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# NON-EQUILIBRIUM MODEL AND EXPERIMENTAL VALIDATION FOR REACTIVE DISTILLATION

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Firstly, a non-equilibrium model is implemented in order to simulate non-ideal multi-component reactive separation processes. This model is characterised by mass and energy transfer description and is completed up by considering hydrodynamics using 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 analysis of this model ends in setting up a sure and stable strategy, especially 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 etherification 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 the catalyst. For each one, the simulation results are in good agreement with the vapour composition and the liquid temperature profile, without any parameter adjustments. In addition, the need of taking into account the reaction contribution in the diffusional layers is clearly shown.

## Introduction

The reactive distillation processes, which combine reaction and gas liquid separation, are of an increasing interest for scientific investigations and industrial applications. Simulation and design of this process is usually carried out by using the equilibrium stage model. The limitation of conventional equilibrium stage efficiency calculations is discussed by Lee & Dudukovic [1], Baur & al. [2], Taylor & Krishna [3], and Wesselingh [4]. These authors assume that the generalised non-equilibrium model should be preferred for the simulation of a column for reactive distillation to the equilibrium model, because the accurate prediction of individual Murphee tray efficiencies (or HEPT for packing) is very difficult in case of the simultaneous multi-component separation and reaction. Moreover, they outlined the limitations of the equilibrium stage modelling, especially with respect to the realisation of multiple steady states phenomena [5]. But the complexity of the non-equilibrium model pushes some teams to make restrictive assumptions to solve the generated equations. Indeed, the analysis of the models suggested in the literature shows differences concerning the writing of the model and its resolution (see Table 1).

A complete model must not, for mixing together the transfer and energy transfer, make any restrictive assumption on the relations of Maxwell-Stefan and must consider the equilibrium and controlled reaction in the phase and film, like the Gorak A. and Kenig E.Y. approach. Our model is

*Table 1 :* Different approaches for the non equilibrium model

| **Authors** | **University** | **Hydrodynamic model** | **Reactions in the film** | **Type of reactions** | **Maxwell-Stefan Resolution** | **Heat transfer** |
|---|---|---|---|---|---|---|
| **Taylor R.**<br>**Krishna R.** | Holland<br>*Amsterdam*<br>*Postdam* | Film theory + Cell model | YES | Controlled | Numerical | YES |
| **Lee J.H**<br>**Dudukovic M.P.** | USA<br>*Washington* | Film theory | NO | Controlled | Analytical | YES |
| **Pagani G.**<br>**Bianchi G.** | Italy<br>*Novara* | Film theory | YES | Controlled and equilibrium | Numerical | NO |
| **Kenig E.Y.**<br>**Gorak A.** | Germany<br>*Dortmund* | Film theory | YES | Controlled and equilibrium | Numerical | YES |

implemented in the same way except for the numerical resolution (see paragraph 3.2). Compared to this complete approach, Taylor R. and Krishna R. [6] do not consider the instantaneous equilibrium reaction. Lee J.H. and Dudukovic M.P. [1] do not take into account the reaction on the film. Or, Pagani G. and Bianchi G. [7] neglect the heat transfer. Moreover, the type of resolution carried out by some authors can generate uncertainties about the precision of the results without a large investigation, such as the linearisation of film.

Experimental validation of the non-equilibrium model was also carried out by various authors [7,8,9,10,11]. Nevertheless, accurate experimental work on reactive distillation is necessary. Indeed, on the articles, it is difficult to have the complete parameter of the model to reproduce these experiments by simulation, like diffusion coefficients, all internal column characteristics ( hold up, specific area,…), kinetic (often depending on the catalyst quantity but is not described like such) or error estimation of analysis measurement. Moreover, the experimental results are not available as data but only presented on graphs. Lastly, many parameters must be measured along the column in order to get a pilot process of reactive distillation. Too many times, the measurements taken on the pilots are confined to input and output data, as mentioned by Taylor R. and Krishna R. [6] in their conclusion of the review on modelling reactive distillation : "...there is need for more experimental work with the express purpose of model validation. In such process studies, parameters need to be measured along the height of RD columns. Too often measurements are confined to feed and product stream conditions. Such data cannot serve as a reliable discriminant of computer-based process models."

The objectives of our study are thus to propose a model without any restrictive assumption but with a reliable and powerful resolution, as well as to develop an experimental pilot for validation.

Thus, this article is divided into three parts. The first part is dedicated to the writing of the non-equilibrium model. First of all the column is described from a macroscopic point of view where it is focused on the interface vicinity to quantify the various transfers between phases. The numerical resolution of the model equations is also briefly exposed in this part. The second part deals with the experimental pilot and the reasons of the material choice. Its design features and its settings are also evoked. The various measurement techniques are thoroughly described and the operational protocols are specified. The experimental validation is the final topic. The numerical results of the model are compared with the experimental values resulting from the pilot of the laboratory for reactive multi-components mixtures.

## Non-equilibrium model theory

Some limits must be fixed to define the limits of our investigation. The implemented model can be applied to any fluid-fluid contactor in which a two-phase transfer takes place. However, this work is focused on reactive distillation and absorption, for which a liquid phase and a vapour phase are in contact. The study is carried out in a steady state and the mixture is considered as a non-ideal multi-component mixture. The reactions can be multiples. There is no assumption concerning the nature and the localisation of the reactions; they can be considered as being instantaneously in equilibrium or controlled by kinetics, and can be slow, therefore they would take place primarily in the bulk of the phases or can be fast, therefore they would take place primarily in the diffusional layer.

