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Rigorous Multicomponent Reactive Separations Modelling: Complete Consideration of Reaction-Diffusion Phenomena

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Résumé — Modélisation rigoureuse de la séparation réactive multiconstituant : prise en compte des phénomènes de diffusion-réaction — Cet article concerne la première étape du développement d'un modèle rigoureux pour la séparation réactive multiconstituant. Ce type de modèle est indispensable pour optimiser les procédés de captage des gaz acides (captage de CO₂, traitement des gaz, etc.) en termes de taille et de consommation d'énergie, lorsque les solvants chimiques sont classiquement utilisés. Dans un premier temps, les deux grandes approches de modélisation sont présentées : le modèle d'équilibre et le modèle de non-équilibre.

Dans un deuxième temps, un modèle de non-équilibre avec une approche rigoureuse des phénomènes de diffusion-réaction est proposé. La théorie de double-film et les équations généralisées de Maxwell-Stefan sont utilisées afin de caractériser les interactions multiconstituants. La chaîne complète des réactions chimiques est prise en compte. Les réactions peuvent être cinétiquement contrôlées ou à l'équilibre chimique, et elles sont considérées à la fois dans le film liquide et dans le bulk liquide.

Dans un troisième temps, la méthode de résolution numérique est décrite. Le couplage des équations généralisées de Maxwell-Stefan avec les équations d'équilibre chimique engendre un système d'équations algèbre-différentielles fortement non-linéaire connu sous le nom DAE index 3. Les DAE sont discrétisées avec des différences finies, car leur intégration sous leur forme différentielle selon la méthode de Gear est complexe. Le système algébrique résultant est résolu numériquement en utilisant l'approche de Newton-Raphson. Enfin, le modèle et les méthodes associées de résolution numérique sont validés avec l'exemple de l'estérification du méthanol. Ce système non-électrolytique permet une analyse intéressante de l'impact de réaction sur le transfert de masse, surtout à l'interface des phases. La résolution numérique du modèle par la méthode de Newton-Raphson donne des bons résultats en termes de temps de calcul et de convergence. Les résultats de simulation montrent que l'impact des réactions à l'équilibre chimique et celui des réactions cinétiquement contrôlées avec une cinétique élevée sur le transfert de masse est relativement similaire. En outre, la loi de Fick est moins adaptée pour les mélanges multiconstituants où certaines anomalies comme la contre-diffusion ont lieu.

Abstract — Rigorous Multicomponent Reactive Separations Modelling: Complete Consideration of Reaction-Diffusion Phenomena — This paper gives the first step of the development of a rigorous multicomponent reactive separation model. Such a model is highly essential to further the optimization of acid gases removal plants (CO_2 capture, gas treating, etc.) in terms of size and energy consumption, since chemical solvents are conventionally used.

Firstly, two main modelling approaches are presented: the equilibrium-based and the rate-based approaches.

Secondly, an extended rate-based model with rigorous modelling methodology for diffusion-reaction phenomena is proposed. The film theory and the generalized Maxwell-Stefan equations are used in order to characterize multicomponent interactions. The complete chain of chemical reactions is taken into account. The reactions can be kinetically controlled or at chemical equilibrium, and they are considered for both liquid film and liquid bulk.

Thirdly, the method of numerical resolution is described. Coupling the generalized Maxwell-Stefan equations with chemical equilibrium equations leads to a highly non-linear Differential-Algebraic Equations system known as DAE index 3. The set of equations is discretized with finite-differences as its integration by Gear method is complex. The resulting algebraic system is resolved by the Newton-Raphson method.

Finally, the present model and the associated methods of numerical resolution are validated for the example of esterification of methanol. This archetype non-electrolytic system permits an interesting analysis of reaction impact on mass transfer, especially near the phase interface. The numerical resolution of the model by Newton-Raphson method gives good results in terms of calculation time and convergence. The simulations show that the impact of reactions at chemical equilibrium and that of kinetically controlled reactions with high kinetics on mass transfer is relatively similar. Moreover, the Fick's law is less adapted for multicomponent mixtures where some abnormalities such as counter-diffusion take place.

NOTATION

A_c	Cross section of column (m^2)	J_i^*	Molar diffusion flux in electrolytic solution ($\text{mol m}^{-2} \text{s}^{-1}$)
a^l	Specific area for a gas-liquid contact ($\text{m}^2 \text{m}^{-3}$)	k_0	Constant of kinetic for esterification reaction ($\text{L mol}^{-1} \text{s}^{-1}$)
C_i	Concentration of component i (mol m^{-3})	k_i^L	Mass transfer coefficient (m s^{-1})
D_{ij}°	Binary diffusion coefficient for a dilute (ideal) phase ($\text{m}^2 \text{s}^{-1}$)	K_i^{th}	Dimensionless gas-liquid equilibrium constant
d_i	Characteristic driving force of diffusion (m^{-1})	K_k^{cha}	Chemical equilibrium constant, correlated by activities
D_{ij}	Binary diffusion coefficient of the i - j pair ($\text{m}^2 \text{s}^{-1}$)	L	Liquid molar flow rate (mol s^{-1})
D_{ij}^*	Correlation constants between the composition gradients and the molar diffusion fluxes	nc	Total number of components in the mixture
D_{iM}	Diffusivity of component i in the mixture ($\text{m}^2 \text{s}^{-1}$)	N_i	Molar flux of component i in film ($\text{mol m}^{-2} \text{s}^{-1}$)
E	Heat flux ($\text{J m}^{-2} \text{s}^{-1}$)	n_i	Mole number (mol)
E_a	Activation energy (J mol^{-1})	n_i^0	Initial mole number (mol)
E_i	Enhancement factor	nrc	Number of kinetically controlled chemical reactions
E_i^{eff}	Efficiency factor of Murphree	nre	Number of instantaneous equilibrium reactions
F	Faraday constant	P	Pressure (Pa)
G	Gas molar flow rate (mol s^{-1})	Q	Heat loss flux ($\text{J m}^{-2} \text{s}^{-1}$)
G^t	Total Gibbs free energy	R	Constant of ideal gas ($\text{J mol}^{-1} \text{K}^{-1}$)
H	Molar enthalpy (J mol^{-1})	r_k	Reaction rate ($\text{mol m}^{-3} \text{s}^{-1}$)
H	Molar enthalpy (J mol^{-1})	T	Temperature (K)
h_i	Partial molar enthalpy (J mol^{-1})	u	Average velocity of components (m s^{-1})
J_i	Molar diffusion flux ($\text{mol m}^{-2} \text{s}^{-1}$)	v_i	Component velocity (m s^{-1})
		x_i	Liquid mole fraction (mol mol^{-1})
		y_i	Gas mole fraction (mol mol^{-1})
		y_i^*	Gas mole fraction in equilibrium with liquid (mol mol^{-1})

z	Diffusion axis (m)
z'	Column's height axis (m)
z_i	Ionic charge
ε^m	Molar liquid hold-up (mol)
ε^*	Dimensionless hold-up (liquid volume per unity of reactor volume)
ν_{ik}	Stoichiometric coefficient of component i in kinetically controlled reaction k
ν_{ik}^*	Stoichiometric coefficient of component i in the instantaneous equilibrium reaction k
μ_i	Chemical potential of component i (J mol ⁻¹)
δ_{ij}	Symbol of Kronecker
χ_k	Conversion rate of the instantaneous equilibrium reaction k per unity of volume (mol m ⁻³ s ⁻¹)
γ_i	Activity coefficient
λ	Thermal conductivity (J s ⁻¹ m ⁻¹ K ⁻¹)
δ_L	Liquid film thickness (m)
δ_G	Gas film thickness (m)
ξ_k	Molar conversion due to instantaneous equilibrium reaction k (mol)
Φ_e	Electrical potential (V)

Index & Subscripts

f	Film
G	Gas
I	Phase interface
J	Discretization pass
L	Liquid
n	Solvent
t	Total

INTRODUCTION

The wide interest in multifunctional unit operations involving reactive separation arises from the world's industrial tendency towards process intensification. Combining reaction and separation mechanisms brings several advantages such as increasing reaction yield and selectivity, overcoming azeotropes and thermodynamic restrictions, and important reductions in energy, water and solvent consumption. Major examples of reactive separations are reactive absorption and reactive distillation.

