

From Reactive Distillation To Reactive Membrane Separation: A Generalized Approach For Feasibility Analysis

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Abstract

A new feasibility analysis methodology generalized from distillation is applied to membrane process. The model is formulated to depict the reactive liquid phase composition on the retentate side of membrane reactors. The effects of both chemical reaction and membrane mass transfer kinetics on the feasible products are elucidated by means of retentate phase diagrams and bifurcation analysis. In the proposed method, the description of flux induced by selective mass transfer effects is subordinate so that the method can be applied to various membrane processes, providing that the flux equation is acquired either by applicable diffusion theories or by experimental membrane characterization. Some examples of ternary and quaternary systems are introduced to illustrate the methodology. It is shown that the selective mass transfer through membranes can change the topology and stationary points of the retentate phase diagrams. This implies the desired products which are not attainable in open distillation can be feasible by means of suitable membranes. Furthermore, a new set of composition variables is introduced to transform the original model equations into an analogous form of open distillation, and leads to the explicit conditions for singular points in membrane process, which are termed as reactive arheotropes.

Keywords: Azeotrope; Arheotrope; Residue curve map; Bifurcation analysis; Membrane reactor; Dusty gas model

Introduction

It is generally agreed that the integration of reaction and separation into a single unit (so called "reactive separation process") may bring potential advantages such as reducing energy and capital cost, enhancing yield and selectivity, breaking thermodynamic restrictions and in-situ purification, etc. However, most of these reactive separation processes are short of feasibility analysis methodologies due to the process complexity, and hence the number of industrial applications is rather low. An exceptional success among these reactive separation processes is reactive distillation, which has been amply studied. One of the first formulations for reactive distillation is the work by Barbosa and Doherty [1], in which they illustrated the chemical equilibrium effect on distillation process with residue curve maps. After that, Venimadhavan et al. [2] introduced the dimensionless group, Damköhler number, to characterize the ratio of reaction rate and escaping flow rate so that it became possible to study the kinetically controlled RCMs in addition to non-reactive and equilibrium reactive cases.

Except reactive distillation, systematic analysis of other reactive separation processes has rarely been developed. For example, reactive membrane separation, a hybrid process combining chemical reaction and membrane separation, attains its wide feasible product spectrum by means of selective membranes, but little literatures provide perspectives on the feasibility analysis of reactive membrane separation, because of the even more complicated blend of chemical reaction and mass transfer kinetics.

In order to understand the effects of membranes on the feasible products, an approach adopted from distillation process is generalized to be applicable for reactive membrane separation [3,4]. A model is formulated to describe the concentration profiles in the retentate liquid phase, in which the chemical reaction takes place, when vacuum is applied on the permeation side. Residue curve maps, or more precisely, "retentate phase diagrams" for membrane process, and bifurcation analysis are applied to elucidate the effects of both chemical reaction and membrane diffusion.

Model Equation of Retentate Phase Diagrams

Considering a batch reactive membrane separation process where a chemical reaction takes place in the liquid phase (as Fig.1a), the governing equation of retentate liquid phase composition can be derived from material balances as [3]:

$$\frac{dx_i}{d\xi} = \left(x_i - \frac{n_i}{n_T} \right) + Da \cdot (v_i - v_T x_i) \cdot \frac{k_f}{k_{f,ref}} \cdot \mathfrak{R} \quad \text{with } i = 1 \dots NC - 1 \quad (1)$$

where ξ stands for the dimensionless time, n_i the component mass flux through the membrane, $n_T = \sum_{i=1}^{NC} n_i$ the total mass flux, v_i is the stoichiometric coefficient of component i ,

and $v_T = \sum_{i=1}^{NC} v_i$ the total mole change of the chemical reaction. k_f denotes the temperature-

dependent rate constant of the forward reaction, and \mathfrak{R} is the dimensionless reaction rate depending on the liquid phase composition; $k_{f,ref}$ is the forward reaction rate constant at a reference temperature. A dimensionless group, the Damköhler number Da , is introduced which is defined as the ratio of the characteristic reaction rate ($H_{r,0} \cdot k_{f,ref}$) and the