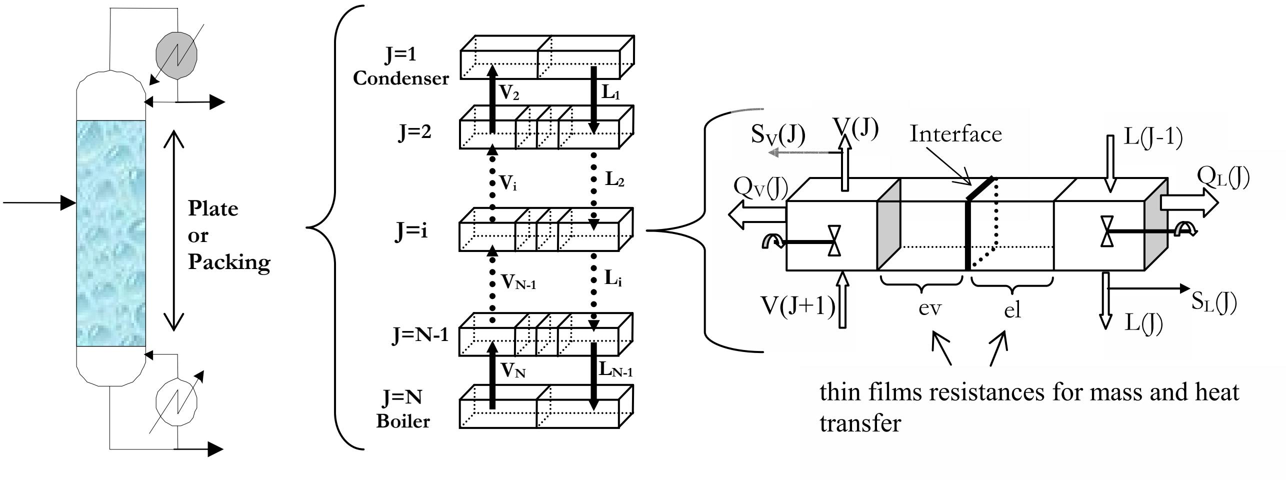

*Figure 1 :* Non equilibrium model

## Column level model

First of all, the "column" model is described, with two kinds of equations: bulk equations and interface equations.

### *Bulk equations*

The stage equations are the traditional equations based on mass balances and energy balances in the bulk phase for each stage [3]. These equations take into account the reactions, and there are no restrictive hypotheses regarding 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 modelling leads to a system of algebraic equations. J represents the stage number.

*Energy balance for vapour and liquid phase*

$$L(J-1).H_L(J-1)-\left(L(J)+S_L(J)\right).H_L(J)+$$
$$+E_L(J)+F_L(J).H_L^F(J)-Q_L(J)=0$$

$$V(J+1).H_V(J+1)-\left(V(J)+S_V(J)\right).H_V(J)+$$
$$+E_V(J)+F_V(J).H_V^F(J)-Q_V(J)=0$$

*Partial mass balance for vapour and liquid phase for the component i (i $\in$ [1,n])*

$$L(J-1).X(i,J-1)-\left(L(J)+S_L(J)\right).X(i,J)+$$
$$+N_L(i,J)+F_L(J).ZF_L(i,J)+\sum_{k=1}^{NRC}\upsilon_{Ik}r_{Ik}=0$$

$$V(J+1).Y(i,J+1)-\left(V(J)+S_V(J)\right).Y(i,J)+$$
$$+N_V(i,J)+F_V(J).ZF_V(i,J)=0$$

### *Interface equation*

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

*Energy fluxes conservation*

$$E_L^I(J)+E_V^I(J)=0$$

*Summation equation for the liquid and vapour*

$$\sum_{i=1}^{n} X^{I}(i,J) = 1$$

$$\sum_{i=1}^{n} Y^{I}(i,J) = 1$$

*Equilibrium equations*

$$Y^{I}(i,J) - KI_{eq}.X^{I}(i,J) = 0 \qquad i \in [1,n]$$

*Mass flux conservation*

$$N_L^{I}(i,J) + N_V^{I}(i,J) = 0 \qquad i \in [1,n]$$

*Chemical equilibrium*

$$mKeq_j \prod_{i=1}^{n} A_i^{\alpha_{ij}^R} - \prod_{i=1}^{n} A_i^{\alpha_{ij}^P} = 0 \qquad i \in [1,n]$$

## Diffusional layer model

A complete model is used to compute heat and mass transfer through the diffusion layer considered in the film theory [11].

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. Neither the diffusion coefficients nor the molar flux are considered to be constant due to the reaction. The complete formulation for mass transfer for n non-ideal components is:

Mass transfer continuity **(1)** :

$$-\frac{\partial N_i}{\partial z} + \sum_{j=1}^{NRC} \upsilon_{ij} R_j + \sum_{j=1}^{NRE} \upsilon_{ij}^{'} \xi_j = 0 \qquad i \in [1,n]$$

Maxwell Stephan diffusion law **(2)**:

$$\sum_{j=1}^{n} \left( \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j}_{T,P} \right) \frac{\partial x_j}{\partial z} = -\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\left(x_i N_j - x_j N_i\right)}{c_t D_{ij}} \qquad i \in [1,n]$$

Equilibrium equation **(3)** :

$$mKeq_j \prod_{i=1}^{n} A_i^{\alpha_{ij}^R} - \prod_{i=1}^{n} A_i^{\alpha_{ij}^P} = 0 \quad j \in [1,NRE]$$