The introduction of a separation function within the reaction zone leads to complex interactions between gas-liquid mass transfer, chemical kinetics and gas-liquid equilibrium. One famous example of multicomponent reactive separation is the acid gases removal from flue gases emitted by power plants. New efficient processes of gas purification contain more complex physico-chemical phenomena which demands as well higher accuracy in terms of process modelling.

The multicomponent interactions can be interpreted as the diffusional competitions of components. Therefore in such systems, the diffusion has to be characterized accurately using generalized Maxwell-Stefan equations. For electrolytic solutions, the impact of ionic charges on diffusion can be considered using the gradient of electric potentials as the second driving force of diffusion.

The use of chemical reactions in separation units can enhance the mass transfer by shifting the physical equilibrium to the product side. This reduces significantly the size of separation units and maintains an intensified process with less cost and more efficiency.

Using more complex solvents in reactive separation units in order to obtain higher efficiencies, deal eventually with a huge chain of chemical reactions of different natures and velocities. In this case, any simplification in terms of reaction mechanism such as considering just one apparent chemical reaction would cause a loss in accuracy. Hence, the present work considers complete chain of chemical reactions. The reactions could be kinetically controlled or at instantaneous equilibrium.

A combined diffusion-reaction model with the possibility of application in ionic mixtures is then needed to ensure the required accuracy for an industrial application.

The first part of this article describes the two major modelling approaches to simulate homogeneous reactive separation: the equilibrium-based and the rate-based approach. Both models are applied to mass and energy transfer, as well as to chemical reactions.

The following parts of the article explain the characterisation of multicomponent interactions and diffusion phenomena in electrolytic and non-electrolytic solutions, as well as the influence of chemical reactions on diffusion and mass transfer.

Afterward, a rigorous rate-based model based on the two-film theory, with almost no simplification in terms of chemical reactions and multicomponent interaction, is argued. The heat transfer is not neglected and is determined by conductive and convective heat flows through the liquid and gas films.

It has to be noticed that the final objective of the present model is to simulate CO₂ capture and gas treatment plants. To reduce greenhouse gases emissions, CO₂ must be removed from flue gases emitted by power plants. To further exploit gas fields with increasingly severe environmental rules, acid gases (CO₂, H₂S, COS, etc.) must be removed from natural gas with very high efficiency. This emphasizes the necessity to develop such accurate modelling.

1 MODELLING APPROACHES

1.1 Equilibrium-Based Approach

The equilibrium stage model has been generally applied to the conventional distillation, where the system is either

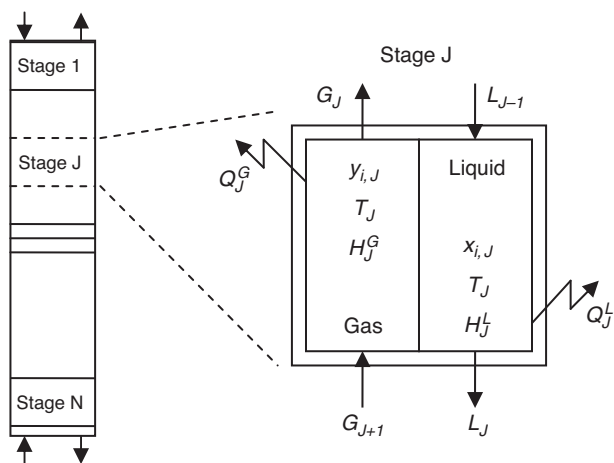


Figure 1

The equilibrium stage in a separation column.

non-reactive or associated with a simple chemical reaction (Seader and Henley, 1981). Its application for reactive distillation has been discussed afterwards by Taylor and Krishna (2000).

The equilibrium stage model divides the column into artificial segments. Figure 1 gives a schematic diagram of an equilibrium stage, where vapour from the stage below is brought into contact with liquid from the stage above. Equilibrium-based model assumes that the leaving liquid and vapour streams are at thermodynamic equilibrium for each stage. The MESH-equations (Material, Equilibrium, Summation and Heat equations) are known to model equilibrium stages.

Reactive separation processes rarely operate close to thermodynamic equilibrium. Dudukovic and Lee (1998) propose a stage efficiency factor in order to rectify the equilibrium assumption and to tend towards non-equilibrium real conditions of distillation. The non-ideal behaviour of the phase in terms of mass transfer can be taken into account *via* the Murphee efficiency (Lockett, 1986):

$$E_i^{eff} = \frac{\bar{y}_{i,J} - y_{i,J+1}}{y_i^* - y_{i,J+1}} \quad (i = 1, nc) \quad (1)$$

where $\bar{y}_{i,J}$: average mole fraction of gas leaving the stage; $y_{i,J+1}$: mole fraction of gas entering the stage; y_i^* : gas composition in equilibrium with liquid leaving the stage.

For packed columns, the Height Equivalent to Theoretical Plate (HETP) is commonly used, where its behaviour is closely related to the behaviour of stage efficiency.

Taylor and Krishna (1993) have stated that for the distillation of multicomponent systems with three or more species, component efficiencies are usually very different.

Some of them have values greater than unity and some less than zero.

Some authors propose methods in order to predict multicomponent efficiencies, but there is no fundamental method for estimating efficiencies or HETPs in reactive distillation of multicomponent mixtures especially when systems contain complex chain of chemical reactions. For example in reactive absorption operations, chemical reactions can lower reactant concentrations, resulting in component efficiencies greater than one.

Gorak *et al.* (1999b) as well as Chakravaty *et al.* (1985) have explained the low accuracy of an equilibrium approach for reactive absorption modelling where more complex reactive behaviours, multicomponent interactions and thermodynamics interfere.

1.2 Rate-Based Approach

The rate-based models for reactive separation follow the principle of non-equilibrium stage, implying that actual rates of chemical reactions and multicomponent mass and mass transfer between phases are taken into account directly. Mass transfer at the phase interface could be described by the two-film theory or the penetration theory (Danckwerts, 1951; Higbie, 1935). This work adapts the two-film theory because of its simplicity.

Figure 2 illustrates a non-equilibrium stage in separation column. The non-equilibrium stage represents a tray or a cross section of a packed column. Regarding Figure 2, bulks are assumed to be well mixed, with no gradient of concentration. The thermodynamic equilibrium at the interface is considered as well.

The consideration of diffusion resistance is realized by means of the film's thickness (δ_G, δ_L). Film thickness can be estimated by simplification, as the ratio between mass transfer coefficient and diffusion coefficient:

$$\delta_{ij} = \frac{D_{ij}}{k_{ij}} \quad (2)$$

The impact of hydrodynamics and internals (*e.g.* in a packed-column) is summarized to the estimation of film thickness (Gorak *et al.*, 1999a; Taylor and Krishna, 2000). Regarding to Equation (2), in multicomponent mixtures there are as many film thicknesses as the number of binary pairs. An average by mole fractions has to be applied to obtain just one film thickness for each phase.

The model balances liquid and gas phases separately considering mass and heat fluxes across the interface. In each bulk phase, the model is expressed by component balances, thermal balances and summation equations.

