

Nonequilibrium models for a multi component reactive distillation column

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Abstract

A nonequilibrium model for multi component separation processes, including liquid or/and gaze reactions, was developed in this paper. This model include the finite mass transfer rate describe by *Maxwell Stephan* equations. It is assumed that the bulk of both the vapour and liquid are perfectly mixed and that the resistance to mass and heat transfer are located in two films at the liquid/vapour interface (film theory). There are no restrictive hypotheses as to the nature and the localisation of the chemical reactions. This models was solved numerically to simulate numerous example in the ProSim™ simulator. So we can do the comparison between the equilibrium stage models (EQ), in which the thermodynamic equilibrium is considered between the two phase, and the nonequilibrium model (NEQ). With reasonable value of Murphee efficiencies the simulation using EQ model is almost equivalent to the NEQ model. It seems to be difficult to estimate efficiencies for multi component reactive mixture, but some NEQ model requirements are equally delicate to predict, like the film thickness for the mass and heat transfer. An other simulation show that the model should use the Maxwell Stephan formulation for mass transfer even if Fick formulation give a good prediction.

1 Introduction

Reactive distillation is a unit operation of great industrial interest. It can reduce capital and production costs by combining two units into once, and this units can improved the selectivity, the heat integration, the conversion, etc... Simulation and design of multi component reactive distillation usually is carried out using the equilibrium stage model. The limitation of conventional equilibrium stage efficiency calculations is discussed by Lee & Dudukovic (1998), Baur & al. (2000), Taylor & Krishna (1993), and Wesselingh (1997). This author assume that the generalised nonequilibrium 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 the case of simultaneous multi component separation and reactions. The non equilibrium model seems to be better because the model takes into account the technique characteristics of the column (type of plate , of packing...), so more near reality. But the non equilibrium model needs model requirements which can be as difficult to find as an efficiency.

In this paper, we describe our non equilibrium model in the first part, and define the model requirements. The second objective of this study is to compare the conventional equilibrium model, including a predicted tray efficiency, and the non equilibrium model. Finally, the traditional Fick approach for the mass transfer is compared to the Maxwell Stephan approach.

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 the vapour and liquid are perfectly mixed and that the resistance to mass and heat transfer are located in two films at the liquid/vapour interface (film theory, Krishna & Standard, 1976 ; Krishna, 1977).

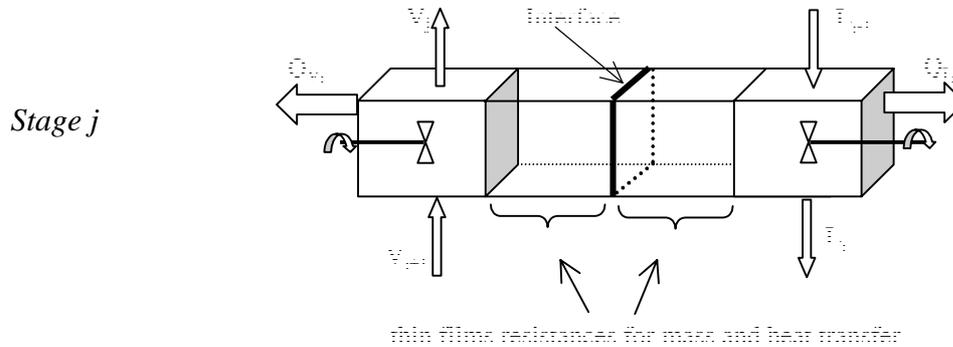


Figure 1 : The nonequilibrium model

Stage equations

The stage equations are the traditional equation of the mass balances and energy balances in the bulk phase for each stage (see Taylor & Krishna (1993)). These equations take account of reactions, and there are no restrictive hypotheses as to the nature and the localisation of the chemical reactions. The bulk variables (compositions, molar fluxes, temperatures, energy fluxes) are different from the interface variables. The temperature of the vapor and the liquid phases are not assumed to be equal.

The entire column is taken to consist of a sequence of such stages. We consider an N stage column where stage 1 can be a total or partial condenser and stage N a reboiler.