The dimension of system **(I)** is 2n+NRE

In a traditional model, only n-1 equations of **(2)** are conserved because of equation dependence. Indeed, equation **(4)** is obtained by summing the n terms in equation **(2)**:

$$\sum_{i=1}^{n} \left( 1 + x_i \frac{\partial \ln \gamma_i}{\partial x_j}_{T,P} \right) \frac{\partial x_1}{\partial z} + \sum_{i=1}^{n} \left( 1 + x_i \frac{\partial \ln \gamma_i}{\partial x_2}_{T,P} \right) \frac{\partial x_2}{\partial z} + \\ + \ldots + \sum_{i=1}^{n} \left( 1 + x_i \frac{\partial \ln \gamma_i}{\partial x_n}_{T,P} \right) \frac{\partial x_n}{\partial z} = -\sum_{i=1}^{n} \sum_{j=1}^{n} \frac{\left(x_i N_j - x_j N_i\right)}{c_t D_{ij}} \qquad \textbf{(4)}$$

With the Gibbs Duhem relation $\sum_{i=1}^{n} x_i \frac{\partial \ln \gamma_i}{\partial x_j} = 0$ and the coefficient symmetry $D_{ij}=D_{ji}$, equation **(4)** becomes: $\sum_{i=1}^{n} \frac{\partial x_i}{\partial z} = 0$ **(5)** which is the differential form of equation 6 $\sum_{i=1}^{n} x_i = 1$ **(6)**.

In our model, the n components formulation is conserved because equation (6) is never written. This formulation is a great advantage; the molar fluxes are needed because they appear in the material balance. With the n components formulation, molar fluxes in a fixed reference are directly derived; we do not need other information [3] unlike the traditional models do.

No assumption is made about the kind or the number of reactions, thus they can be controlled by kinetics or instantaneously equilibrium. In addition, the mass transfer rate changes 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.

*Heat transfer continuity*

$$\frac{dE}{dz} = 0 \qquad \textbf{(7)}$$

*Energy definition*

$$E = -\lambda \nabla T + \sum_{i=1}^{n} N_i H_i \qquad \textbf{(8)}$$

The diffusional layer model is formed by equations (1),(2),(3),(7) and (8).

### *Numeric resolution*

The complete model consists of partial and algebraic equations and we can find different resolution methods in the literature. Lee J.H. and Dudukovic M.P. [1] write an approximate analytical solution for the diffusional layer model described by Maxwell Stefan diffusion. Discretisation is used to write the bulk phase equations with the set of model equation, Newton's method and homotopy continuation are used. The homotopy-continuation method was found superior to the Newton-Raphson method in guaranteeing the desired solution for the non-equilibrium model. But this kind of approach is not acceptable for the complete model without assumptions.

Gorak A. [12,13] and Taylor R. [14] suggest that in order to obtain a numerical solution of such a problem, discretisation in regard to the axial (column height) and normal (film thickness) co-ordinates should be carried out. With this kind of resolution, a step discretisation analysis in the film is needed. Indeed, several discretisations should be tested for the determination of the required number of film grid points. These number segments depend on the reaction kinetic rate. Moreover, the segment width should be varied to take into account the large variable profiles and to optimise time calculation and numerical convergence. In our case, this problem is avoided. Even if the discretisation in regard to the axial is used, the diffusional layer model equations are solved by integration based on the Gear method extended by Petzold L. R. [15] to DAE systems. With this numerical tool the integration step and method order are automatically adjusted.

So, the numeric resolution was achieved in two steps according to the model. This resolution was thoroughly described in a previous article [11].

*Resolution of the diffusional layer model*

The diffusional layer model equations (DAE system) are solved by a DAE integration based on the Gear method and implemented by Le Lann J.M. [16]. The integration of system DAE is made from the interface to the bulk by using interface variables as boundary conditions (molar compositions, mass and energy fluxes, temperature). The outcomes are: the molar and energy fluxes, temperature and the compositions in the diffusional layer. In order to use a DAE integrator effectively there are two main numerical problems to overcome:

*Initialisation procedure (Figure 2)*

First of all, a hardy procedure leading to a coherent initial state (i.e. all algebraic equations must be satisfied at z=0) before starting the integration has to be used. The algebraic equations are the chemical equilibrium equations (eq3). The boundary values which must thus check these equations are the molar fractions and enhancement of equilibrium reaction. This calculation procedure is used to evaluate these boundary variables if the equilibrium reactions are present in the film. If not, the diffusional layer model consists of a pure differential system without any consistency problems of the boundary values.

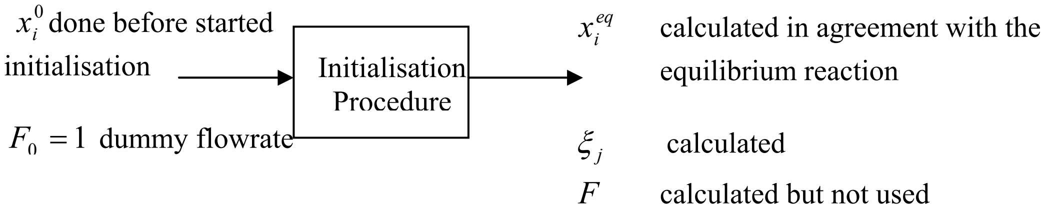

*Figure 2 :* Consistancy of boundary values

Our procedure is based on the transformation of a set of fraction $x^0$ in a set of fraction $x^{eq}$ satisfying equation (3). To perform this calculation the following system is solved:

$$F_0 x_i^0 - F x_i^{eq} + \sum_{j}^{NRE} \upsilon'_{ij} \xi_j = 0 \qquad i \in [1,n] \qquad \textbf{(9)}$$

$$K_j = \prod_{i=1}^{n} {x^{eq}_i}^{\alpha_{ij}} \qquad j \in [1,NRE] \qquad \textbf{(10)}$$

$$1 - \sum_{j=1}^{n} x_j^{eq} = 0 \qquad \textbf{(11)}$$

Then, at z=0, $x^{eq}$ are used as boundary values.