The influence of chemical reaction on mass transfer is conventionally considered by using the enhancement factor,

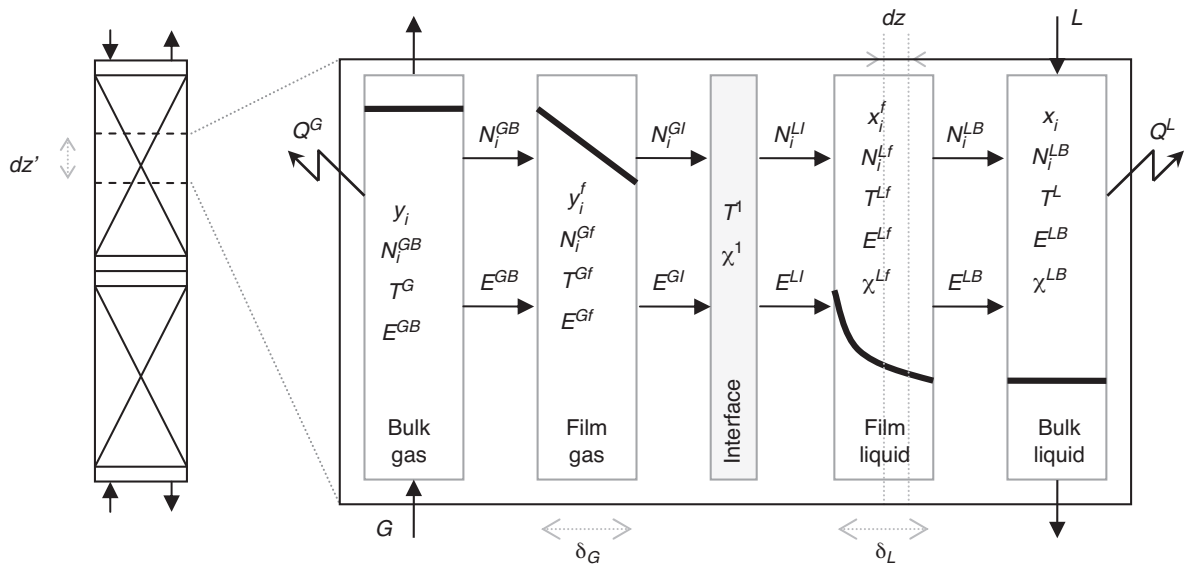


Figure 2

The non-equilibrium (rate-based) stage in a reactive separation column, based on the two film theory.

E_i (Eq. 3). This factor is the ratio of mass transfer with and without chemical reaction:

$$N_i^L = k_i^L E_i(x_i^f|_i - x_i) \quad (3)$$

Versteeg *et al.* (2007, 1989), Gorak *et al.* (2001), Hikita *et al.* (1972) and DeCoursey (1982) have provided analytical expressions of enhancement factor for few simple reaction schemes. To apply the enhancement factor for multicomponent reactive separation modelling, multiple assumptions are necessary. These assumptions are for example the equality of all binary diffusion coefficients, or the consideration of only one transferring component. For a complex chain of chemical reactions the estimation of enhancement factor is not simple and does not maintain the desired accuracy.

The molecular diffusion is generally characterized by Fick's law. However Fick's law is strictly valid for binary mixtures or for diffusion of infinite dilute specie i in multicomponent mixture, and in the absence of external forces.

Authors such as Toor (1957) and Valerio *et al.* (1995) have proposed to generalize Fick's law for multicomponent mixtures, in order to consider the effect of all composition gradients on each molar diffusive flux (Eq. 4). However, the resulting D'_{ij} coefficients do not reflect the physical sense of diffusion coefficient:

$$J_i^{Lf} = -C_t^L \sum_{j=1}^{nc-1} D'_{ij} \nabla x_j^f \quad (4)$$

2 DIFFUSION IN MULTICOMPONENT MIXTURE

2.1 Non Electrolytic Solutions

The Maxwell-Stefan (MS) equations make available a rigorous modelling of molecular diffusion when the mixture contains three or more components with different sizes and natures. MS equations take into account the accurate interactions in non-ideal phase, as well as the possible presence of other external forces such as electrical forces. Wesselingh and Krishna (1997) have done a complete study on diffusion in multicomponent mixtures. The MS equations connect diffusion fluxes of components to the gradients of their chemical potentials (Taylor and Krishna, 1993):

$$\frac{x_i^f}{RT^{Lf}} \nabla \mu_i^{Lf} = - \sum_{j=1}^{nc} \frac{(x_i^f N_j^{Lf} - x_j^f N_i^{Lf})}{C_t^L D_{ij}^L} \quad (i = 1, nc) \quad (5)$$

D_{ij} are the binary diffusion coefficients. For a non-ideal liquid phase, the binary diffusion coefficient is related to a gradient of chemical potential. Considering an ideal gas phase, D_{ij} is related to a gradient of mole fraction which is similar to the Fick's law. Then, binary diffusion coefficients can be used for Maxwell-Stefan relations, and there is no need to correlate new diffusion coefficients.

The effect of non-ideality on the binary diffusion coefficient can be translated by composition-dependency of the binary diffusion coefficient in non-ideal phase. The non-ideal binary diffusivities are estimated from their value for an ideal dilute phase (D_{ij}^0), and by adding the composition impact. The

non-ideal correction can be realized *via* Vignes relationship (Vignes, 1966):

$$D_{ij} = (D^{\circ}_{ij})^{1-x_i} (D^{\circ}_{ji})^{x_i} \quad (6)$$

The liquid phase is considered as a non-ideal phase. It is commonly recommended to write the Maxwell-Stefan equations in terms of mole fraction gradients (Slattery, 1981). For an isothermal isobaric diffusion we have:

$$\sum_{j=1}^{nc} \left(\delta_{ij} + x_i^f \frac{\partial \ln \gamma_i}{\partial x_j^f} \right)_{T,P,x_k (k \neq j)} \nabla x_j = - \sum_{j=1}^{nc} \frac{(x_i^f N_j^{Lf} - x_j^f N_i^{Lf})}{C_i^L D_{ij}^L} \quad (7)$$

($i = 1, nc$)

with, δ_{ij} as the Kronecker symbol:

$$\begin{cases} \delta_{ij} = 1 & (i = j) \\ \delta_{ij} = 0 & (i \neq j) \end{cases} \quad (8)$$

Taylor and Krishna (2000) replace one Maxwell-Stefan equation by the summation of mole fractions. In this case, the mole fraction of the last component is obtained by the summation equations for both phases. The difficulty is then to choose a reference component. In contrast with this approach, we take into account all the Maxwell-Stefan equations. It is because, by integrating all the nc Maxwell-Stefan equations, the vanishing sum of compositions' gradients signifying the constant summation of mole fractions through the film, is obtained:

$$\sum_{j=1}^{nc} \nabla x_j = 0 \quad (9)$$

Therefore, there is no need to rewrite the constant sum of mole fractions as a new explicit equation. Keeping the nc -equations structure of Maxwell-Stefan equations, a coherent numerical resolution of model can be realized.

The gas phase is considered as an ideal phase. So the terms containing the gradient of activity coefficient can be neglected. The gradient of chemical potential is reduced to a gradient of mole fraction in an ideal phase. Therefore, the Maxwell-Stefan equations for the gas phase take the following form:

$$\nabla y_i^f = - \sum_{j=1}^{nc} \frac{(y_i^f N_j^{Gf} - y_j^f N_i^{Gf})}{C_i^G D_{ij}^G} \quad (i = 1, nc) \quad (10)$$

2.2 Electrolytic Solutions

According to the Maxwell-Stefan equations (Eq. 5), the left part describes the gradient of chemical potential which is considered as the only driving force for diffusion in absence of other external forces such as gravity. It is a more accurate representation of driving forces, because it considers likewise the non-ideality effects of the chemical potential expression.

