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# Non equilibrium model and experimental validation for reactive distillation

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## Abstract

Firstly, a non equilibrium model is developed in order to simulate non ideal multi-component reactive separation processes. This model is characterised by mass and energy transfer description completed up by hydrodynamics consideration based on the film theory model. The Maxwell Stefan approach is used for the description of mass transfer without restrictive hypotheses. Moreover, there are no restrictive hypotheses about the type and localisation of the chemical reactions. Secondly, the numerical analyse of this model end in the setting up of a sure and stable strategy, specially to the differentiation index and the initialisation coherence. Thirdly, an experimental apparatus is set up in order to validate the numerical results. It represents a section of a packing distillation column fed by two fully controlled flows. The experiments were performed for the homogeneously catalysed esterification of acid acetic and methanol to produce methyl acetate and water. Several runs have been realised by varying the flow rates and compositions of the feeds, as well as the concentration of catalyst. For each one, the simulation results are in good agreement with the vapour composition and the liquid temperature profile, without any parameter adjustment. In addition, the need of taking into account reaction contribution in the diffusional layers is clearly proofed.

## 1.Introduction

The reactive distillation processes which combine reaction and gas liquid separation are of increasing interest for scientific investigation and industrial application. Nowadays, simulation and design of multi component reactive distillation is carried out using the non equilibrium stage model (NEQ model) due to the limitation of conventional equilibrium stage efficiency calculations for equilibrium model (Lee & Dudukovic (1998), Baur & al. (2000), Taylor & Krishna (1993), and Wesselingh (1997)). So, the NEQ model is developed by numerous authors. But there is a lack of experimental data in order to validate the model. Some input/output measurements are available but they provide little information about the behaviour inside the column. With this in mind, our paper is focus on the NEQ models and experimental validation.

The first part deals with our non equilibrium model; focused on the diffusional layer near the interface, where complete multi component reactive mass and heat transfer is described. The numeric resolution, avoid the bootstrap problem, is discussed in the second part. Finally, our experimental pilot and the different experiments to validate the model are presented in the last part.

## 2. Nonequilibrium model theory

A schematic representation of the non equilibrium model (NEQ) is shown in Fig.1. This NEQ stage may represent a tray or section of packing. It is assumed that the bulk of both vapour and liquid phase are perfectly mixed and that the resistance to mass and heat transfer are located in two thin films at the liquid/vapour interface (film theory, Krishna & Standard, 1976 ; Krishna, 1977).

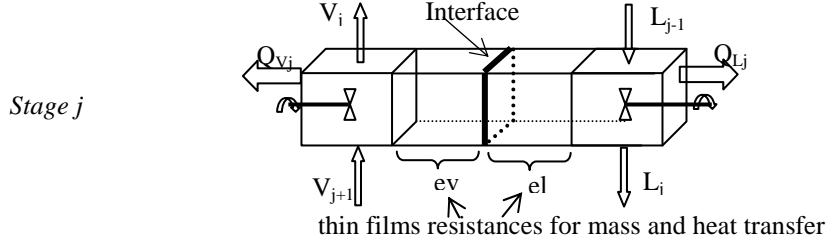


Figure 1 : The nonequilibrium model

### 2.1. Bulk equations

The stage equations are the traditional equations based on mass balances and energy balances in the bulk phase for each stage (see Taylor & Krishna (1993)). These equations take into account reactions, and there are no restrictive hypotheses as to the nature and the localisation of the chemical reactions. The bulk variables (composition, molar flux, temperature, energy flux) are different to the interface variables. The temperature of the vapour and the liquid phases are not assumed to be equal. The entire column represented as a sequence of such stages.

### 2.2. Interface equation

The interface equations link the two phases. Physical equilibrium is assumed at the vapour liquid interface for each component. Moreover, the mass and energy transfer fluxes through the interface should be continuous.

### 2.3. Mass and heat transfer

A novel model is used to compute heat and mass transfer through the diffusion layer considered in the film theory. Indeed, the fluid is considered as an n component reactive non ideal mixture. The balance equations for simultaneous heat and mass transfer are written in steady state, taking into account the reactions.