*Index reduction*

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 also to reduce the differentiation index to 1 (see Annex).

### *Resolution of the column level model*

Equations of the column level model lead to a system of differential and algebraic equations with boundary conditions at each end. Discretisation method is used and the resulting algebraic system is solved by *Newton*'s method. Those general balances use the values resulting from the integration of the diffusional level model equations.

## Results

A Fortran code was implemented in the ProSim Plus™ simulator. This simulation software is able to give results in terms of profiles along the column of various variables such as the molar compositions, temperatures and flow-rates.

## Experimental validation

An experimental pilot plant was developed in order to validate the simulation results.

## Materials

The glass column consists of four packed sections with glass raschig rings. The total packing height is about one meter and the column diameter is 8 cm. This column has no boiler and no reflux. It represents the reactive section where the top liquid flow and bottom vapour flow are totally controlled. The experimental pilot plant is shown in Figure 3. The top liquid flow is pre-heated close to its bubble temperature by an electric preheater ④ and a dry evaporator ① (power 8 kW) generates the bottom vapour flow (see Figure 3). A vapour sample and the liquid temperature can be measured at each end of the packing sections. The vapour sampling is done via a gutter placed on the lower part of a Teflon support. This shelters a capillary needle from the down flowing liquid. For the liquid temperature measurement, a gutter is placed on the higher part so that it can collect the falling liquid where a thermocouple of type J is placed. Therefore, the liquid temperature and vapour compositions are measured along the column.

The samples analysis is done by gas chromatography with an FID detector. The absolute error generated by this method is ± 0.015 of the mass fractions. The measurement error on the liquid temperature is evaluated according to the type of thermocouple and the calibration with $\Delta T = \pm(0.0025 * T + 0.2)$.

The operational variables such as the feed flow rate, the feed temperature, and the column temperature profile are measured by a process control unit.

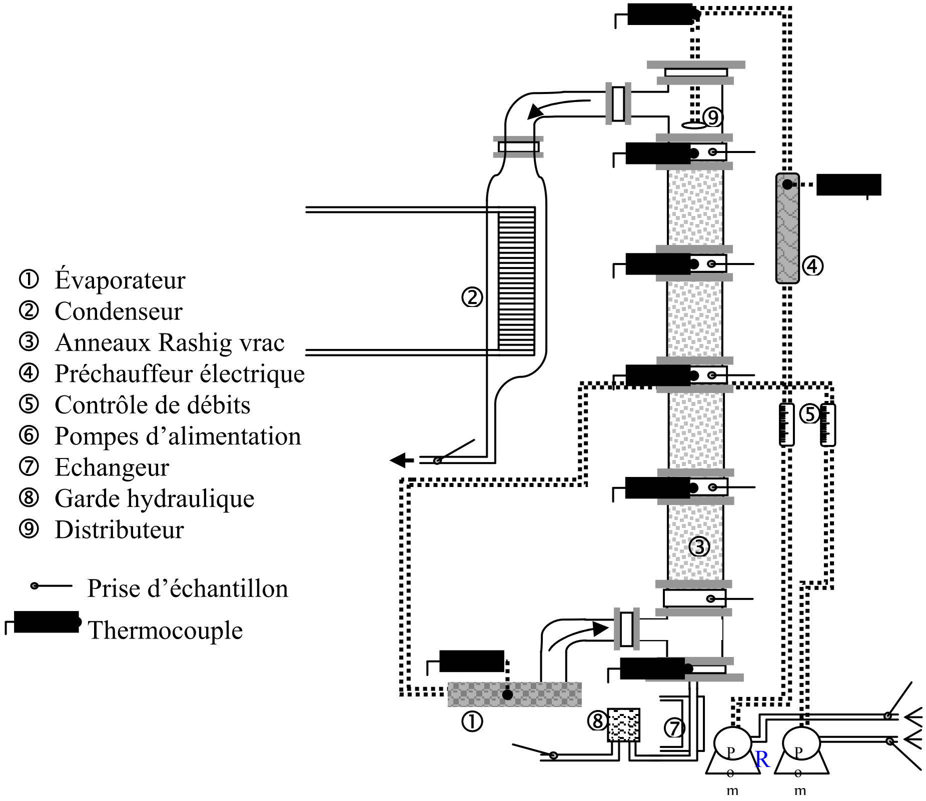

*Figure 3 :* Experimental pilot plant

## Experiments

*Specific experiment for heat losses determination*

In spite of the heat insulator around the column, heat losses are inevitable. It is significant to evaluate them for simulation. The evaporator is supplied by the pump ⑦ of constant water flow. The column is not fed at the head of the column. If there is no loss, all the vapour generated by the evaporator must be recovered at the head of the column to condenser ②**.** On the other hand, in case of heat losses, part of the vapour condenses in the column and is recovered in the bottom of the column. This residue flow-rate corresponds to the heat losses which can be evaluated at 250 Watts.

The experiments were performed for the homogeneously catalysed etherification of acid acetic and methanol to produce methyl acetate and water. Sulphuric acid is chosen as the homogeneous catalyst. The catalyst is fed into the column through the liquid feed in the top of the column with a shower ⑨. Four experiments have been carried out by changing the flow rates (ranging from 4.34 kg/h to 8.35 kg/h for the liquid feed and from 2.89 kg/h to 6.34 kg/h for the vapour feed), as well as the concentration of catalyst, in order to modify the rate of the reaction. Experiment 5 is carried out to represent a section of the simulated column. The different conditions of the experiments are shown in Table 2. For each run, the partial and global mass balance is tested in order to validate the consistency of the measurements.