In electrolytic mixtures, the gradient of electrical potentials due to the presence of ionic species has to be integrated in MS equations as the second driving force for diffusion (Newman, 1991). Hence, the generalized driving force takes the following form:

$$d_i = \frac{x_i^f}{RT^f} \nabla \mu_i^f + x_i^f z_i \frac{F}{RT^f} \nabla \Phi_e \quad (i = 1, nc) \quad (11)$$

The diffusive molar fluxes (J_i) are described with respect to the mobile Cartesian coordinate of velocity reference. For a non-electrolytic mixture, reference velocity is the average of components' velocity with respect to their molar fraction ($u = \sum_{i=1}^{nc} x_i v_i$). In this case, total diffusive fluxes are vanished.

$$J_i = C_i (v_i - u) \quad (12)$$

$$\sum_{i=1}^{nc} J_i = \sum_{i=1}^{nc} C_i v_i - \sum_{j=1}^{nc} C_j v_j = 0 \quad (13)$$

On the contrary, for an electrolytic solution, the reference velocity is usually the solvent velocity (v_n). So, new diffusive molar fluxes with respect to the solvent's movement have to be introduced:

$$J_i^* = C_i (v_i - v_n) \quad (14)$$

$$\sum_{i=1}^{nc} J_i^* \neq 0 \quad (15)$$

The generalized Maxwell-Stefan equations could be similarly expressed in term of diffusive molar fluxes:

$$\frac{x_i^f}{RT^f} \nabla \mu_i^f + x_i^f z_i \frac{F}{RT^f} \nabla \Phi_e = - \sum_{j=1}^{nc} \frac{(x_i^f J_j^* - x_j^f J_i^*)}{C_i D_{ij}} \quad (16)$$

($i = 1, nc - 1$)

Regarding Equation (16), due to the presence of a second driving force, the constant sum of mole fractions through the film is not verified as it has been verified for non-electrolytic systems (Eq. 9).

Two approaches exist. Either to introduce explicitly the constant sum of mole fractions, or to introduce the vanishing sum of the second driving force (gradient of electrical potential) which would be simplified as the electroneutrality condition:

$$\sum_{j=1}^{nc-1} x_j^f z_j = 0 \quad (17)$$

We take into account the latter approach. So, the last Maxwell-Stefan equation describing the neutral solvent ($z_n = 0$) is replaced by the electroneutrality condition.

The electroneutrality condition which is in fact a simplified form for the sum of external electrical forces would be physically justified for an isobaric system at mechanical equilibrium, where there is no temporal derivative of velocities.

3 PHYSICAL AND CHEMICAL EQUILIBRIUM

The classical approach of determining thermodynamic equilibrium conditions of several phases in equilibrium with each other, which is addressed by Walas (1985), is not sufficient when the chemical equilibrium exists similarly at the phase interface. Hence, a combined problem of determining equilibrium points in a multiphase mixture at chemical equilibrium conditions has to be studied.

The effect of chemical equilibrium reactions on a two-phase equilibrium has been argued at length by Doherty (1990). In their first paper (Barbosa and Doherty, 1987a), the influence of a single reversible chemical reaction on a vapour-liquid equilibrium has been represented. Furthermore, in their second paper (Barbosa and Doherty, 1987b), they have introduced a set of transformed composition variables that are particularly useful to construct thermodynamic diagrams for reacting mixtures. In this case, actual flows and compositions are replaced by transformed ones. The advantage of this method is that the chemical and physical equilibrium problem in a reactive mixture is identical to a strictly physical equilibrium model, and the existing algorithms can be used to solve the equation. However, this approach could not be applied to kinetically controlled chemical reactions and its use is limited for chemical reactions at instantaneous equilibrium.

In multicomponent mixtures when several reactions take place, the chemical equilibrium has to be described separately in the model. Hence, the model is not the same and it has to take into account the chemical equilibria as new algebraic equations, which make the numerical resolution of the model more complex.

The chemical equilibrium is characterized by the minimization of Gibbs free energy (Smith, 1980). The mathematical problem is the minimization of non-linear system of equations under constraints:

$$\min \left\{ G^t = \sum_{i=1}^{nc} n_i \mu_i(T, P, x_{j=1,nc}) \right\} \quad (18)$$

$$n_i = n_i^0 + \sum_{k=1}^{nre} \nu'_{ik} \xi_k \geq 0 \quad (i = 1, nc) \quad (19)$$

As described in Equation (19), the change in mole number is a function of molar conversion due to instantaneous equilibrium reactions. The Gibbs free energy is then an indirect function of instantaneous molar conversion (ξ_k) and its minimization leads to the chemical equilibrium equations as shown below:

$$K_k^{ch,a} = \prod_{i=1}^{nc} (\gamma_i x_i)^{\nu'_{ik}} \quad (k = 1, nre) \quad (20)$$

4 CHEMICAL REACTIONS AND HEAT TRANSFER

As discussed in Section 1.2, the enhancement factor approach is not adapted for multicomponent reactive systems. The present work proposes to take into account the complete chain of chemical reactions.

The continuity of molar fluxes at phase interface is applied, if there is no instantaneous equilibrium reaction at gas-liquid interface:

$$N_i^{Lf} \Big|_l = N_i^{Gf} \Big|_l \quad (i = 1, nc) \quad (21)$$

For instantaneous equilibrium reactions at interface, the inequality of molar fluxes at phase interface has to be applied. In this case, the difference between gas and liquid molar fluxes at phase interface is due to the rate of interfacial instantaneous equilibrium reaction which is characterized as a new set of variables χ_k :

$$N_i^{Lf} \Big|_l a^l - N_i^{Gf} \Big|_l a^g + \sum_{k=1}^{nre} \nu'_{ik} \chi_k^l = 0 \quad (i = 1, nc) \quad (22)$$

Chemical equilibrium equation has to be written as well, whenever an instantaneous equilibrium reaction takes place. This is ensured by means of components' activities at phase interface:

$$K_k^{ch,a} = \prod_{i=1}^{nc} (\gamma_i x_i^f)^{\nu'_{ik}} \quad (k = 1, nre) \quad (23)$$

If chemical reactions are sufficiently fast, they could take place in the liquid film. They can be kinetically controlled or at instantaneous equilibrium, and their impact on mass transfer is formulated in partial material balances:

$$\nabla N_i^{Lf} = \sum_{k=1}^{nrc} \nu_{ik} r_k^f + \sum_{k=1}^{nre} \nu'_{ik} \chi_k^f \quad (i = 1, nc) \quad (24)$$

The former term (r_k^f) represents the rate of a kinetically controlled reaction. The latter term (χ_k^f) is the rate of an instantaneous equilibrium reaction.

If chemical reactions at instantaneous equilibrium exist in film, the chemical equilibrium equation has to be verified as well within the reactive film:

$$K_k^{ch,a} = \prod_{i=1}^{nc} (\gamma_i x_i^f)^{\nu'_{ik}} \quad (k = 1, nre) \quad (25)$$

The molar fluxes remain uniform in the gas film as this phase is considered non-reactive:

$$\nabla N_i^{Gf} = 0 \quad (i = 1, nc) \quad (26)$$

Coupling Maxwell-Stefan equations (Eq. 7) and partial mass balance (Eq. 24) with the presence of instantaneous chemical equilibrium (Eq. 25), we get a highly non-linear set of Differential and Algebraic Equations, which has to be solved numerically.

Most studies on rate-based modelling of homogeneous reactive separation make numerous assumptions either on multicomponent mass transfer or on reactive events, in order to simplify the model's system of equations. The present work does not use these simplifications and solves the model's set of equations using some numerical strategies.