For mass transfer, the Maxwell Stefan diffusion law is used, in a novel formulation. Neither the diffusion coefficients, nor the molar flux due to the reaction, are considered to be constant. The complete formulation for mass transfer for n non ideal components is :

$$\text{Mass transfer continuity (1) : } -\frac{\partial N_i}{\partial z} + \sum_{j=1}^{\text{NRC}} v_{ij} R_j + \sum_{j=1}^{\text{NRE}} v_{ij}' \xi_j = 0 \quad \text{for } i \text{ from } 1 \text{ to } n$$

$$\text{Maxwell Stefan diffusion law (2) : } \sum_{j=1}^n \left( \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T,P} \frac{\partial x_i}{\partial z} = -\sum_{j=1}^n \frac{(x_i N_j - x_j N_i)}{c_t D_{ij}}$$

for  $i$  from 1 to  $n$

$$\text{Equilibrium equation (3) : } K_j = \prod_{i=1}^n a_i^{\alpha_{ij}} \quad \text{for } j \text{ from } 1 \text{ to } \text{NRE}$$

In our model, a n component formulation is proposed without using the summation equation. This choice is discussed in a previous paper (Rouzineau et al, 2001).

No assumption is made on the type or the number of reactions, thus they can be controlled by kinetics or instantaneously equilibrium. So, in addition, the mass transfer rate change due to the chemical reaction.

For the heat transfer, the *Dufour* and *Soret* effects are neglected and the diffusion heat rate is evaluated by *Fourier's* law.

### 3.Numeric resolution

The numeric resolution has been achieved in two steps. First of all, the system due to the mass and heat transfer in the diffusion layer (DAE system) is solved by a DAE integration based on Gear method (Le Lann, 1998). With this integration, we obtained the molar and energy fluxes and the compositions in the diffusional layer. To efficiently use a DAE integrator there are two main problems to overcome. First of all, a robust procedure leading to a coherent initial state (ie. all algebraic equations must be satisfied) before starting the integration has to be used. And secondly, an automatic substitution procedure is used to reduce the number of mass balances in order to take into account the chemical equilibrium constraints and to reduce the differentiation index to 1. This resolution has been described in a previous paper (Rouzineau et al, 2001). The initial values are the interface values.

Secondly, the general balances in both phases and at the interface leads to a system of differential and algebraic equations with boundary conditions at each end. So a discretisation method is used and the resulting algebraic system is solved by a traditional *Newton's* method. This general balances use values resulting from the integration of the equations in the diffusional layer.

### 4.Experimental validation

An experimental pilot has been developed to have comparison with simulation results.

#### 4.1.Materials

The glass column consist of four packed section with glass rashig rings. The totally packing height is about one meter and the column diameter is 8 cm. This column has no reboiler and no reflux. It represent the reactive section where the top liquid flow and bottom vapour flow are totally controlled. The top liquid flow is pre-heated and a dry evaporator generate the bottom vapor flow (see figure 2). Vapour sample and liquid temperature can be measured on each packing section. The operational variables such as feed flow rate, feed temperature, and column temperature profile are controlled by a process control unit.

#### 4.2.Experiments

The experiments were performed for the homogeneously catalysed esterification of acid acetic and methanol to produce methyl acetate and water. Sulphuric acid is chosen as homogeneous catalyst. This catalyst is feed by the shower ⑨. Five experiments have been realised by changing the flow rates (range from 4.34 kg/h to 8.35 kg/h for liquid feed and range from 2.89 kg/h to 6.34 kg/h for vapour feed) and compositions of the feed, as well as the concentration of catalyst, in order to modify the rate of reaction. For each run, the partial and global mass balance are tested in order to validate the measurements..

### 4.3.Simulation

Calculations were made for the above systems with our non equilibrium model. The thermodynamics data specification are provided by DECHEMA and UNIQUAC model is used. The reaction is considered like a reaction controlled by kinetics and the rate constant is given by a study in our laboratory. It depends of the quantity of catalyst. So the expression is :  $r = 333.3[H^+] \exp\left(\frac{-E_a}{RT}\right) \left[ C_{Ac\acute{e}tate} C_{Eau} - \frac{C_{Acide} C_{M\acute{e}thanol}}{K_e} \right]$  with  $[H^+]$  in ml/l<sub>solution</sub>

The estimation of the film thickness is obtained from the average values for the binary mass transfer and diffusion coefficient, estimated by traditional correlation (Onda (1968) correlation for the mass transfer coefficient, Fuller and Wilke Chang correlation for the vapour and liquid diffusion coefficient)

