

COLUMN PROFILES FOR MEMBRANE COLUMN SECTIONS

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Abstract

A novel graphical method of analysing continuous membrane separation systems has been developed. The method is applicable to all counter- and co-current membrane modules – single-stage, cascades, and membrane columns. All configurations can be broken down into “column sections”, no matter how complex the arrangement. Each column section, which resembles a typical single-stage separator, is modelled using the difference point equation. The difference point equation tracks the change in the retentate composition down the length of the column section. For demonstration purposes, a simple constant relative permeability flux model is employed to determine the permeate composition as well as the continually changing retentate flow. All possible operating conditions of a column section are explored. Each condition is a result of the relationships between the flows and compositions at the top of a column section. Using the difference point equation, column profiles for each condition can be plotted. The behaviour of the profiles is discussed both mathematically and graphically. This innovative way of investigating membrane processes provides a unique way of synthesizing and designing them.

Keywords: Membrane Separation, Continuous, Graphical, Design, Column Profile.

1. Introduction

Novel separation methods and techniques have been the focus for engineers in recent decades. Membrane-based separations are one of the many fresh approaches that have come about in the light of designing more economical and environmentally attractive processes. A vast array of different types of membranes have been developed for various applications^{1,2}. Furthermore, numerous unit operations and cascades, including the membrane column³, as shown in Figure 1(a), have been developed and investigated. The column is filled with hollow-fibre membranes, resembling the design of a shell-tube heat exchanger. A high pressure is maintained on one of side in order to allow permeation through the membrane to the low-pressure side. To allow the recycle streams to flow, a compressor, as well as a retentate recycle, is necessary^{3,4}. Most publications pertaining to membrane columns assume binary mixtures for separation⁵⁻⁷. There is a lack of a generalized method for the synthesis and design of separation of ternary, and higher order, mixtures with the use of membrane columns, or any membrane-based process for that matter.

Peters et al.⁸ began to address this need by introducing Membrane Residue Curve Maps (M-RCMs). Although graphically produced for ternary systems, the ideas and methods are applicable to higher order mixtures, and are not restricted to one type of membrane. Applications of these maps to both batch and continuous process were later introduced⁹. The maps have shown their worth when designing reflux separators, including membrane columns. The aim of this article is to furnish the reader with a graphical method of analyzing and visualizing profiles for membrane separators, including the membrane column. With this, one is able to synthesize and design any membrane separation circuit, no matter how complex in its arrangement.

Consider a membrane column, such as the one given in Figure 1(a). Analyzing the entire membrane column as a whole, limits one's possibilities to only that particular configuration. This is not useful when it comes to *synthesizing* a separation sequence, especially if it is intended to be optimal. Therefore, a different approach is taken: Any membrane column or cascade can be divided into column sections (CS).

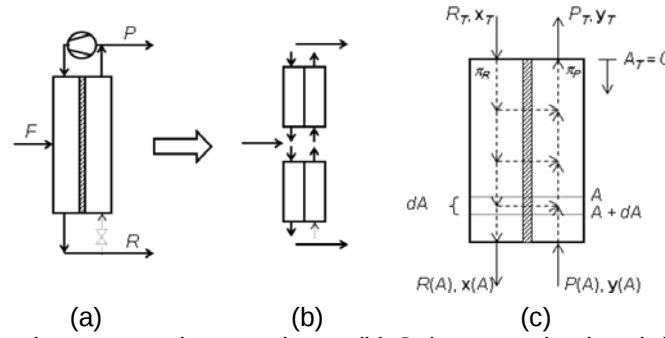


Figure 1. (a) A continuous membrane column. (b) Column section breakdown. (c) Generalized membrane column section. Refer to Nomenclature section for notation details.