*Table 2 :* Operating conditions for the five experiments

| | | **Experiments** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **Exp.1** | | **Exp. 2** | | **Exp.3** | | **Exp.4** | | **Exp. 5** | |
| | | Liquid | Vapour | Liquid | Vapour | Liquid | Vapour | Liquid | Vapour | Liquid | Vapour |
| **Flow** (kg/hr) | | 4.84 | 5.63 | 4.34 | 2.89 | 4.34 | 2.89 | 8.35 | 6.34 | 7.74 | 6.129 |
| **Mass Fraction** | Acid | 0.760 | 0.000 | 0.760 | 0.000 | 0.760 | 0.000 | 0.760 | 0.000 | 0.519 | 0.043 |
| | MeOh | 0.000 | 0.980 | 0.000 | 0.980 | 0.000 | 0.980 | 0.000 | 0.980 | 0.095 | 0.587 |
| | Ester | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.121 | 0.249 |
| | $H_2O$ | 0.240 | 0.020 | 0.240 | 0.020 | 0.240 | 0.020 | 0.240 | 0.020 | 0.265 | 0.121 |
| $k_0[H^+]$ (l/mol/s) | | 400 | | 550 | | 1100 | | 1100 | | 200 | |

## Simulation

Simulations were made by our non-equilibrium model. The thermodynamics data specifications are provided by the DECHEMA database. The UNIQUAC model is used to represent the non-ideal liquid phase. Dimerisation is considered for the vapour phase. The reaction is considered as a reaction controlled by kinetics and the rate constant depends on the catalyst quantity [ref]:

$$r = k_0\left[H^+\right]\exp\left(\frac{-E_a}{RT}\right)\left[C_{Acétate}C_{Eau} - \frac{C_{Acide}C_{Méthanol}}{K_e}\right]$$

with $[H^+]$ in ml/$l_{solution}$ and $E_a$=10000 cal/mol , $k_0$=333.3 l/mol/s, $K_e$=5.2 The value for the different experiments are given in Table 2.

The film thickness estimation is obtained from the average values for the binary mass transfer and diffusion coefficient, estimated by the traditional correlation (Table 3). The different parameters for the simulation can be found in Table 3.

## Results and exploitation

For each run, the experimental and calculated values of the outputs (flow rates, concentrations), the vapour composition and the liquid temperature profiles are compared. A good agreement is systematically seen without the need of any

*Table 3 :* Simulation parameters

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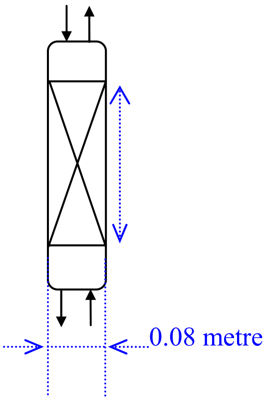
**Mixture:**
Number of components: 4
Components: Acetic Acid – Methanol – Methyl Acetate – Water
Thermodynamic Model:
*Heat of vaporization: Clausius - Clapeyron*
*Equation of state: Association (polymerisation)*
*Vapour tension: Antoine*
*Activity coefficient: UNIQUAC*
*Binary interaction parameters (cal/mol)*

| | | |
|---|---|---|
| 1 2 | -23.094 | 30.803 |
| 1 3 | -449.604 | 747.594 |
| 1.4 | -383.266 | 601.033 |
| 2 3 | -115.025 | 676.392 |
| 2.4 | 54.337 | 47.106 |
| 3.4 | 789.996 | 117.211 |



**Reaction:**
Number of reaction: 2
Reaction: Acetic Acid + Methanol → Methyl Acetate + Water **1**
Methyl Acetate + Water → Acetic Acid + Methanol **2**

**Kinetics:**

$$r_1 = 333.33[H^+]exp\left(\frac{-10000}{RT}\right)*C_{Acetique}C_{Méthanol}$$ r mol/l/s and R cal/mol/K

$$r_2 = 64.10[H^+]exp\left(\frac{-10000}{RT}\right)*C_{Acétate}C_{Eau}$$ $[H^+]$ ml for litre of solution

**Type of column:**
Column: Raschig packing
Diameter: 0.08 m
Numeric discretisation: 30 non equilibrium stages
Losses thermal: 250 W in liquid phase

**Correlations :**

| | |
|---|---|
| Mass transfer coefficients : | Onda [17] |
| Binary coefficients diffusion : | Fuller for vapour phase<br>Wilke et Chang for the liquid phase |
| Hold-up : | Mersmann et Deixler (Kister, [18]) |
| Inter facial area : | Onda [17] |

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*Table 4 :* Experimental measurement and mass balances

| **Global mass balance (kg/h)** | liquid | vapour | Total |
|---|---|---|---|
| input | 4.34 | 2.89 | 7.23 |
| output | 5.00 | 2.20 | 7.20 |
| | | Absolute error | 0.03 |
| | | **Relative error** | **0.41%** |