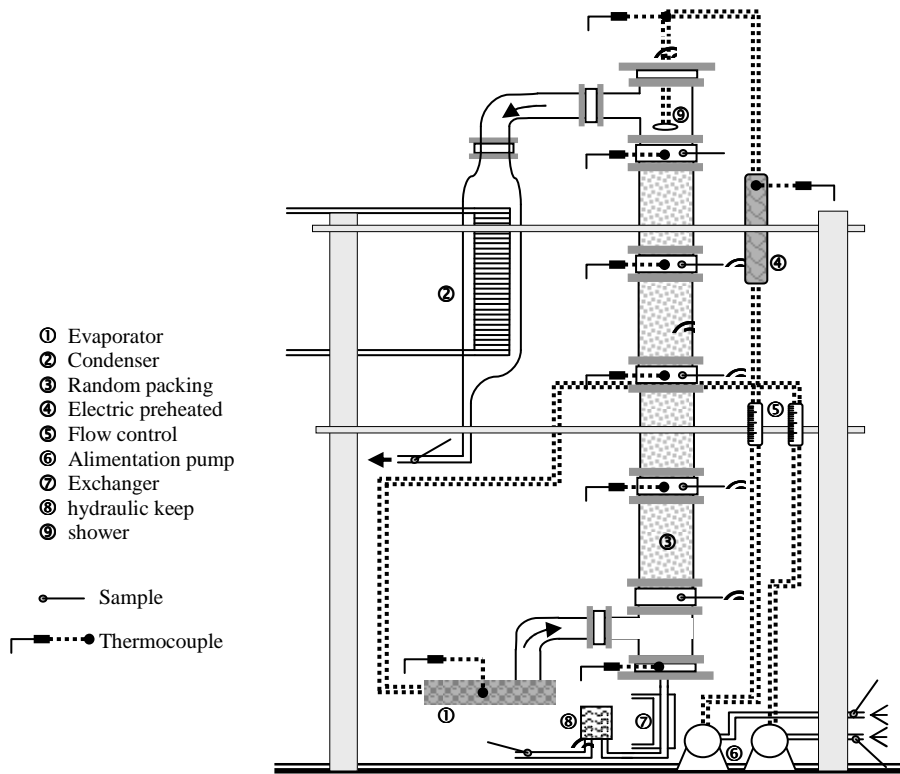


Figure 2: Experimental pilot plant

### 4.4.Results and exploitation

For each run, the experimental and calculate values of outputs (flow rates, concentrations), the vapour composition and liquid temperature profiles are compared; a good agreement is systematically observed without need of parameter adjustment. For illustration, one run is detailed. The liquid feed is water and acid acetic (0.76 mass) mixture with a flow of 4.34 kg/hr, and the vapour feed is pure methanol with a flow of 2.89 kg/hr. The flow of the catalyst is about 32g/hr. The conversion of Acetic Acid is about 26%, so the reaction is notified and the concentration gradient are important along the column height. The non equilibrium model show a quite good accordance to the experiment, with the consideration of measurement error (figure 3 shows compositions profiles along the column for one run and for simulation).

An other simulation is done without taking into account reaction contribution in the diffusional layers. The profile compared with experimental and simulated with reaction in the film are shown in figure 4. It is clear that the results are different, so the importance of taking into account the reaction in the diffusional film is underlined. And faster the reaction is greater the gap between this two cases is.