The modelling leads to a system of differential and algebraic equations, which are solved after discretisation using *Newton's* method.

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 account of the reactions.

The traditional model uses the Fick Formulation :

$$N_i = -c_i D_{im} \frac{\partial x_i}{\partial z} + x_i N_t \quad 0 \leq z \leq e$$

Unfortunately, this description is limited to two component mixtures because it does not take the interactions between the different components into account; moreover the non ideality for the driving force is not considered.

So, 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 n non ideal components is :

$$\sum_{j=1}^n \left(\delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \right) \frac{\partial x_i}{\partial z} = - \sum_{j=1}^n \frac{(x_i N_j - x_j N_i)}{c_i D_{ij}} \quad 0 \leq z \leq e$$

No assumption is made on the type or the number of reactions, thus they can be controlled by kinetics or 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.

These steady state differential equations are solved by a DAE integrator which allow conserving the n Maxwell Stephan formulation.

The complete model can used as well as the Maxwell Stephan formulation as the Fick Formulation. This allow different simulations with the two law to compare (see result paragraph 3).

Interface equation

The interface equations link the two phases. We assume physical equilibrium at the vapor liquid interface for each component. Moreover, the mass and energy transfer rate through the interface should be continuous.

Model requirements

The complete model needs more requirements because of the more complete description of the equipment. For physical chemical properties, the model is linked to the Prophy™ thermodynamic library and integrated into the ProSim™ simulator. The properties (thermal conductivity, densities, viscosity, surface tension, etc...) is calculated by this library. Moreover, for the NEQ model, the column equipment must be described. : the column diameter, plate or packing characteristics. On the other hand, for the EQ model, only the number of stages and two physical properties (vapor liquid equilibrium and enthalpies) are needed. The drawback of this model is the evaluation of the efficiencies for the plate or the HEPT for the packing column in the case of multi component reactive mixture. The NEQ model include also some delicate concepts; indeed for this model we should evaluated the vapor and liquid film thickness (el and ev, see Fig. 1), and the interfacial area. The difference model requirements between two models is shown in Fig. 2.