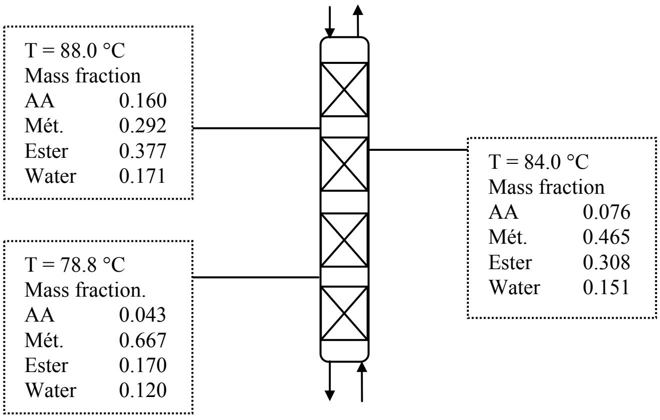
⬚ Experimental measurement

| **Partial mass balance** | **Acid Acetic** | **Methanol** | **Methyl Acetate** | **Water** | *Temperature* **°C** | |
|---|---|---|---|---|---|---|
| **Liquid input** | | | | | 95.1 | |
| Mass fraction | 0.760 | 0.000 | 0.000 | 0.240 | | |
| Partial flow rate g/h | 3298.400 | 0.000 | 0.000 | 1041.600 | | |
| Partial flow rate mol/h | 54.973 | 0.000 | 0.000 | 57.867 | | |
| **Vapour input** | | | | | | |
| Mass fraction | 0.000 | 0.980 | 0.000 | 0.020 | | |
| Partial flow rate g/h | 0.000 | 2832.200 | 0.000 | 57.800 | | |
| Partial flow rate mol/h | 0.000 | 88.506 | 0.000 | 3.211 | | |
| **Liquid output** | | | | | 73.9 | |
| Mass fraction | 0.371 | 0.408 | 0.054 | 0.167 | | |
| Partial flow rate g/h | 1855.000 | 2040.000 | 270.000 | 835.000 | | |
| Partial flow rate mol/h | 30.917 | 63.750 | 3.649 | 46.389 | | |
| **Vapour output** | | | | | | |
| Mass fraction | 0.243 | 0.166 | 0.360 | 0.231 | | |
| Partial flow rate g/h | 534.600 | 365.757 | 792.110 | 507.533 | | |
| Partial flow rate mol/h | 8.910 | 11.430 | 10.704 | 28.196 | | |
| input output difference | | | | | | |
| Molar | -15.147 | -13.326 | 14.353 | 13.507 | Molar error | **Relative error / reactive** |
| average | -14.237 | | 13.930 | | -0.306 | **2.15%** |

| Conversion Acetic Acid | 26.11% |
|---|---|

| **Global energy balance** | Liquid | Vapour | Total |
|---|---|---|---|
| Input (Watt) | -11411.23 | -5178.82 | -16590.05 |
| Output (Watt) | -10697.72 | -6166.67 | -16864.39 |
| | | Difference | -274.34 |
| | | Energy lost (Watt) | 250.00 |
| | | Absolute error | -39.34 |
| | | Relative error | 8.87% |

**Vapour mass fraction and liquid temperature measerement aloung the column**



parameter adjustment. The comparison between the predicted and measured mass fraction for all five experiments is provided in Figure 4. The maximum absolute deviation is 0.026 and the average absolute deviation is 0.0096. This is satisfactory considering the measurement experimental error, which is more or less 0.015 of these mass fractions.

For illustration, experiment 3 is analysed. The liquid feed is water and acetic acid (0.76 mass) mixture with a flow rate of 4.34 kg/hr, and the vapour feed is pure methanol with a flow rate of 2.89 kg/hr. The flow rate of the catalyst is about 32g/hr. The following Table 4 shows the different experimental measurements and the different mass and energy balances. The global mass balance error for this experiment is 0.4 % and 2.1 % for the partial mass balance. The output vapour temperature is not measured, so the energy balance can only be carried out by admitting that the top vapour exit is dew. These results guarantee us the quality of the experiment as well as the control of the operating conditions. The error on this energy balance is 8.87 %.

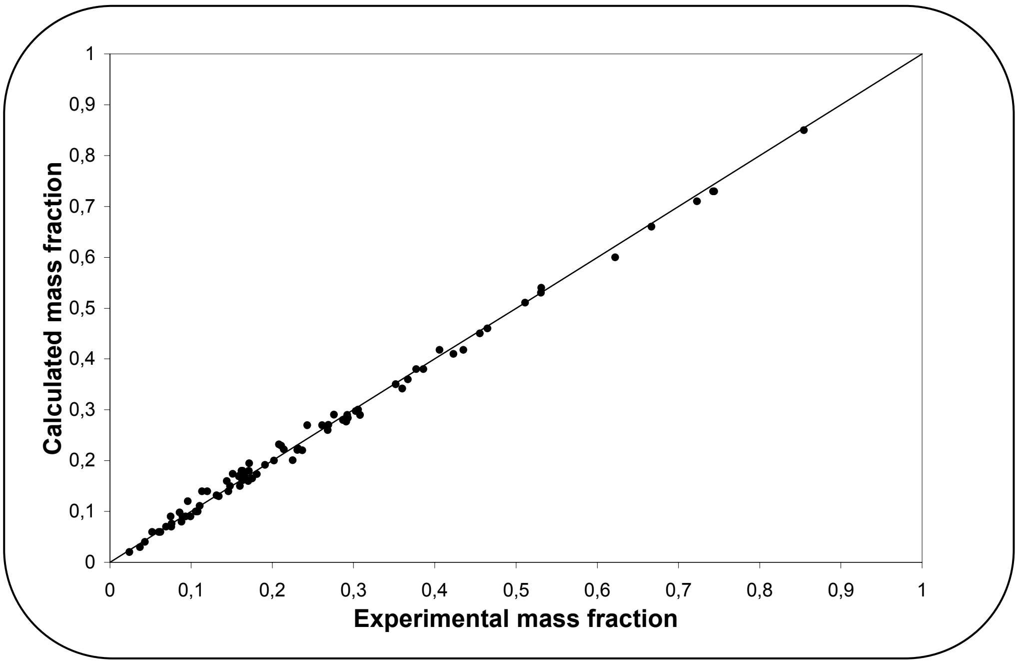


*Figure 4 :* Predicted versus experimental mass fraction along the column for the five experiments

The conversion of acetic acid is about 26%, therefore the reaction is shown and the concentration gradients are important along the column height. Figure 5 shows composition profiles along the column for run 3 and for the simulation. The non-equilibrium model shows quite good agreement with the experiment, considering the measurement error.