A generalized CS is defined as a *length of column between points of addition and removal of material and/or energy*¹⁰. This definition is general, and applicable to most, if not all, counter- and co-current applications, including membrane permeation. Figure 1(b) shows an example of a CS breakdown for the membrane column given in Figure 1(a). Similar breakdowns can be done for any other arrangement. Thus, provided the assumptions of operation are clear and defined, a CS introduces a novel way of investigating membrane separations.

2. Theory

A schematic representation of a membrane CS is shown in Figure 1(c). Throughout the paper, it is assumed that: (i) All flows and compositions at the top (T) of a column section are known and constant. (ii) The permeate pressure is set sufficiently close to vacuum ($\pi_p \approx 0$), thus permeation will be mono-directional. (iii) Permeation only occurs through the membrane in direction that is perpendicular to the flow of the retentate stream, as indicated in Figure 1(c). Using overall and component material balances, it can be shown, after some algebraic manipulation, that the Difference Point Equation (DPE) is obtained:

$$\frac{d\mathbf{x}}{dA} = \left[\frac{\Delta}{R(A)} + 1 \right] [\mathbf{x} - \mathbf{y}(\mathbf{x})] + \frac{\Delta}{R(A)} [\mathbf{X}_\Delta - \mathbf{x}], \text{ with} \quad (1)$$

$$\Delta = P(A) - R(A) \text{ is the } \mathbf{net\ molar\ flow} \text{ inside the CS [mol/s], and} \quad (2)$$

$$\mathbf{X}_\Delta = \frac{P(A) \cdot \mathbf{y}(A) - R(A) \cdot \mathbf{x}(A)}{\Delta} \text{ is the } \mathbf{difference\ point} \text{ [-]}. \quad (3)$$

The DPE (equation 1) mathematically models how the retentate composition ($\mathbf{x}$) varies as a function of position (A) in a general membrane CS. To solve it, it is necessary to understand how $\mathbf{y}$ is related to $\mathbf{x}$. For a gas separation membrane operating at almost vacuum conditions ($\pi_p \approx 0$), it can be shown that:

$$y_i = \frac{\alpha_{ij}^M x_i}{\sum_i \alpha_{ij}^M x_i} \quad (4)$$

where α_{ij}^M is known as *membrane selectivity*, and is assumed constant for the scope of this article. Knowledge of how the retentate flow is changing as a function of position is required, since material is being transferred mono-directionally (from R to P only). By using the appropriate differential balances across a strip of membrane area, it can be shown that:

$$\frac{dR(A)}{dA'} = -\sum_i \alpha_{ij}^M x_i \text{ with } A' = A \frac{\pi_R P_{ref}'}{d} \text{ being a normalized form of } A. \quad (5)$$

In this paper, component B is the reference (ref) component, and the following relative permeabilities have been assumed throughout: $\alpha_{AB}^M = 3$, $\alpha_{BB}^M = 1$, and $\alpha_{CB}^M = 1.5$. Thus, using equations 4 and 5, in the DPE, one can solve for, and graphically interpret the retentate profile for a specified CS.

The DPE is derived on a mass balance basis and is not dependent on the type of membrane used. Whilst solving it requires knowledge regarding the membrane flux, the form of the DPE is *general*. In the sections which follow, possible operating conditions for a CS are detailed. Each condition is a result of the relationships between R_T and P_T , as well as $\mathbf{x}_T$ and $\mathbf{y}_T$.

3. Column Section Profiles: Operating Condition 1

Let us briefly consider a special case of operation of the membrane CS shown in Figure 1(c) where:

$$P_T = R_T \text{ and } \mathbf{y}_T = \mathbf{x}_T \quad (6)$$

This is saying that both flows and compositions are the same at the top of the CS, resulting in a total reflux column.⁹ The conditions of this case result in $\Delta = 0$, and thus the DPE (equation 1) becomes:

$$\frac{d\mathbf{x}}{dA} = [\mathbf{x} - \mathbf{y}(\mathbf{x})] \quad (7)$$

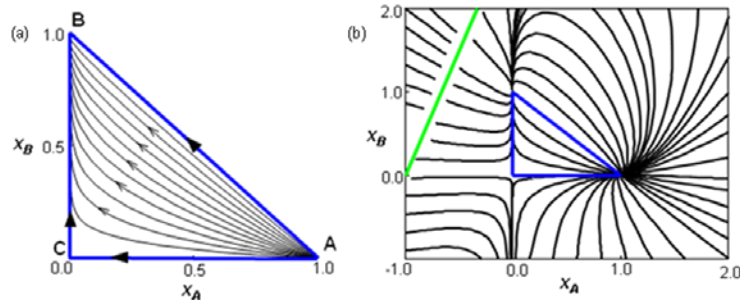


Figure 2. (a) Membrane Residue Curve Map⁸ (M-RCM) for an A-B-C system with $\alpha_A = 3$, $\alpha_C = 1.5$. (b) Entire M-RCM. MBT in blue, discontinuity line in green.

Equation 7 is the Membrane Residue Curve equation as identified by Peters et al.⁸. Solving this set of equations, in conjunction with the flux model (equation 4), for a range of initial conditions ($\mathbf{x}^0$) allows one to produce a Membrane Residue Curve Map (M-RCM) as shown in Figure 2(a).

The Mass Balance Triangle (MBT), as shown in blue in Figure 2(a), represents the region of physically achievable profiles in ternary systems. Although describing a real process, the DPE at infinite reflux, is merely a mathematical equation. This equation is not bound by any physically relevant initial conditions, and it is possible to evaluate it at initial values of $\mathbf{x}$ outside the MBT, making it possible to populate the entire x_A – x_B space, as shown in Figure 2(b). The profiles lying outside the MBT may not be physically achievable, but the relevance of this map is important, as will be discussed in the next section. The nature and location of the stationary points in this map also provide insight into the behaviour of the curves – the reader is referred to Holland et al.^{11,12} for a more information on these.

4. Column Section Profiles: Operating Condition 2

Suppose we still have the CS configuration as depicted in Figure 1(c), with

$$P_T = R_T \text{ but } \mathbf{y}_T \neq \mathbf{x}_T \quad (8)$$

Expanding the general DPE (equation 1), and manipulating accordingly, it can be shown that:

$$\frac{d\mathbf{x}}{dA} = [\mathbf{x} - \mathbf{y}(\mathbf{x})] + \beta(A) \cdot \delta_T \text{ with } \beta(A) = \frac{R_T}{R(A)} \text{ and } \delta_T = \mathbf{y}_T - \mathbf{x}_T \quad (9)$$

δ_T is known as the *difference vector* taken at the top of the CS. If values of the δ_T and R_T are arbitrarily chosen (say $[0.1 \ -0.05]$ and 100 mol/s respectively), then a membrane profile can be generated for a given initial composition. Using a value of $\mathbf{x}_T = [0.3, 0.3]$, and integrating down the length of the column, the profile displayed in Figure 3 results.

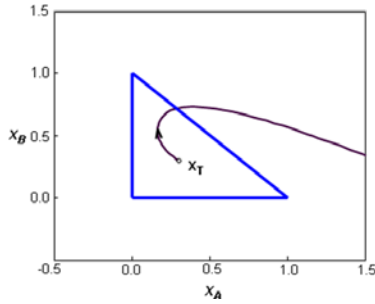


Figure 3. Membrane column profile for Case 2. $R_T = 100$ mol/s, $\delta_T = [0.1, -0.05]$, $\mathbf{x}_T = [0.3, 0.3]$.