The heat balance within the film is described by the continuity of heat fluxes in the absence of external heat sources. The heat of reaction does not appear in the heat balance since enthalpies are referred to their elemental state:

$$\nabla E^{Lf} = 0 \quad (27)$$

$$\nabla E^{Gf} = 0 \quad (28)$$

Heat fluxes E^{Lf} and E^{Gf} are expressed as the integration of conductive and convective heat flows through the films:

$$E^{Lf} = \left[-\lambda \nabla T^{Lf} + \sum_{i=1}^{nc} N_i^{Lf} h_i^{Lf} \right] \quad (29)$$

$$E^{Gf} = \left[-\lambda \nabla T^{Gf} + \sum_{i=1}^{nc} N_i^{Gf} h_i^{Gf} \right] \quad (30)$$

5 RIGOROUS RATE-BASED MODEL FOR MULTICOMPONENT REACTIVE SEPARATION

Reactive separation operations have generally a multicomponent nature. The non-ideal thermodynamics and the diffusional competitions in film are accompanied by chemical reactions. A rigorous model consists of sub-models for thermodynamics, hydrodynamics, reactions and simultaneous mass and heat transfer.

Here, the mass transfer between phases is described as the combination of the two-film theory (Sect. 1.2) and the Maxwell-Stefan formulation of molecular diffusion (Sect. 2). The diffusion is assumed to be one-dimensional through the film's thickness. For each phase, a molar averaged film thickness is used as the "overall" film thickness.

The simplifications according to the present model concern the process's hydrodynamics. The model does not apply the equations of momentum; and the necessary hydrodynamic parameters have been estimated using empirical correlations.

Regarding the non-equilibrium stage of separation column (Fig. 2) for a packed-column, the steady-state balance equations including the reaction source terms are:

$$\frac{d}{dz'} (L x_i) + \left(\begin{array}{l} -N_i^{LB} a' + \left[\sum_{k=1}^{nrc} v_{ik} r_k \right] \varepsilon^* + \\ \left[\sum_{k=1}^{nrc} v'_{ik} \chi_k^B \right] \varepsilon^* \end{array} \right) A_c = 0 \quad (i = 1, nc) \quad (31)$$

$$\frac{d}{dz'} (G y_i) + N_i^{GB} a' A_c = 0 \quad (i = 1, nc) \quad (32)$$

The dimensionless hold-up (ε^*) depends on the flows and is calculated via empirical correlations. The term r_k indicates the rate of a kinetically controlled chemical reaction, and the term χ_k^B corresponds to the tau of an instantaneous equilibrium reaction in liquid bulk for which the chemical equilibrium equations have to be included:

$$K_k^{ch,a} = \prod_{i=1}^{nc} (\gamma_i x_i)^{v'_{ik}} \quad (k = 1, nrc) \quad (33)$$

The energy balances for the gas and liquid bulk-phases are as follows:

$$\frac{d}{dz'} (L H^{LB}) + (Q^L - E^{LB}) a' A_c = 0 \quad (34)$$

$$\frac{d}{dz'} (G H^{GB}) + (Q^G - E^{GB}) a' A_c = 0 \quad (35)$$

The set of equations describing film's simultaneous mass and heat transfer (film model) associates Maxwell-Stefan equations (Eq. 7, 10), differential mass balances within the film (Eq. 24, 26) and chemical equilibrium equations in the film (Eq. 25) in order to maintain concentration and molar flux profiles in the film, and in order to determine concentrations (x_i, y_i) and molar fluxes: ($N_i^{Lf}|_{\delta_L}, N_i^{Gf}|_{\delta_G}$) at the boundary of the film region.

The film model contains in addition the differential heat balances in the film (Eq. 27, 28) and the energy contribution equations through the film region (Eq. 29, 30) in order to give temperature and heat flux profiles in film, and in order to determine the temperatures ($T^{Lf}|_{\delta_L}, T^{Gf}|_{\delta_G}$) and heat fluxes ($E^{Lf}|_{\delta_L}, E^{Gf}|_{\delta_G}$) at the boundary of the film region.

The differential equations of the film model should be completed by the boundary conditions relevant to the film. The boundary conditions specify the values of the mixture at both film boundaries. We maintain finally a vector-type boundary value problem in order to obtain the film's profiles as functions of the film co-ordinate. The boundary value problem has to be solved in conjunction with all other film model equations such as the MS equations and the chemical equilibrium equations, to determine the component fluxes.

The boundary conditions of the film model at film's thickness ($z = \delta_G, z = \delta_L$) near the bulk-phase have been listed as follows:

$$N_i^{LB} - N_i^{Lf}|_{\delta_L} = 0 \quad N_i^{GB} - N_i^{Gf}|_{\delta_G} = 0 \quad (i = 1, nc) \quad (36)$$

$$x_i - x_i^f|_{\delta_L} = 0 \quad y_i - y_i^f|_{\delta_G} = 0 \quad (i = 1, nc) \quad (37)$$

$$T^L - T^{Lf}|_{\delta_L} = 0 \quad T^G - T^{Gf}|_{\delta_G} = 0 \quad (38)$$

$$E^{LB} - E^{Lf}|_{\delta_L} = 0 \quad E^{GB} - E^{Gf}|_{\delta_G} = 0 \quad (39)$$

According to the phase interface boundary-condition, The G-L phase equilibrium is considered:

$$y_i^f|_i - K_i^{th} x_i^f|_i = 0 \quad (i = 1, nc) \quad (40)$$

K_i^{th} values are evaluated at the pressure, temperature and composition of the interface from appropriate thermodynamic models, which would be the same models used for an equilibrium-based model.

For interfacial instantaneous equilibrium reactions, the inequality of molar fluxes (Eq. 22) is assumed. In this case, chemical equilibrium equations at gas-liquid interface have to be involved (Eq. 23).

The continuity of heat fluxes and temperature are considered at the interface as follows:

$$E^{Lf}|_i - E^{Gf}|_i = 0 \quad (41)$$

$$T^{Lf}|_i - T^{Gf}|_i = 0 \quad (42)$$

The summation of mole fractions is written at the interface.

$$\sum_{i=1}^{nc} x_i^f|_i - 1 = 0 \quad \sum_{i=1}^{nc} y_i^f|_i - 1 = 0 \quad (i = 1, nc) \quad (43)$$

Regarding the vanishing sum of compositions' gradients (Eq. 9), the constant sum of mole fractions remains verified through the film region and in the bulk phase.

When the chemical reactions are at instantaneous equilibrium, the chemical equilibrium conditions have to be considered. In this case, we introduce the conversion rates of instantaneous equilibrium reactions (χ) in order to provide the coherent number of variables and equations in model. Adding the chemical equilibrium equations, the model's system of equations becomes a set of Differential-Algebraic Equations (DAEs).

For the simulation of multicomponent reactive separation, two coupled sets (models) of Differential-Algebraic Equations have to be solved. The first set of Differential-Algebraic Equations (film model) describes simultaneous mass and heat transfers accompanied with all the reaction events and equilibrium considerations through the film regions. The second set of Differential-Algebraic Equations (bulk model) describes partial balance equations and the possible chemical equilibrium conditions in bulk phases for each segment (stage) of column. Figure 3 represents the conjunction between these two models at the film's

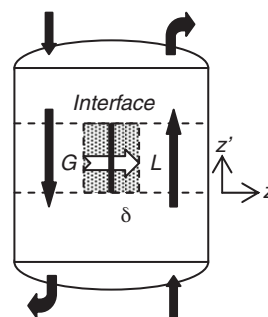


Figure 3
Coupled transfers in rate-based model (film versus bulk).

boundary-conditions. δ in Figure 3 represents the film thickness.

The DAE set of equations of film model can be solved analytically or numerically, regarding the nature and the degree of non-linearity of equations. Table 1 shows different resolution strategies according to the rate-based modelling of multicomponent reactive separation.

Analytical resolution of film model is possible considering lots of physico-chemical assumptions. Hikita *et al.* (1972) propose an analytical solution for two-step instantaneous chemical reaction between the dissolved gas and a liquid-phase reactant. Their analytical approach has been based on the following considerations: the chemical equilibrium constants of the first and second step reactions are very large; diffusivities of all species are equal; and reaction factor is given with an approximate expression.