A maximum deviation of 1°C appears between the experimental and calculated profiles of the liquid temperature (Figure 6). This remains acceptable considering the precision of the thermocouples. The simulation also gives acceptable results in terms of output flow rates (average deviation of 2%).

An other simulation is done without taking into account the reaction results in the diffusional layers. The profiles are compared with the experimental and simulated results with reaction in the film, as shown in Figure 7. It is clear that the results are different, so the importance of taking into account the reaction in the diffusional film is obvious. Furthermore, the faster the reaction is, the greater the gap is between these two cases.

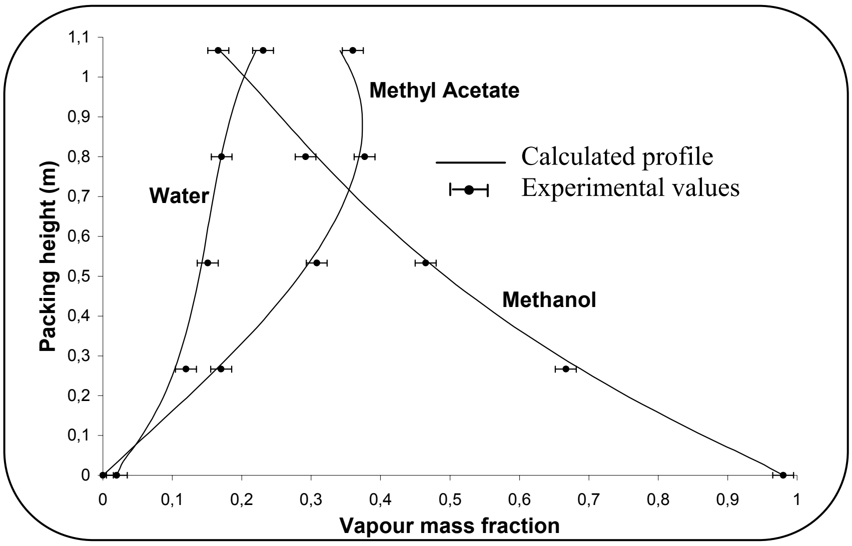


*Figure 5 :* Experimental and calculated composition profile

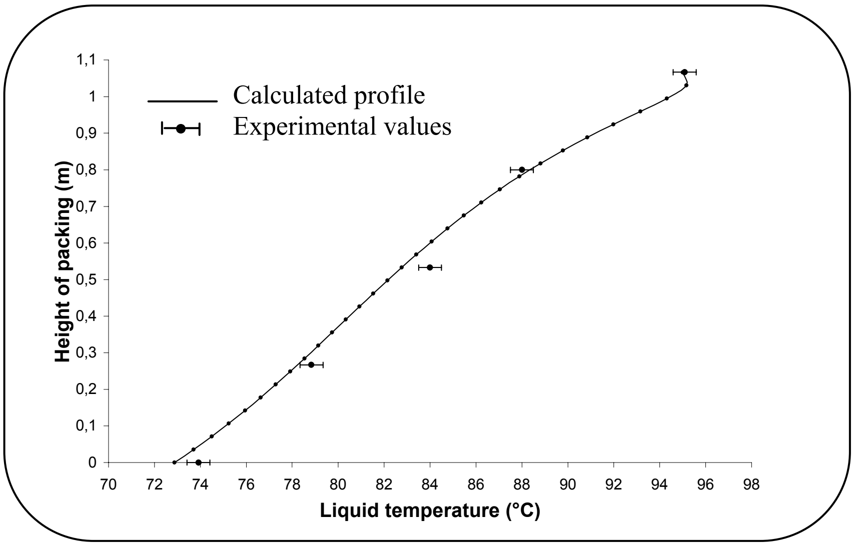


*Figure 6 :* Experimental and calculated liquid temperature profile

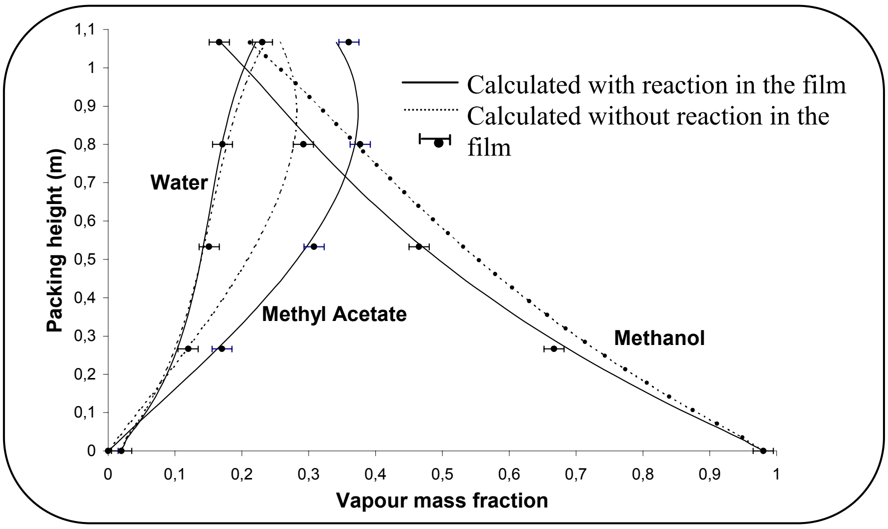


*Figure 7 :* Composition profile with and without reaction in the film

## Conclusion

We have developed a non-equilibrium model for multi-component reactive separation techniques. This model is solved numerically by a hardy strategy. The originalities of this model are the Maxwell Stefan formulation, which is solved in the 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 the column where inlet fluxes are controlled, and local temperatures and compositions profiles are measured accurately. For each experiment, which concerns the production of methyl acetate, the results of the steady state simulation are in good agreement with the experimental data and demonstrate the importance of taking into account the reaction in the diffusionnal layer. Therefore, the non-equilibrium model seems to be a well-adapted tool for the simulation, design and optimisation of reactive distillation.