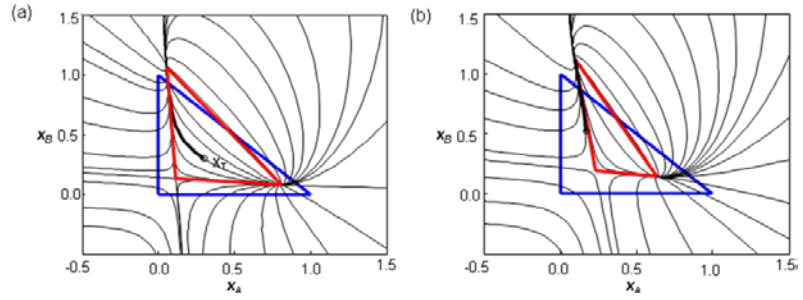


Figure 4. Shifted M-RCMs. The blue triangle represents the MBT, the red shows the transformed triangle. (a) $\beta(A=0) = 1$, (b) $\beta(A) = 1.667$. $\delta_T = [0.1, -0.05]$, $\mathbf{x}_T = [0.3, 0.3]$. Actual membrane profile (see Figure 3) is tangent to bold profile at the point indicated.

This type of curve is unique and behaves very differently from those obtained in the M-RCM (Figures 2(a) and (b)). The behaviour of the profile can be understood by analysis of the DPE for the operating conditions of this case (equation 9). Although the curve has no physical meaning once it crosses the AB-boundary, a great deal of useful information can be extracted from the trajectory it follows.

The DPE for this case (equation 9) is a combination of the separation vector, $\mathbf{s} = \mathbf{x} - \mathbf{y}$, and the difference vector, δ_T . The equation is similar to the one used in Case 1 (equation 7), except now that there is an additional vector term that gives rise to new topological features. If this were Case 1, then $\delta_T = 0$. $\beta(A)$ is a scalar multiplier preceding δ_T , and is a ratio of the retentate flow at the column top to that at a point corresponding to A . If the column was operating under the assumption of constant molar overflow, then $\beta(A)$ is unity. However, this assumption is not true for membrane permeation, and $\beta(A) = 1$ at the top of the column only, and $\beta(A) > 1$ at any point down the length of the column, since the retentate flow is losing material from the column top.

Consider, for a moment, what topological effects would occur if $\beta(A)$ were to remain constant at a value of 1. If this were the case, then the resulting map is shown in Figure 4(a). It is noticed that map obtained has similar topological features to the M-RCM (Figure 2(b)). However, it has been shifted, and the nodes are in different positions. As discussed by Holland et al.¹², the three nodes are connected by straight lines due to the collinear nature and direction of the eigenvectors at each node, thus forming a triangle. The blue triangle indicates the MBT, as well as the location of the nodes when $\beta(A) = 0$ (total reflux). The red triangle represents the “transformed” triangle, connecting the 3 nodes appropriately. It can be noticed that previously non-achievable profiles have moved into the physically possible (MBT) space. This shift arises from the addition of δ_T in the M-RCM equation. The magnitude and direction of δ_T affects the way in which the map is transformed.

If $\beta(A)$ was constant, the column profile would follow the bold curve in Figure 4(a), commencing at $\mathbf{x}_T$. However, $\beta(A)$ is not a constant value, and it becomes larger down the length of the column. This implies that the trajectory of the column profile shown in Figure 3 will be tangent to the appropriate curve that passes through the $\mathbf{x}_T$ on the shifted plot when $\beta(A) = 1$, i.e. the bold curve in Figure 4(a).

As permeation begins, $\beta(A) > 1$, and the shifted map shown in Figure 4(a) will, in fact, shift again! Since $\beta(A)$ is continually changing, the map itself is going to constantly transform. i.e., at a certain A , it will occur that $\beta(A) = 1.667$. The corresponding map at this value is shown in Figure 4(b). The actual membrane column profile that exists (Figure 3) is not one of the curves shown Figure 4(b), but is tangent to the curve that goes through the point when the retentate flow is such that $\beta(A) = 1.667$. This point is easily determined from the data associated with the membrane column profile, and is plotted in Figure 4(b). The corresponding curve is shown in bold – it is along the one side of the transformed triangle. It is interesting to note that this particular curve was originally outside the MBT, and has now been shifted in, and forms part of the column profile.