characteristic escaping total flux $n_{T,ref}$

$$Da \equiv \frac{H_{r,0} \cdot k_{f,ref}}{n_{T,ref}} \quad (2)$$

Eq.(1) portrays the retentate phase diagrams for non-reactive ($Da = 0$), equilibrium reactive ($Da \rightarrow \infty$) as well as kinetically controlled ($0 < Da < \infty$) conditions. Open distillation can be interpreted as a special case of membrane process when there is no selective mass transfer effect; in such a case, the flux ratio (n_i / n_T) equals to the vapor mole fraction y_i , which is assumed to be in phase equilibrium with x_i , and the total molar flow rate is usually denoted as V , which is proportional to the total vapor pressure of the system. The considered batch process is the equivalent of a continuous membrane process, as depicted in Fig.1b [4]. There, the time coordinate is replaced by the axial coordinate. Therefore, the phase diagrams acquired from the batch process can be directly used for continuous process design.

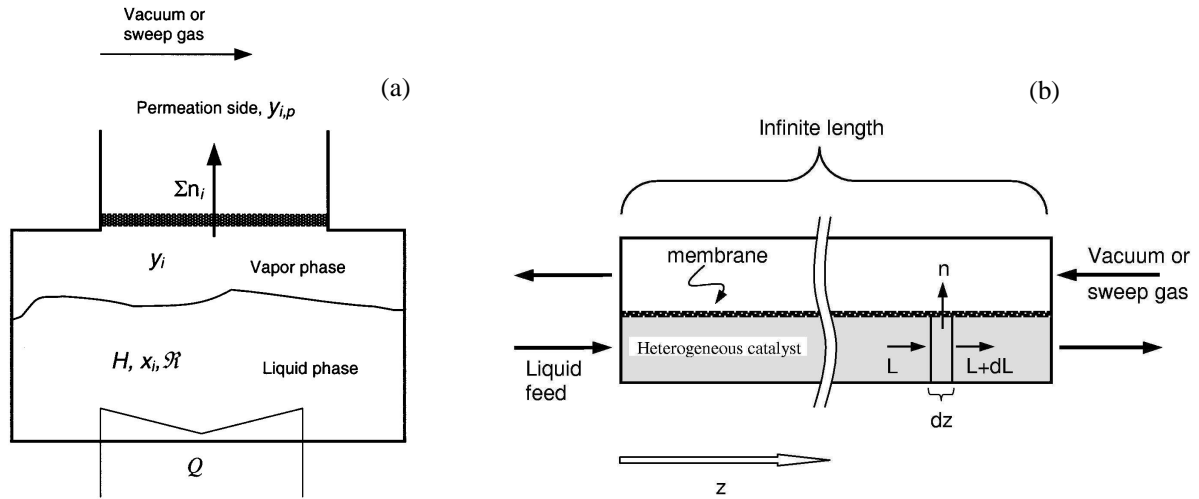


Fig.1: Considered reactive membrane separation process, (a) a batch reactive membrane separation, (b) equivalent continuous process.

Singular Point Analysis

The singular points of Eq. (1) are of special interest because those points structure the topology of the retentate phase diagrams. Thus, bifurcation analysis of these points yields fast information on the feasibility of a certain process variant. By introducing a new set of composition variables [3], Eq.(1) can be cast into an analogous form as in distillation:

$$\frac{dX_i}{d\tau} = X_i - Y_i \quad \begin{array}{l} i = 1 \dots NC - 1 \\ i \neq k \end{array} \quad (3)$$

where k marks a reference component. X_i , Y_i are the transformed liquid and vapor composition variables defined as following:

$$X_i = \frac{(v_k x_i - v_i x_k)}{(v_k - v_T x_k)}, \quad Y_i = \frac{(v_k n_i - v_i n_k)}{(v_k n_T - v_T n_k)} \quad \begin{matrix} i = 1 \dots NC - 1 \\ i \neq k \end{matrix} \quad (4)$$

and τ as the dimensionless time coordinate. At the singular points the transformed vapor and liquid phase mole fraction are equal:

$$X_i = Y_i \quad \begin{matrix} i = 1 \dots NC - 1 \\ i \neq k \end{matrix} \quad (5)$$

The compositions fulfilling Eq.(5) are called *reactive azeotropes* [3]. The azeotropic loci form a curve on which all singular points are located; this curve is called “potential singular point curve” (PSPC). The shape and location of PSPC are determined by the reaction stoichiometry, the vapor-liquid phase equilibrium of the considered mixture, and the mass transfer properties of applied membrane.