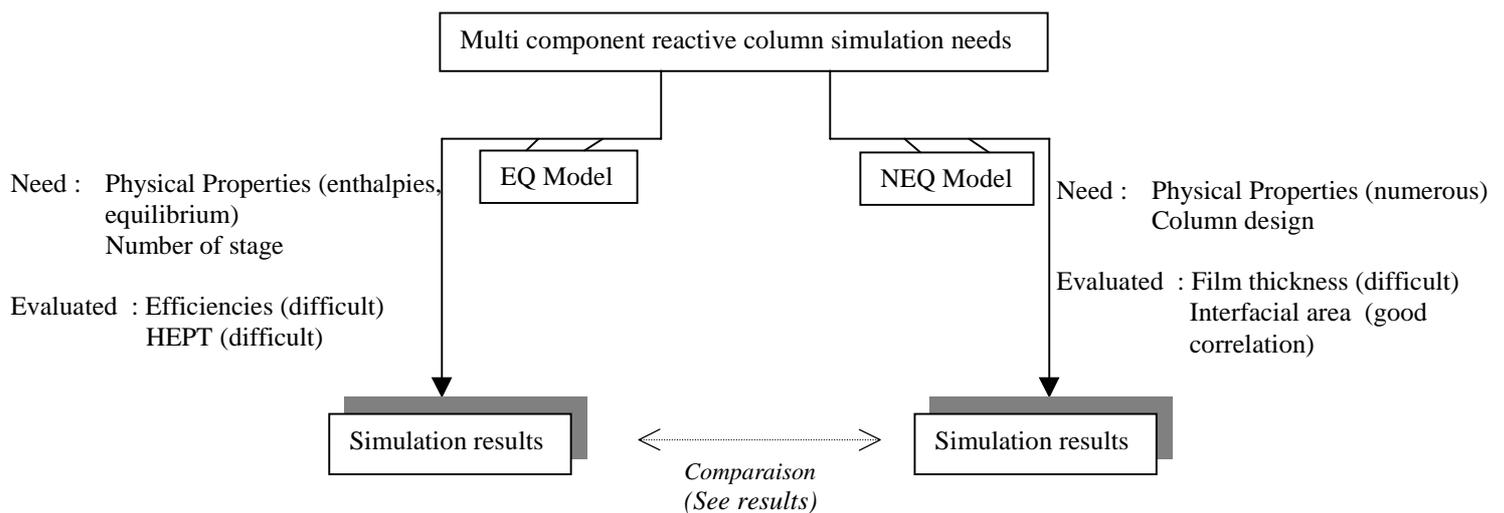


Figure 2 : Model requirements for EQ model and NEQ model

3 Simulations results

We will discuss two examples to show the non equilibrium simulation column in practice :

- Reactive distillation plate column with Acetic Acid – Water – Acetic Anhydride non ideal mixture; this example permit the comparison between EQ and NEQ model.
- Extractive distillation packing column with acetone – Methanol – Water non ideal mixture; this example show the difference between Maxwell Stephan and Fick formulation for the mass transfer.

Comparison EQ and NEQ model

Example parameters

The example is a reactive distillation where the Acetic Anhydride react with Water to obtain 2 moles of Acetic Acid. The reaction rate is given by Marek (1956).

The column has 15 sieve trays with a feed at 6. The specifications feed and operator conditions are the same than Higler & al. (1999). The binary interactions parameters (Wilson model) are given by Higler & al. (1999).

Simulations

The first simulation is the NEQ model where the vapor film thickness is fixed at 10^{-4} meters and the liquid film thickness is fixed at 10^{-5} meters. The correlation to calculate the interfacial area is the Zuiderweg Method.

To compare with EQ model , this model simulation was performed using the Murphee tray efficiencies :

- EQ simulation with Murphee efficiencies are assumed to be 1.0
- EQ simulation with Murphee efficiencies are predicted by correlation (MacFarland, 1972)
- EQ simulation with Murphee efficiencies are calculated from the results of the non equilibrium model

The correlation of MacFarland predict efficiencies ranging from 0.69 to 0.72 for Acetic Anhydride, from 0.67 to 0.83 for Water and from 0.69 to 0.99 for Acetic Acid. So, as there are one efficiency for a plate, we choose 0.7 for the simulation. The Murphee efficiencies calculated from the results of the non equilibrium model are shown in Fig. 3; ranging from 0.54 to 1.14.

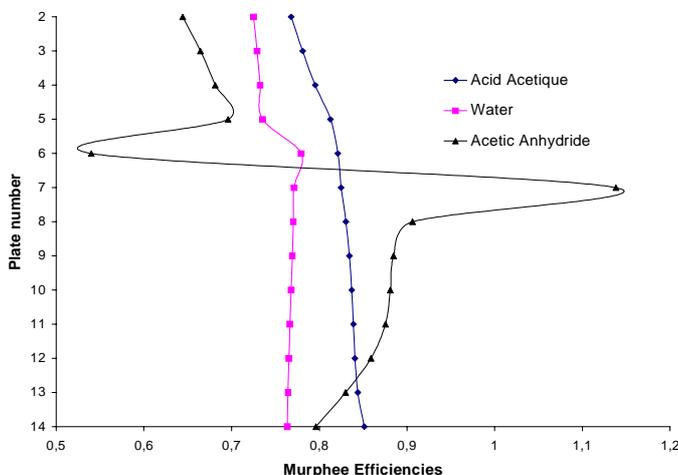


Fig.3 : Murphee efficiencies calculated from the results of the non equilibrium model.

This indicates that the conventional prediction of Murphee efficiencies from an empirical correlation may not be reliable for multicomponent reactive mixture in this case.

The Acetic Acid molar fraction profile is shown in Fig. 4 for the different simulations (the conclusion is the same for the other constituents). The EQ model profile with good prediction efficiencies (here 0.7 by Macarland) is almost similar. In this case, the prediction of EQ model is equivalent to the NEQ model.