It can be concluded that: *Every point on the membrane column profile is tangent to a curve on a transformed map going through that point. The transformed map corresponds to the appropriate $\beta(A)$ value at that point.* Figure 5(a) shows discrete points on the column profile and the associated

tangent curves at the indicated $\beta(A)$ -values. Each of the “constant $\beta(A)$ ” curves run to their stable pinch.

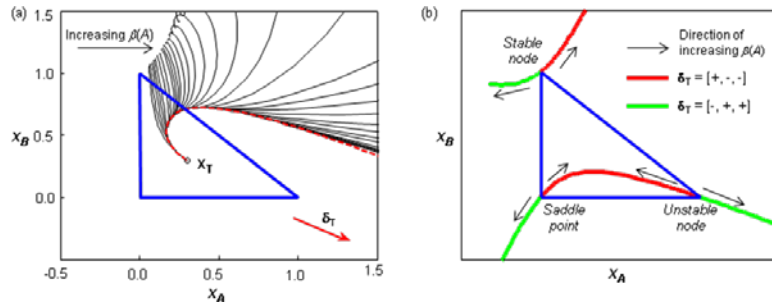


Figure 5. (a) Tangency of curves to the column profile. Each curve corresponds to a different $\beta(A)$ -value, and is allowed to run to its stable pinch point. (b) Pinch Point Loci for $\delta_T = [+ , - , -]$.

As $\beta(A)$ increases, the membrane column profile tends to maintain a similar direction to the “constant $\beta(A)$ ” curve for longer. This is expected since, the DPE for this case (equation 9) dictates that, as $\beta(A) \rightarrow \infty$, the difference vector (δ_T) becomes dominant, suppressing the effect of the separation vector ($\mathbf{s}$). Thus, the left-hand side of the differential equation becomes a constant vector (for each $\beta(A)$) which has the direction of δ_T . As the trajectory proceeds, its ultimate direction becomes that of δ_T , as shown. Thus, varying the direction of the difference vector will decide the ultimate direction of the membrane column profile, provided $A \rightarrow \infty$.

In Figure 5(a) that there is a trend occurring with the pinch points of each “constant $\beta(A)$ ” curve. Due to the direction of integration, the point where each of these curves pinch would be their stable node. It is not only the stable node that moves, but the unstable and saddle points shift as well. A locus of all these points can be generated, as shown in Figure 5(b). The general shape of the pinch point loci depends on the sign of each of the terms δ_T ¹².

When plotting the membrane column profile in Figure 3, a randomly chosen $\mathbf{x}_T$ and R_T were chosen. Of course, any positive flowrate for R_T is feasible, as is any point within the MBT is a possible top retentate composition. Figure 6(a) displays column profiles for a set $\mathbf{x}_T = [0.3, 0.3]$, varying R_T as indicated. Figure 6(b), on the other hand, shows a range of column profiles for select $\mathbf{x}_T$'s at a constant $R_T = 100 \text{ mol/s}$. It can be seen that, in Figure 6(a), irrespective of starting point or flowrate, all curves ultimately end up progressing in the same direction, namely $\delta_T = [0.1, -0.05]$. But the smaller R_T is, the faster $\beta(A)$ becomes larger, resulting in the δ_T dominating in the DPE sooner. What is interesting to note is that, by adjusting $\mathbf{x}_T$ and R_T , it is possible to obtain a profile to runs directly into a pure component. Consider the $R_T = 20 \text{ mol/s}$ profile in Figure 6(a) that passes through pure A. Interestingly enough, component A is the most permeable component, and is expected to permeate the fastest. However, due to the operating conditions of Case 2, it is evident that one can synthesize any membrane column to achieve desired products!

In Figure 6(b), the initial direction of each curve is determined by the curve going through the same point on the $\beta(A) = 1$ map (Figure 4(a)). This map has been superimposed on Figure 6(b). Curves commencing in the regions outside shifted triangle, but inside the MBT, initially move in a different direction to the profiles that begin within the shifted triangle. This is due to the nature of the profiles in Figure 4(a) in that region (they were shifted into the space!).

