant at 20 bar and so the effect of stage cut on permeate and reject compositions was studied. Membrane separation has been simulated with the model and the results can be observed in Figures 6-9. The effect of stage cut on reject and permeate compositions is shown in these figures. The concentrations of hydrocarbons are low due to due to their small amounts present in the permeate stream. The results obtained by ABM model with the mathematical model and experimental results reported in literature [23, 24] are compared. It can be investigated that there is very good agreement between the model predictions and the experimental results.
Table 6. Operating Parameters for Separation of Multicomponent Mixture, Taken from S.P. Kaldis et al. [23].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_h$</td>
<td>20 bar</td>
</tr>
<tr>
<td>$P_l$</td>
<td>1 bar</td>
</tr>
<tr>
<td>$d$</td>
<td>2.53 mm</td>
</tr>
<tr>
<td>$Q_f$</td>
<td>15 Nl/h</td>
</tr>
</tbody>
</table>

Table 7. Operating Parameters for Separation of a Multicomponent Mixture, Permeabilities Taken from S.P. Kaldis et al. [23].

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole fraction at inlet</th>
<th>Permeability $\times 10^{-4}$ $(\text{cm}^3(\text{STP})/\text{cm}^2/\text{s/cm Hg})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.675</td>
<td>2.9</td>
</tr>
<tr>
<td>Methane</td>
<td>0.167</td>
<td>0.037</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.043</td>
<td>0.0064</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.115</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Figure 7. Effect of stage cut on reject and permeate composition of $\text{H}_2$. 
Figure 8. Effect of stage cut on reject and permeate composition of CO₂.

Figure 9. Effect of stage cut on reject and permeate composition of CH₄.
5. CONCLUSION

The key emphasis of this study is the identification of proper numerical methods for the simulation of co-current flow, since this is of main significance for an precise calculation of permeate and reject composition in a membrane gas separation processes. Therefore, different state of the art numerical methods of solving coupled differential equation with initial value problems, namely Bogacki–Shampine method, Dormand–Prince method, Adams-Bashforth-Moulton method, numerical differentiation formulas, modified Rosenbrock formula of order 2, Trapezoidal rule with free interpolant and Trapezoidal rule with backward difference formula of order 2 are compared. The presented numerical results show a strong dependence of the computed behavior of the here considered membrane gas separation process on the selected numerical method. It can be concluded that the physical and chemical knowledge of the process, formulated in the model equations, does not stringently determine the computed process behavior [25].

Serious effects follow from the applied numerical method on the identification of model parameters from experimental data. These problems are fixed by adjusting the step size and tolerance level in MATLAB. Thus it can be summarized, that stable and fast behavior of Adams-Bashforth-Moulton method based on numerical integration can be identified as a proper numerical method giving accurate results and requiring an acceptable computational effort for the simulation of co-current flow, where permeation composition is one of the dominating phenomena. Future work needs to be focused on the further development of the model proposed using multiple permeation unit and membrane modules in order to obtain a better description of permeate and reject composition.

Figure 10. Effect of stage cut on reject and permeate composition of C$_2$H$_6$. 
Nomenclature

- $n$: number of components
- $A$: area
- $K_i$: permeability of the $i^{th}$ component
- $P_h$: total pressure on the high pressure side
- $P_l$: total pressure on the permeate side
- $P_r$: pressure ratio $P_h/P_l$
- $Q_f$: feed flow rate
- $Q^0$: reject flow rate
- $Q^p$: permeate flow rate
- $W$: width of the membrane
- $A$: dimensionless area
- $q^h$: flow rate at any point on the high pressure side
- $q^l$: flow rate at any point on the low pressure side
- $\bar{q}^h$: dimensionless flow rate at any point on the high pressure side
- $x_i^f$: mole fraction of the $i^{th}$ component in feed
- $x_i^0$: mole fraction of the $i^{th}$ component in reject
- $x_i^p$: mole fraction of the $i^{th}$ component in permeate
- $y_i$: variable mole fraction of $i^{th}$ component on the high pressure side at any point
- $y_i$: variable mole fraction of the $i^{th}$ component on low pressure side at any point

Greek

- $\Phi$: stage cut
- $\delta$: thickness
- $\gamma_i$: permeability ratio with respect to the most permeable component
- \{\}: the set of values for all components, e.g., $\{x_i\}, \{y_i\}$, etc.

Subscripts

- $i, j, k$: $i^{th}, j^{th}, k^{th}$ component
- $h$: high
- $l$: low

Superscripts

- $f$: feed
- $0$: outlet on reject side
- $P$: permeate

REFERENCES