The numerical approaches are also applied for various case studies. The recent works are generally based on effective diffusivities in order to overwhelm the problem of highly non-linear Maxwell-Stefan equations. In addition, recent numerical approaches use an enhancement factor to characterize the reactions' effect. Therefore our rigorous approach to rate-based modelling, means the complete consideration of physico-chemical effects in models involving all multicomponent diffusional and reactive events, is original.

TABLE 1
Different approaches to rate-based modelling of multicomponent reactive separation

Authors	Hydrodynamic model	Reaction in film	Nature of reaction	Strategy of resolution	Heat transfer
Taylor and Krishna (1993)	Two-film	+	Kinetically controlled	Numerical film discretization	+
Dudukovic and Lee (1998)	Two-film	-	Kinetically controlled	Analytical	+
Pagani <i>et al.</i> (2001)	Two-film	+	Kinetically controlled/Equilibrium	Numerical effective diffusivity	-
Gorak <i>et al.</i> (1999a)	Two-film	+	Kinetically controlled/Equilibrium	Numerical effective diffusivity	+

The conversion rate of instantaneous equilibrium reactions (χ) is in fact an algebraic variable of DAE system of equations, whose differential terms is hidden in the equation of chemical equilibrium. To make appear these hidden differential terms, it is necessary to differentiate frequently the algebraic equations of chemical equilibrium in order to obtain a pure system of differential equations. The number of necessary differentiations to transform the DAE system into a pure differential system of equations is known as the index of differentiation. With respect to the DAE system of film model, the index of differentiation is 3. The high index of differentiation in film model signifies the complex relation between conversion rate of instantaneous equilibrium reaction (χ) and algebraic equation of chemical equilibrium (Eq. 25).

For a high index of differentiation, the DAE system integration using the Gear method (Gear, 1971) through the axis of independent differential variable is complex. This leads to discretize the film regions by finite differences with a backward-difference approximation, in order to transform the DAE system of equation into a pure algebraic set of equations. Figure 4 gives a schematic picture of liquid film discretization.

The bulk model forms a DAE system of index 2, while the instantaneous chemical equilibrium conditions exist. The bulk model can be similarly discretized by finite differences in order to generate a set of pure algebraic equations.

Newton-Raphson is the widely used approach to solve nonlinear set of algebraic equations describing conventional separation processes. To overcome the convergence problem,

it is necessary to limit the changes in increment in the variable values. Limiting variable regeneration in each iteration is particularly important when the values of variables conflict with their expected physical magnitude.

The Newton-Raphson method demands the evaluation of partial derivatives of all the equations with respect to all variables. Because of the difficulty in the estimation of partial derivatives of thermodynamic properties with respect to temperature and composition, almost all derivatives are obtained analytically. The resulting Jacobian matrix with a block tridiagonal structure can be solved using the Thomas algorithm (Seader and Henley, 1981). This numerical approach ensures a quadratic convergence as well as a reasonable calculation time, using a proper initial guess.

In the present model, an accurate estimation of mass transfer coefficients, interfacial areas, liquid hold-ups, etc. is needed. The thermodynamic properties are used not only for the calculation of phase equilibrium but also to estimate the driving forces in mass transfer for taking into account the effects of non-ideality.

The effect of non-ideal thermodynamics manifests in the composition-dependency of activity coefficients (γ_i). Generally used relations such as Margules and Van Laar are less accurate to reflect the composition impact on activity coefficients, however they are considered as the simplest approaches with respect to the newer ones, *e.g.* Wilson, NRTL and UNIQUAC. For electrolytic solutions some recent approaches as SOUR-WATER (Edwards) or UNIQUAC multisolvent electrolytic (UQMS) can be applied.

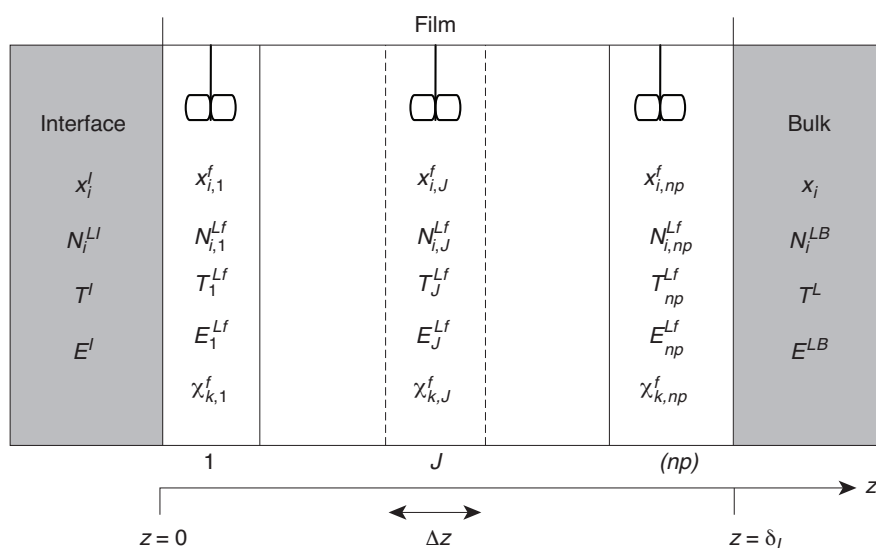


Figure 4

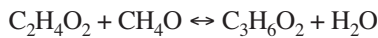
Schematic picture of discretized liquid film with instantaneous chemical equilibrium conditions.

6 TESTING NUMERICAL CONCLUSIONS FOR ESTERIFICATION OF METHANOL

The introduction of instantaneous equilibrium reactions, accompanied by chemical equilibrium equations, makes more complex the numerical resolution of a model. This is due to the formation of the DAE system of equations. The instantaneous reactive behaviour of a mixture is often observed in reactive absorption operations with electrolytic systems, in which we face more complexities such as ion formation, existence of electrical driving force of diffusion, different number of real species in each phase, and lack of some empirical physico-chemical properties.

Therefore, the first step to validate the present model is to simulate a basic example of non-electrolytic system assuming a fictive instantaneous equilibrium reaction. The esterification of methanol has been previously studied by Doherty *et al.* (2003) and Agreda *et al.* (1990) and has been well documented. So, this example is retained to validate all numerical conclusions according to our rigorous approach of rate-based modelling.

The liquid-phase is governed by the following equation:



The equilibrium constant of reaction is given by Doherty *et al.* (1998) as a function of temperature:

$$\ln(K^{ch,a}) = -0.8226 + \frac{1309.8}{T} \quad (44)$$

Agreda *et al.* (1990) as well as Sawistowski and Pilavakis (1979) propose the following expression (Eq. 45) to estimate the reaction rate of esterification of methanol. The necessary parameters have been given in Table 2.

$$r = k_0 \exp\left(\frac{-E_a}{RT}\right) \left[C_{MA} C_W - \frac{C_{AA} C_{MeOH}}{K^{ch,a}} \right] \quad (45)$$

TABLE 2

Reaction rate parameters for the esterification of methanol

$E_a = 10000 \text{ cal mol}^{-1}$
$k_0 = 1.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$
$R = 1.989 \text{ cal mol}^{-1} \text{ K}^{-1}$

The UNIQUAC model (Prausnitz *et al.*, 1999) is taken to estimate the activity coefficients.

Table 3 gives binary parameters of UNIQUAC model for this system.