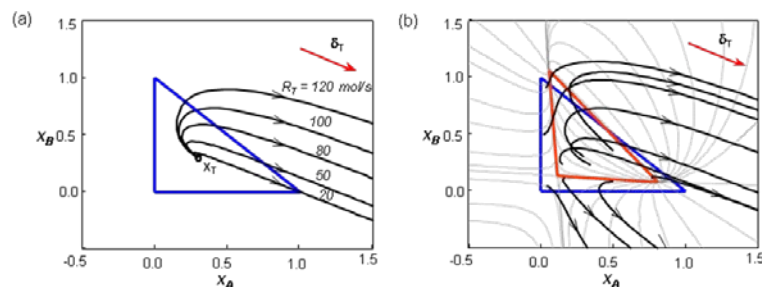


Figure 6. Column Profiles for selected values of (a) R_T with $\mathbf{x}_T = [0.3, 0.3]$, (b) $\mathbf{x}_T$ with $R_T = 100 \text{ mol/s}$. Figure 4(a) has been superimposed.

Residue curves (Case 1) cannot cross by definition and nature of the equations which describe them. However, it is evident from Figure 4(b) that membrane column profiles do intersect. The reason for this is the varying flowrates within the column section. If one profile intersects another profile, then they share the same compositional values, but will have different flows. The result is that each curve will map out different paths. No two curves will intersect and move of in the same direction.

In the discussions on the column profile thus far, we have allowed the curves to cross the MBT boundary, which is not physically possible. However, visualizing it has allowed one some valuable insight into the behaviour the profiles. Such information would be unattainable and misinterpreted if one were to look within the bounds of the MBT only. In reality, each profile would terminate at the boundary it intersects. When this occurs, one component equals zero, meaning that particular species has completely permeated through the membrane, leaving behind a binary mixture. The profile will then continue from the point of intersection with the boundary along the straight line boundary in the direction towards the least permeable component of the two remaining species.

5. Applications and Conclusion

A novel graphical method of analysing continuous membrane systems has been developed. It has been shown that any membrane configuration of membrane separators, no matter how complex in its arrangement, can be broken down into column sections. Each CS, which resembles a typical single-stage separator, is modelled using the DPE. The DPE tracks the change in the retentate composition down the length of the CS. For demonstration purposes, a simple constant relative permeability flux model was employed to determine the permeate composition as well as the continually changing retentate flow. All possible operating conditions of a column section have been explored, only two of which are discussed in this paper. Using the DPE, column profiles for each condition were plotted. The behaviour of the profiles was discussed both mathematically and graphically.

The profiles generated provide valuable insight into the operation of all membrane processes, even the simplest single-stage module. Being able to graphically visualize the change in the retentate composition, assists a design engineer in making necessary and informed decisions. With this novel method, one is now able to synthesize and design more informed and creative configurations. Being able to break down any membrane arrangement to its simplest form, allows one to isolate and evaluate the individual building blocks, thereby permitting an optimal design to emerge. This method is also very useful in the design of hybrid systems involving membrane separators.

Nomenclature

All symbols in **bold** are vectors

A is the dimensionless membrane area [-],

P is the permeate flowrate [mol/s],

R is the retentate flowrate [mol/s],

$\mathbf{X}_\Delta$ is the difference point [-]

α_{ij}^M is the membrane selectivity

π_R is the retentate (high) pressure [Pa],

τ refers to quantities at the top of the CS

d is membrane thickness [m],

P is the species permeability [mol.m/s.m².Pa]

$\mathbf{x}$ is the composition of the retentate phase [-],

$\mathbf{y}$ is the composition of the permeate phase [-],

Δ is the net molar flow in a column section [mol/s]

π_P is the permeate (low) pressure [Pa],

CS is Column Section

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