Description of Flux Through Membranes

One important significance of Eq.(1) is that the flux equation can be determined subordinately. For different membranes, the feasibility analysis can be performed directly based on the corresponding description of flux, which is either given by applicable diffusion theories or acquired by membrane characterization experimentally. In the following examples, the permeation flux is described by the explicit expression with the partial pressure as the driving force:

$$(n) = \frac{1}{RT} \cdot k_{11} [\kappa] \cdot (y \cdot P - y_p \cdot P_p) \quad \text{with} \quad \kappa_{ij} \equiv \frac{k_{ij}}{k_{11}} \quad (6)$$

where $[\kappa_{ij}]$ is the normalized $NC \times NC$ -dimensional matrix of effective binary mass transfer coefficients κ_{ij} , y_p and P_p denote the vector of mole fractions and the total pressure on the membrane permeate side, respectively. Here, the first main diagonal element k_{11} is taken as the reference coefficient. When vacuum is applied on the permeate side, the partial pressures of the diffusing components on the permeate side are negligible ($P_p \rightarrow 0$).

For the sake of simplified analysis, in the following examples the $[\kappa]$ -matrix of constant elements is considered. The example of a practical membrane diffusion mechanism, the dusty gas model, can be referred to [4].

Example I: Ternary Systems

Retentate Phase Diagrams

Considering the reactive ternary mixture A/B/C undergoing a single reversible chemical reaction in ideal liquid phase:



The chemical equilibrium constant is assumed to be independent of temperature $K = 0.2$; the relative volatilities are assumed to be $\alpha_{BA} = 5$, $\alpha_{CA} = 3$. Figs.(2a) & (2b) show the phase diagrams at $Da=1$ for reactive distillation and reactive membrane separation, respectively. It

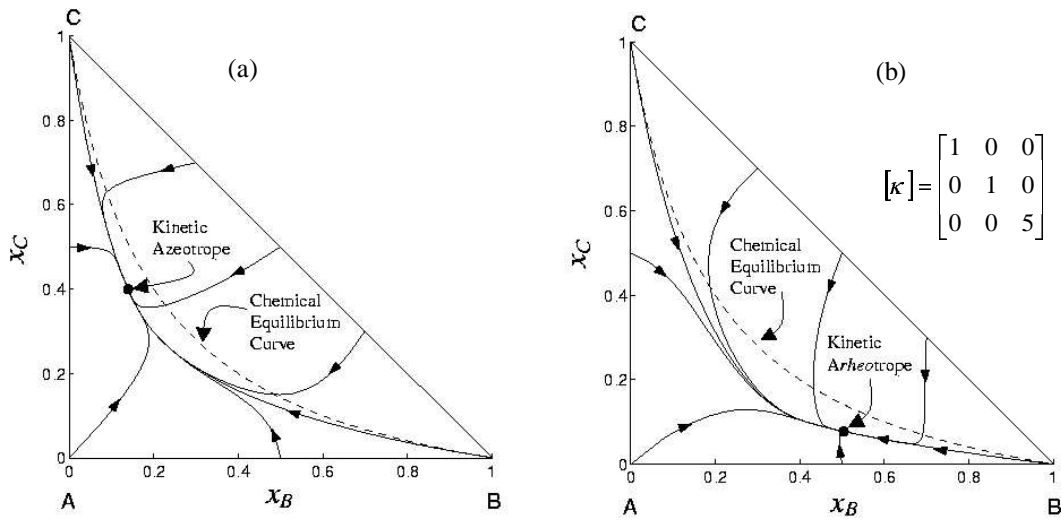


Fig.2: Kinetically controlled phase diagrams ($Da=1$) for ternary system $A \leftrightarrow B + C$; $K = 0.2$; constant relative volatilities: $\alpha_{BA} = 5.0$; $\alpha_{CA} = 3.0$. (a) Reactive distillation, (b) Reactive membrane separation. Legend: \circ Unstable Node, \square Saddle Point, \bullet Stable Node

can be seen that a selective membrane which preferentially removes the byproduct C, can significantly shift the singular point from the “kinetic azeotrope” toward the desired product B corner, to the “kinetic arheotrope”.