## SYMBOLS

| | |
|---|---|
| $\lambda$ | Thermal conductivity of the mixture (cal/m/K/hr) |
| $\nu'_{ij}$ | Stœchiometric coefficients of component i for equilibrium reactions control j |
| $\gamma_i$ | Activity coefficient component i |
| $\alpha_{ij}$ | Order of component i in equilibrium reaction j |
| $\delta_{ij}$ | Kroneker symbol |
| $\nu_{ij}$ | Stœchiometric coefficients of component i for control reactions j |
| $\xi_j$ | Enhancement of equilibrium reaction j (mol/m$^2$/hr) |
| $A_i$ | Activity component i |
| $c_t$ | Total concentration (mol/m$^3$) |
| $D_{ij}$ | Maxwell Stefan binaries diffusion coefficient i-j (m$^2$/hr) |
| E | Density of energy flux (cal/m$^2$/hr) |
| E(J) | Energy flux of stage J (cal/hr) |
| E(J) | Energy flux of stage J (cal/hr) |
| $E_a$ | Activation energy |
| el | Liquid film thickness (m) |
| ev | Vapour film thickness (m) |
| F(J) | Molar flow rate of the stage alimentation J (mol/hr) |
| H(J) | Molar enthalpy of mixture of stage J (cal/mol) |
| $H^F(J)$ | Molar enthalpy of mixture alimentation of stage J (cal/mol) |
| $K_e$ | equilibrium constant for etherification |
| $Keq_j$ | Chemical equilibrium constant of the equilibrium reaction j |
| $K_j$ | Equilibrium constant for equilibrium reaction j |
| L(J) | Liquid molar flow rate for the stage J (mol/hr) |
| n | Number of components |
| N(i,J) | Molar flux of component i of the stage J (mol/hr) |
| $N_i$ | Molar flux component i (mol/m$^2$/hr) |
| NRC | Number of control reactions |
| NRE | Number of equilibrium reactions |
| Q(J) | Heat release of stage J (cal/hr) |
| R | constant perfect gas = 1.989 cal/mol |
| r | reaction rate of estherification (mol/l/hr) |
| $r_{ik}$ | Rate of reaction for the constituent i in the reaction k (mol/hr) |
| $R_j$ | Rate of reaction j (mol/m$^3$/hr) |
| S(J) | Output flow rate of side stream of stage J (mol/hr) |
| T | Temperature (K) |
| V(J) | Vapour molar flowrate for the stage J (mol/hr) |
| X(i,J) | Liquid molar fraction of component i of stage J |
| $x_i$ | Molar fraction component i |
| Y(i,J) | Vapour molar fraction of component i of stage J |
| z | Space coordinate (m) |
| | ZF(i,J) Molar fraction of component i for the feed of stage J |

## INDEX

L : Variable concerning the liquid phase

V : Variable concerning the vapour phase

## EXPONENT

I : Variable concerning the interface

P : Products

R: Reactive

## Annex:

Substitution procedure 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.

The equation **(1)** of mass balance is:

$$-\frac{\partial N_i}{\partial z}+\sum_{j=1}^{NRC}\upsilon_{ij}R_j+\sum_{j=1}^{NRE}\upsilon'_{ij}\xi_j=0$$

With the matrix formulation:

$$\begin{pmatrix} -1 & & 0 \\ & \ddots & \\ 0 & & -1 \end{pmatrix}\begin{pmatrix}\frac{dN_1}{dz}\\ \cdot \\ \cdot \\ \frac{dN_n}{dz}\end{pmatrix}+\begin{pmatrix}\upsilon_{1,1}\cdots\cdots\cdots\upsilon_{1,NRC}\\ \cdot \\ \cdot \\ \cdot \\ \upsilon_{n,1}\cdots\cdots\cdots\upsilon_{n,NRC}\end{pmatrix}\begin{pmatrix}R_1\\ \cdot \\ \cdot \\ \cdot \\ R_{NRC}\end{pmatrix}+\begin{pmatrix}\upsilon'_{1,1}\cdots\cdots\cdots\upsilon'_{1,NRE}\\ \cdot \\ \cdot \\ \cdot \\ \upsilon'_{n,1}\cdots\cdots\cdots\upsilon'_{n,NRE}\end{pmatrix}\begin{pmatrix}\xi_1\\ \cdot \\ \cdot \\ \cdot \\ \xi_{NRE}\end{pmatrix}=0$$

With a pivot strategy, we can obtain equation **(1)** with this formulation:

$$\begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \ddots & 0 \\ \vdots & \ddots & \ddots & 0 \\ \vdots & & 0 & 1 \\ \vdots & & \vdots & a_1 \\ 0 & \cdots & 0 & a_{n-NRE} \end{pmatrix}\begin{pmatrix}\xi_1\\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \xi_{NRE}\end{pmatrix}=(A)\begin{pmatrix}\frac{dN_1}{dz}\\ \cdot \\ \cdot \\ \cdot \\ \frac{dN_n}{dz}\end{pmatrix}+(B)\begin{pmatrix}R_1\\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ R_{NRC}\end{pmatrix}$$

So, the advancement of the equilibrium reaction becomes explicit, and we can substitute their value in the other equation. So, the 2n+NRE dimensional system **(1)** is reduced to a 2n dimensional system. Moreover, the differentiation index of the DAE system is reduced to 1.

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