An other simulation is effected with higher film thickness. The vapor film thickness is fixed at 10^{-3} meters and the liquid film thickness is fixed at 10^{-4} meters. This implies great mass transfer

rate. The gradients of the concentrations in the resistance film are very important. The correlation of MacFarland predict efficiencies ranging from 0.69 to 0.71 for Acetic Anhydride, from 0.70 to 0.78 for Water and from 0.73 to 0.91 for Acetic Acid. The Murphee efficiencies calculated from the results of the non equilibrium model are ranging from -1.39 to 0.73 (with average value 0.2). So, an EQ model simulation is effected with Murphee efficiencies at 0.2. The results are shown in Fig. 5. In this case the prediction of MacFarland is so far of the NEQ model. The EQ model profile with prediction efficiencies at 0.2 is almost similar. In the case with great mass transfer it seems to be difficult to predicted the efficiencies to simulate with EQ model; the traditional correlation can not be predicted the real efficiencies of the plates.

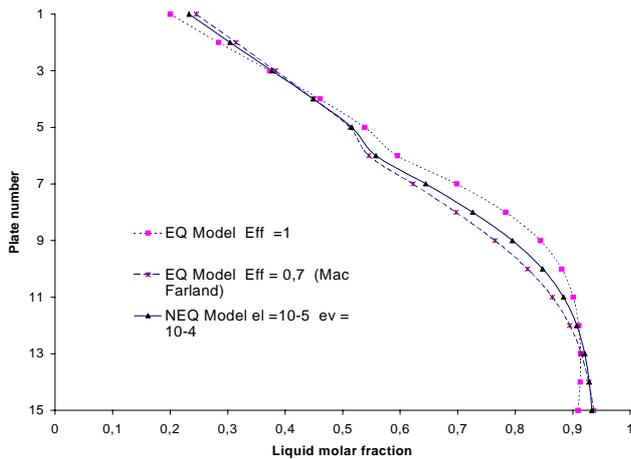


Figure 4 : Liquid Acetic Acid profile Simulation 1

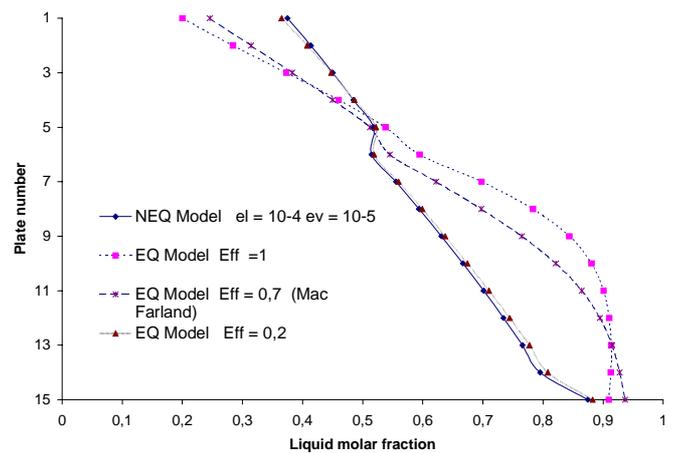


Figure 5 : Liquid Acetic Acid profile Simulation 2

However , the results of simulation 2 with $el = 10^{-4}$ and $ev = 10^{-3}$ are very different from the experimental results of Marvek (1956) and simulation results of Higler & al. (1999). The first simulation is better and seems correct; so, this example shows that the thickness of the resistance film is a sensitive parameter. Moreover, with good prediction of Murphee efficiencies, the prediction of the EQ model simulation is almost equivalent to the non equilibrium model simulation.

Description with Fick Formulation and Maxwell Stephan Formulation

Example parameters

This example is an extractive distillation of an Acetone - Methanol mixture using Water as the solvent. The column is a two height random packing column and 0.5 meters for diameters. The flow sheet and the feed alimentation are shown in Fig.6.

Simulations

Two simulations are effected with the NEQ model : with the Fick formulation and with Maxwell Stephan formulation for the mass transfer in the thin films. Vapor film thickness is fixed at 10^{-4} meters and the liquid film thickness is fixed at 10^{-5} meters. The interfacial area for the packing is calculated by Onda correlation.