The binary diffusivities in liquid phase are first estimated for infinite dilution phase using Wilke and Chang method (Reid *et al.*, 1987). Then they are corrected by Vignes relation (Reid *et al.*, 1987) in order to take into account the non-ideal effects. The estimation of binary diffusion

TABLE 3

Binary parameters UNIQUAC:
MA (Methyl Acetate), MeOH (Methanol), W (Water), AA (Acetic Acid)

$a_{ij} \text{ (cal mol}^{-1}\text{)}$	$j = \text{MA}$	$j = \text{MeOH}$	$j = \text{W}$	$j = \text{AA}$
$i = \text{MA}$	0	585.4818	789.9959	806.8436
$i = \text{MeOH}$	-54.3376	0	95.2593	-40.7254
$i = \text{W}$	117.2113	-10.3767	0	-305.4517
$i = \text{AA}$	-467.1250	-51.0491	427.7405	0

TABLE 4

Binary liquid diffusivities in dilute phase at $T = 365.7 \text{ K}$
and $P = 1 \text{ atm}$ (Wilke and Chang)

$D_{ij}^L \text{ (m}^2 \text{ s}^{-1}\text{)}$	$j = \text{AA}$	$j = \text{MeOH}$	$j = \text{MA}$	$j = \text{W}$
$i = \text{AA}$	3.511E-09	4.665E-09	9.940E-09	3.116E-09
$i = \text{MeOH}$	4.470E-09	5.939E-09	1.266E-08	3.967E-09
$i = \text{MA}$	2.987E-09	3.969E-09	8.456E-09	2.651E-09
$i = \text{W}$	3.173E-09	4.216E-09	8.983E-09	2.816E-09

TABLE 5

Binary gas diffusivities in dilute phase at $T = 365.7 \text{ K}$
and $P = 1 \text{ atm}$ (Fuller)

$D_{ij}^G \text{ (m}^2 \text{ s}^{-1}\text{)}$	$j = \text{AA}$	$j = \text{MeOH}$	$j = \text{MA}$	$j = \text{W}$
$i = \text{AA}$	9.836E-06	1.397E-05	8.370E-06	2.189E-05
$i = \text{MeOH}$	1.397E-05	1.921E-05	1.196E-05	2.963E-05
$i = \text{MA}$	8.370E-06	1.196E-05	7.126E-06	1.868E-05
$i = \text{W}$	2.189E-05	2.963E-05	1.868E-05	4.574E-05

coefficients in gas phase is realized by Fuller equation (Reid *et al.*, 1987) assuming the phase as ideal. Tables 4 and 5 give some values of binary diffusivities in dilute liquid and gas phases.

Methanol (MeOH) is the main component of the inlet gas (98% vol). It is absorbed by Acetic Acid (AA) at 76 wt.% in a packed column. Corresponding operating conditions have been given in Table 6. The column is divided into 30 non-equilibrium stages. The last stage (stage 30) represents the bottom-column where the initial gas enters and the first stage (stage 1) represents the top-column where the liquid solvent is fed.

Figure 5 gives the component mole fractions in the column. Almost all the methanol is absorbed between stages 30 and 20. The Newton-Raphson method provides a quadratic and quick convergence in less than ten iterations.

Two regimes of chemical reaction (reaction at instantaneous equilibrium and reaction with high kinetics) have been studied in order to show clearly the impact of chemical reaction rate and nature on mass transfer especially at the gas-liquid interface.

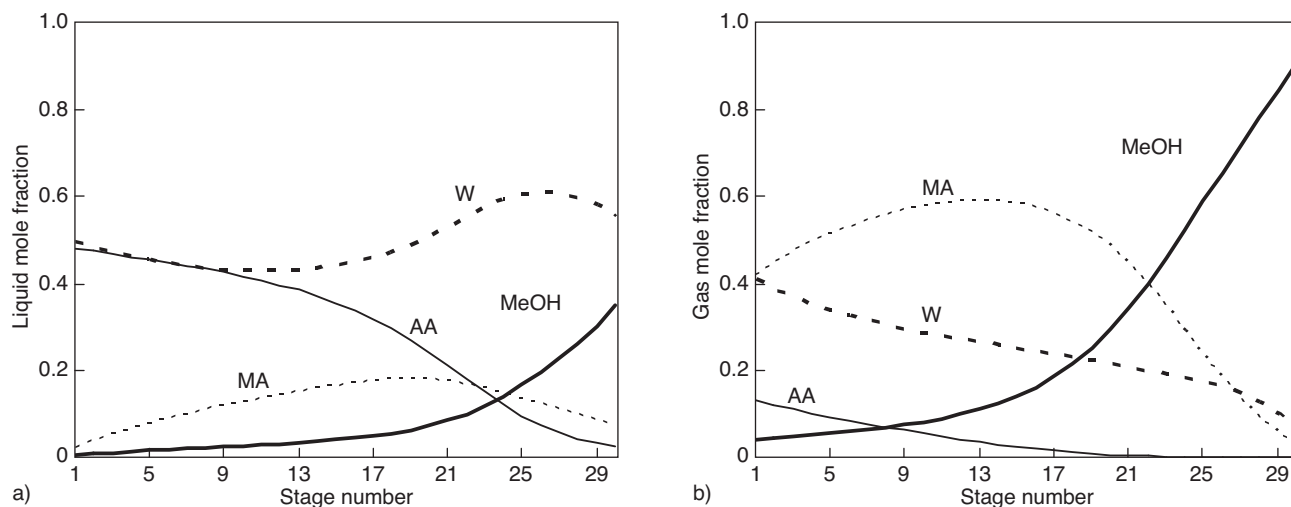


Figure 5

Simulation results of esterification column based on Maxwell-Stefan formulation within films: a) Bulk liquid; b) Bulk gas.

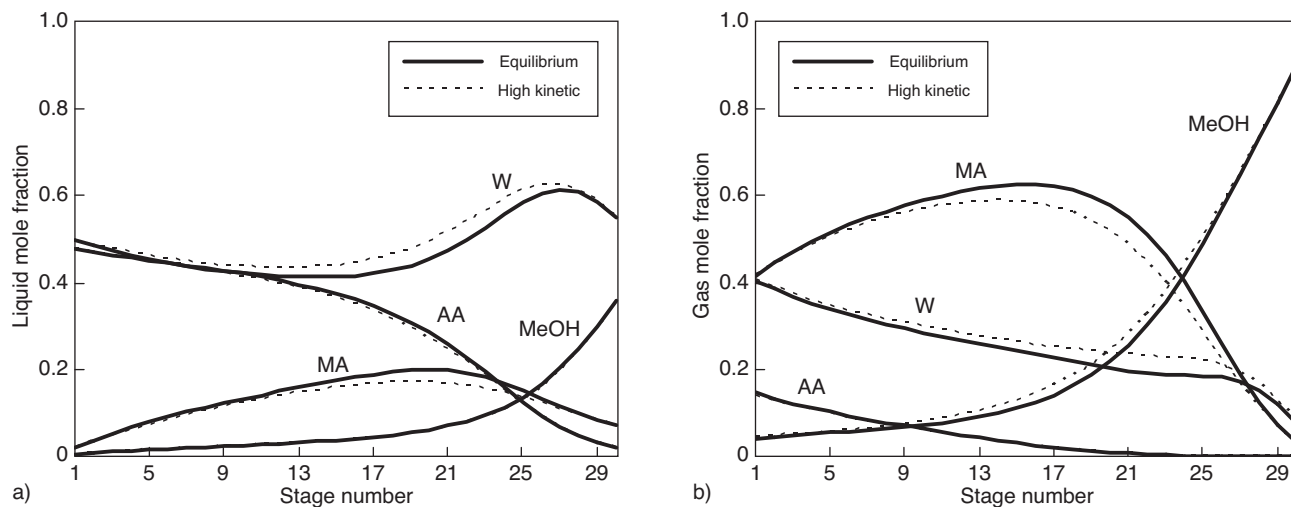


Figure 6

Similarity between the reaction with extremely high kinetic, and the instantaneous equilibrium one: a) Bulk liquid; b) Bulk gas.