Singular Point Analysis & PSPC

The PSPC described by Eq.(5) is depicted as in Fig.3. It is shown that the PSPC of the considered system is a vertical hyperbola (Fig.3a), while the C-selective membrane rotates it to become a horizontal one (Fig.3b) such that the stable node branch approaches the desired B vertex. More detailed discussion and additional examples of practical ternary systems are available in [3].

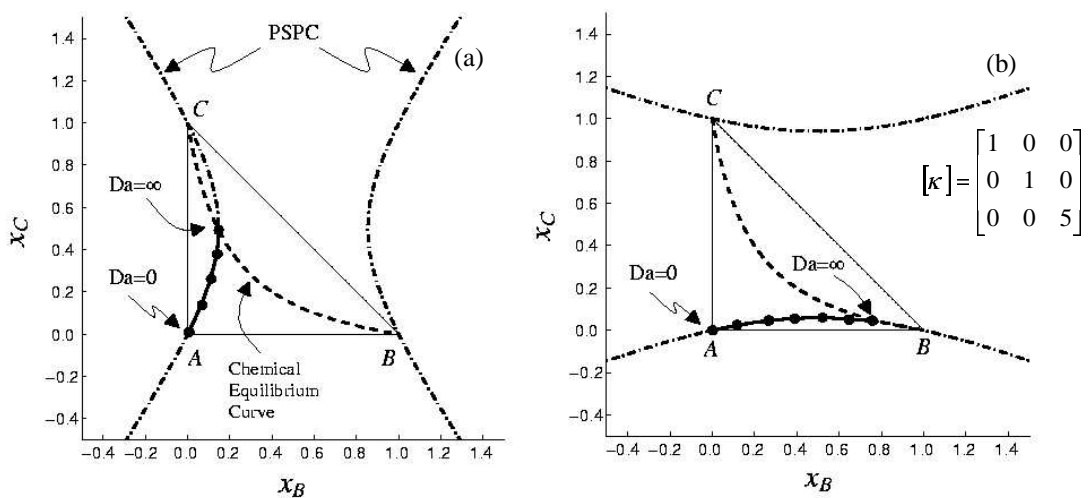
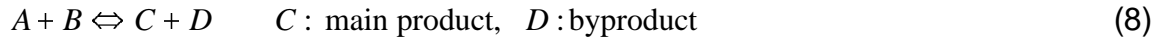


Fig.3: Potential singular point curve (PSPC) and bifurcation behavior for ternary system $A \leftrightarrow B + C$; $K = 0.2$; constant relative volatilities: $\alpha_{BA} = 5.0$; $\alpha_{CA} = 3.0$. (a) Reactive distillation, (b) Reactive membrane separation. Legend: (\bullet) Stable node branch.

Example II: Quaternary Systems

Retentate Phase Diagrams

Similarly, the effect of a selective membrane on the quaternary mixture A/B/C/D undergoing a single reversible chemical reaction in the ideal liquid phase is considered:



The chemical equilibrium constant is assumed to be independent of temperature $K = 12$; the relative volatilities are assumed to be $\alpha_{BA} = 1.7$, $\alpha_{CA} = 3.9$, $\alpha_{DA} = 4.2$.

Fig.4a shows the residue curve map of reactive distillation at kinetically controlled chemical reaction, $Da = 1$, there appears a quaternary saddle point (kinetic azeotrope). The quaternary saddle point forms two boundaries with the unstable nodes C and D such that the residue curves originate from C and D move towards the saddle point and eventually converge to A and B, respectively. When a selective membrane which retains more desired product C than the other three, e.g. $\kappa_{CC} = 0.2$, the membrane changes the sequence of effective volatilities. Thus, C becomes the stable node, A and B are the saddle points and D remains the unstable node permanently.