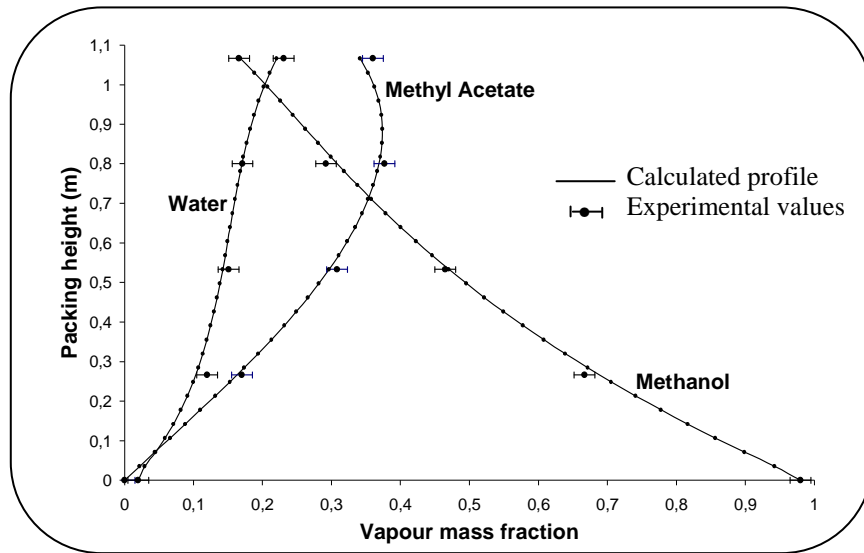


Figure 3 : Experimental and calculated composition profile

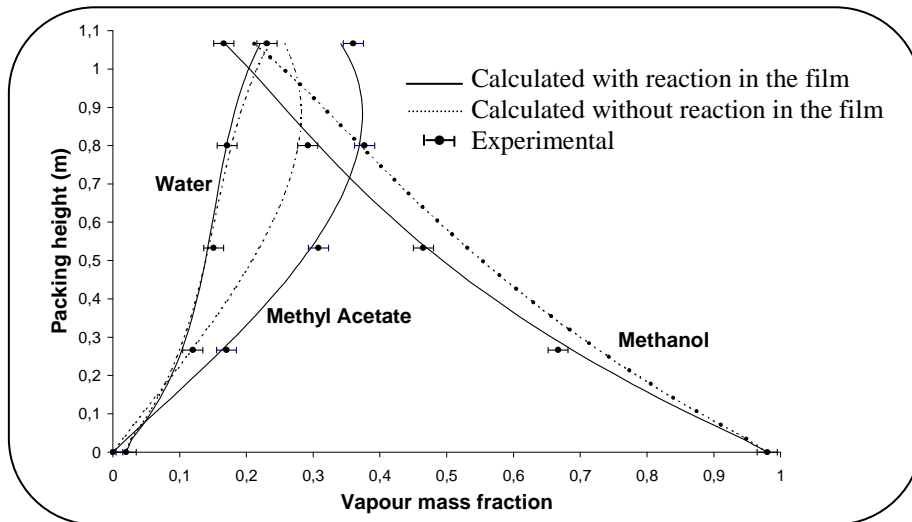


Figure 4 : Composition profile with and without reaction in the film

## 5. Conclusion

We have developed a non equilibrium model for multi component reactive separation techniques. This model is solved numerically by a sure and stable strategy. The

originalities of this model are the Maxwell Stefan formulation which is solved in this complete formulation and the absence of restrictive assumptions concerning the reaction. To validate the model, an experimental pilot has been developed. It is a part of column where inlet flux are controlled, and local accurate temperatures and compositions profiles are measured. For each experiments, which concern the production of methyl acetate, the results of steady state simulation are in good agreement with the experimental data and demonstrate the importance to take into account the reaction in the diffusional layer. So, the non equilibrium model seems to be a well adapted tool for the simulation, design and optimisation of reactive distillation.

## Nomenclature

$a_i$	Activity component i
$c_t$	Total concentration ( $\text{mol}/\text{m}^3$ )
$D_{ij}$	Maxwell Stefan binaries diffusion coefficient i-j ( $\text{m}^2/\text{s}$ )
$E_a$	Activation energy = 10000 cal/mol
$K_e$	equilibrium constant for esterification = 5.2
$K_j$	Equilibrium constant for equilibrium reaction j
$N_i$	Molar flux component i ( $\text{mol}/\text{m}^2/\text{s}$ )
n	Number of constituents
NRE	Number of equilibrium reactions
NRC	Number of control reactions
$R_j$	Rate of reaction j ( $\text{mol}/\text{m}^2/\text{s}$ )
R	constant perfect gas = 1.989 cal/mol
r	reaction rate of esterification ( $\text{mol}/\text{l}/\text{s}$ )
$x_i$	Molar fraction component i
z	Space coordinate (m)
$\gamma_i$	Activity coefficient component i
$\nu_{ij}$	Stoichiometric coefficients of component i for control reactions j
$\nu_{ij}$	Stoichiometric coefficients of component i for equilibrium reactions control j
$\alpha_{ij}$	Order of component i in equilibrium reaction j
$\xi_j$	Enhancement of equilibrium reaction j ( $\text{mol}/\text{m}^2/\text{s}$ )

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