If we increase sufficiently the kinetics of a kinetically controlled chemical reaction, its behaviour would be similar to a chemical reaction at instantaneous equilibrium. So, a simple way to analyze the results of simulation based on an instantaneous equilibrium reaction is to compare them with the results of a similar simulation based on kinetically controlled reaction with a sufficiently high kinetic constant.

Figure 6 shows the similarity between the two approaches. In this figure, composition profiles through the column's height have been illustrated for two different regimes of reaction: reaction at instantaneous equilibrium, and kinetically controlled reaction with high kinetics. The differences

appear at intermediate stages where the maximum reaction rate is observed. Increasing the reaction rate for a kinetically controlled reaction is numerically limited, that's why two reaction approaches do not fit totally according to Figure 6.

To focus on mass transfer in film, Figure 7 gives Acetic Acid (AA) molar flux profiles in a film for a fixed stage. Results show the progressive shape of change in molar flux through the interface, from a moderated kinetically controlled reaction to an instantaneous equilibrium reaction.

Regarding Figure 7, for a kinetically controlled reaction, the model respects the continuity of interfacial molar fluxes.

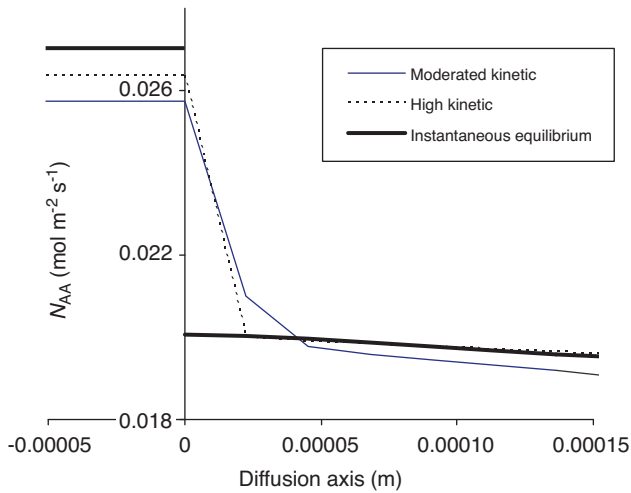


Figure 7

Equality and inequality of Acetic Acid's molar flux at the interface for three different reactive behaviours (Positive values of horizontal axis represent liquid film).

TABLE 6
Operational conditions for reactive separation column

	Initial gas rich in MeOH		
	mol.s ⁻¹	x (mol.mol ⁻¹)	
AA	0	0	T = 65 °C P = 1 atm
MeOH	2.4769E-2	0.98	
MA	0	0	
W	5.0550E-4	0.02	
Total	2.5275E-2	1	
	Initial liquid solvent		
	mol.s ⁻¹	x (mol.mol ⁻¹)	
AA	1.5257E-2	0.4872	T = 95 °C P = 1 atm
MeOH	0	0	
MA	0	0	
W	1.6060E-2	0.5128	
Total	3.1317E-2	1	

On the contrary, for an instantaneous equilibrium reaction, the model applies the discontinuity of molar fluxes. This assumption tries to rectify explicitly the difference between liquid and gas interfacial molar flux for extremely fast chemical reactions.

Figure 8 gives composition profiles in film for a fixed stage. Acetic Acid's (AA) composition gradient is positive while its molar flux is also positive. This phenomenon is known as counter-diffusion and can not be described with Fick's law.

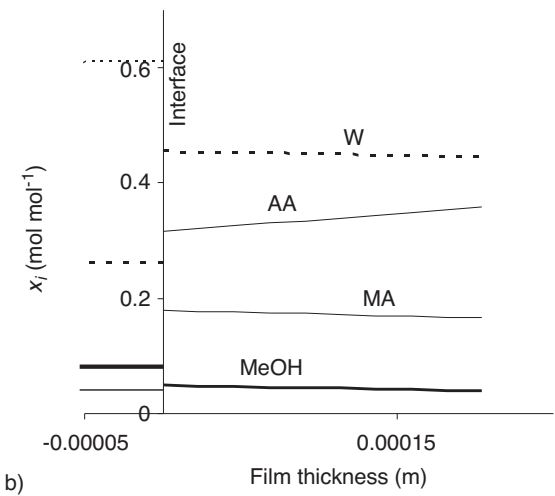
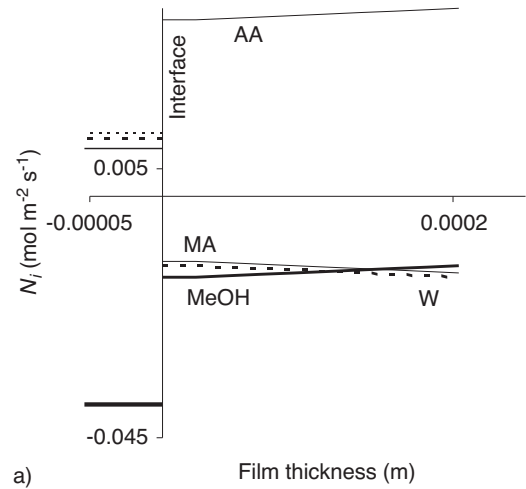


Figure 8

Counter-diffusion of Acetic Acid (AA) in liquid film. a) Molar flux profile in film; b) Mole fraction profile in film, (positive values of horizontal axis represent liquid film).

Some phenomena such as osmotic diffusion (diffusion of component despite the absence of a driving force), the counter/reverse diffusion (diffusion in a direction opposite to that dictated by its driving force) and the diffusion barrier (zero diffusion flux despite a large driving force) can take place in multicomponent mixtures where components are of different size and nature. It would be inadequate to describe these abnormalities with the Fick's law. That's why the Maxwell-Stefan formulation is more adapted for multicomponent mixtures.

CONCLUSION

The paper reviews rigorous rate-based modelling of multi-component reactive separation. The integration of chemical reaction and separation results in high yield and efficiency of the separation unit. That is why attentions are mostly focused nowadays on the rigorous modelling of such processes.

According to the rigorous rate-based approach, a direct consideration of multicomponent diffusion and chemical reactions is provided. A detailed description covers simultaneous mass and heat transfer, and reaction events including reaction-diffusion coupling under steady-state conditions.

Film transfer is described, on the basis of the two-film theory, while all chemical reactions are taken into account. The use of enhancement factor has been avoided since this approach is limited to simple reactive systems. Generalized Maxwell-Stefan equations have been retained in order to describe multicomponent diffusion complexities.

A rigorous rate-based model consists of rigorous sub-models for thermodynamics, hydrodynamics, reactions and simultaneous mass and heat transfer. Our first approach towards rigor in terms of modelling concerns the modelling methodology for complex diffusion-reaction conditions. In this case no physico-chemical simplification is considered with regard to diffusion and reaction. Here, the limitations are mostly due to the hydrodynamics simplifications.

The resulting model generates a highly non-linear DAE system of equations of index 3, whose integration under differential form using Gear method is not realistic. Therefore the model has been discretized with finite differences in order to transform the system of equations into a pure system of algebraic equations, to be resolved numerically by Newton-Raphson method.

Here, the model and the associated methods of numerical resolution are validated for the example of esterification of methanol. This archetype non-electrolytic system permits an interesting analysis of reaction impact on mass transfer, especially near the phase interface. The numerical resolution of the present model by Newton-Raphson method provides a fast and quadratic convergence in less than ten iterations.

The simulations show that the impact of reactions at chemical equilibrium and that of kinetically controlled reactions with high kinetics on mass transfer is relatively similar. Moreover, Fick's law is less adapted for multicomponent mixtures where some abnormalities such as counter-diffusion take place.

The present model will also be applied to reactive separation units with electrolytic solutions such as the multicomponent absorption of acid-gases in amine electrolytic solvents. Calculations will be compared with experimental data obtained with a small pilot plant which is under construction.

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