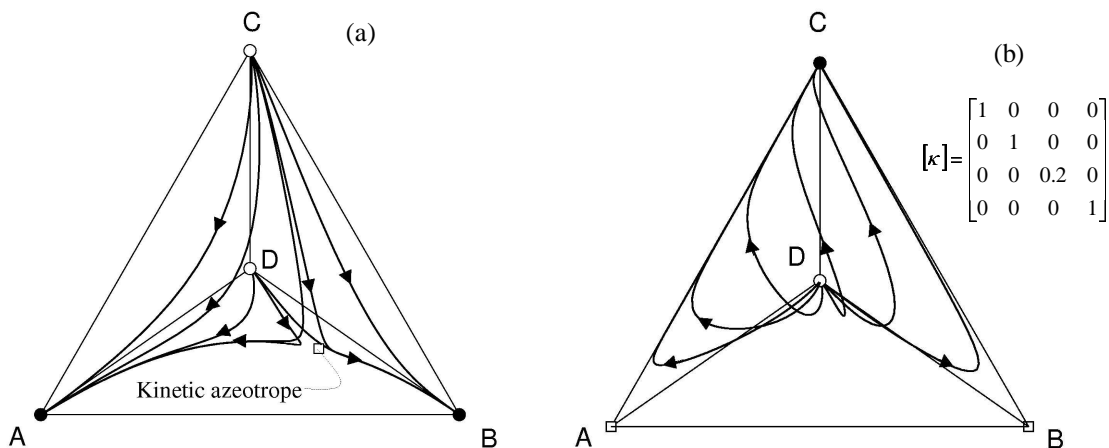


Fig.4: Kinetically controlled phase diagrams ($Da=1$) for quaternary system $A + B \rightleftharpoons C + D$; $K = 12$; constant relative volatilities: $\alpha_{BA} = 1.7$; $\alpha_{CA} = 3.9$; $\alpha_{DA} = 4.2$. (a) Reactive distillation, (b) Reactive membrane separation.

Legend: o Unstable Node, □ Saddle Point, ● Stable Node

Singular Point Analysis & PSPC

For the considered quaternary case, the PSPC is determined by solving the following set of equations simultaneously:

$$X_A = Y_A, \quad X_B = Y_B \quad (9)$$

where the main product C is chosen as the reference component. At the given set of relative

volatilities, the PSPC of distillation process is depicted in Fig.5a. For completeness, the PSPC is also shown outside the composition space. One branch of the PSPC passes through the composition tetrahedron and connects the B, C vertices. The quaternary saddle point emerges from the B vertex and moves along this PSPC branch with the increasing Damköhler number. It intersects the equilibrium surface and thus results in the reactive azeotrope at $Da \rightarrow \infty$. As for the pure component vertices, A and D remain the stable and unstable nodes, respectively, at any Damköhler number, while B changes from a saddle point to a stable node if $Da > 0.411$. The pure C vertex is a saddle point when $Da < 0.921$, and turns into an unstable node if the Damköhler number exceeds the critical value. For $\kappa_{CC} = 0.2$ (Fig.5b), both branches of the PSPC do not move into the composition tetrahedron, but only intersect the four pure component vertices. For this case, A and B are saddle points, C is the stable node and D is the unstable node permanently.

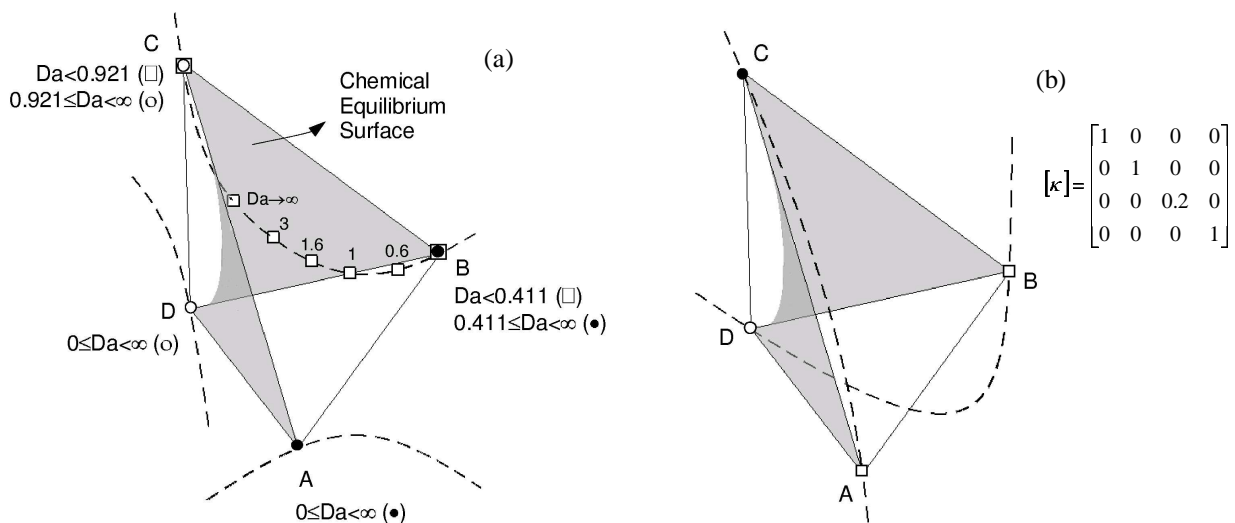


Fig.5: Potential singular point curve (PSPC) and bifurcation behavior for quaternary system $A + B \leftrightarrow C + D$; $K = 12$; constant relative volatilities: $\alpha_{BA} = 1.7$; $\alpha_{CA} = 3.9$; $\alpha_{DA} = 4.2$. (a) Reactive distillation, (b) Reactive membrane separation.

Legend: ○ Unstable Node, □ Saddle Point, ● Stable Node

For the selection of suitable membrane materials, it is helpful to track the location of the feasible product composition in dependence on the membrane mass transfer coefficients. For instance, Fig.6 shows the bifurcation behaviour with respect to the relative mass transfer coefficient κ_{CC} . At equilibrium controlled conditions (i.e. $Da \rightarrow \infty$), the quaternary singular point moves from the reactive azeotrope ($\kappa_{CC} = 1$) towards the B-C edge as shown in Fig.6. When κ_{CC} is smaller than the critical value $0.436 (= \alpha_{BA}/\alpha_{CA})$, the quaternary branch vanishes within the composition space, and pure B changes from a stable node into a saddle point, while pure C from an unstable into a saddle point. When κ_{CC} becomes smaller than the value $0.256 (= 1/\alpha_{CA})$, C becomes the only stable node of the system, replacing the original stable node which was pure A. Further details and practical examples of quaternary systems are available in [4].

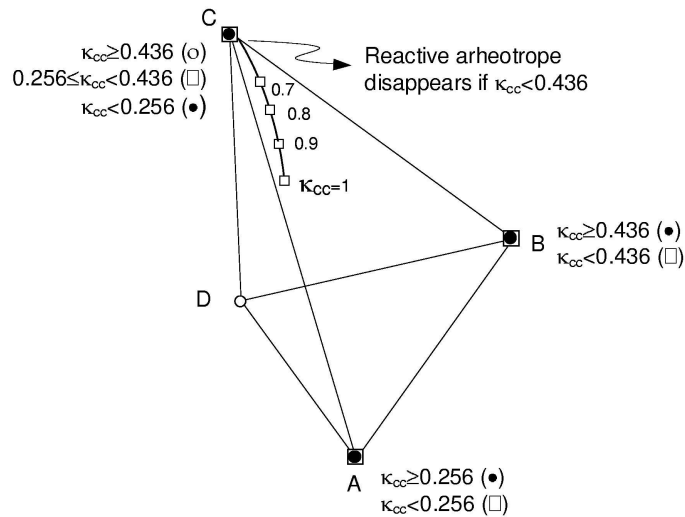


Fig.6: Bifurcation behavior with respect to κ_{CC} (at $Da \rightarrow \infty$) for quaternary system $A + B \leftrightarrow C + D$; $K = 12$; constant relative volatilities: $\alpha_{BA} = 1.7$; $\alpha_{CA} = 3.9$; $\alpha_{DA} = 4.2$.

Legend: o Unstable Node, □ Saddle Point, ● Stable Node

Conclusion

The vision of this work is to develop a methodology such that the feasibility analysis of membrane reactors can be carried out directly based on the characterisation of the membranes. It is worth while notifying that the proposed concept could be also applied to other reactive separation processes, in which the mass transfer kinetics instead of phase equilibrium have to be considered. With the proposed method, the similar feasibility analysis as has been done for reactive distillation can be implemented for membrane reactors.

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