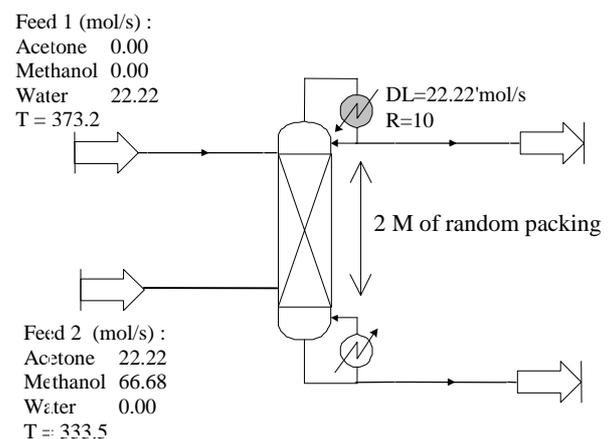


Figure 6 : Spécifications for extractive distillation

Maxwell Stephan binaries diffusion coefficients D_{ij} is calculated by Fuller correlation for the vapor and by Wilke-Chang and Vignes correlation for the liquid. Diffusion coefficients of component i in mixture m D_{im} for the Fick formulation is predicted by Blanc's law for the vapor and evaluated Perkins and Geankoplis for the liquid.

The two simulations results are shown in Figure 7. We can notice a difference between the two laws. This is due to the drawback of the Fick law :

- the interactions between Acetone Water and Methanol does not take into account
- the non ideality of mixture (here UNIQUAC data fom Taylor R. 1993) is not considered with Fick formulation

Moreover, the diffusion coefficients are different between the two formulation of mass transfer.

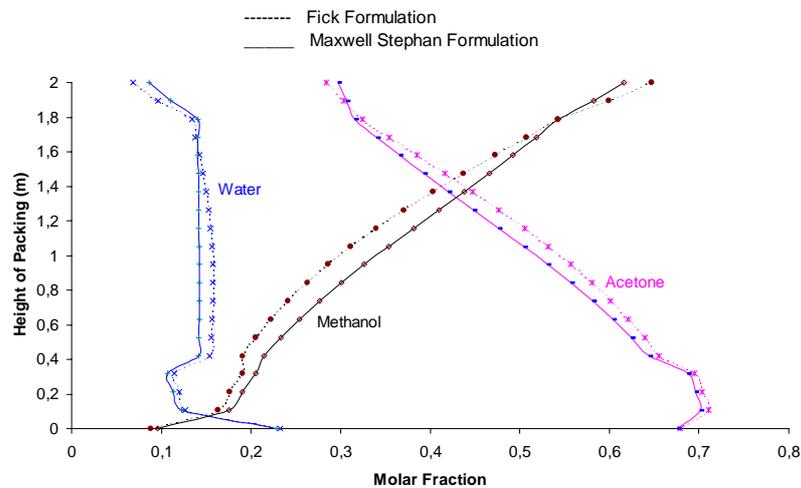


Figure 7 - Liquid phase composition profiles with Fick Formulation and Maxwell Stephan Formulation

However, the traditional Fick formulation is correct to predict the composition profile; indeed the difference with Maxwell Stephan is not very important. The real Fick formulation inconvenient is the prediction of the diffusion coefficients D_{im} which are more abstracts that Maxwell Stephan binaries diffusion coefficients D_{ij} .

4 conclusion

We have developed a non equilibrium model for multi component reactive separation techniques. This model was solved numerically and then included in the ProSim™ environment.

The originality of this model is the Maxwell Stephan formulation which is solved in this complete formulation. The non equilibrium model was tested and compared with the classical equilibrium model. We can find the same results with the EQ model, but it is difficult to estimate Murphee efficiencies for a multi component reactive mixture. NEQ model simulation is effected with Fick law and Maxwell Stephan law for the mass transfer. The classical Fick formulation can predict concentration profile but this law is not enough general for non ideal multi component mixture.

We are actually developing an experimental pilot study in order to determine the more efficient model.

Nomenclature

c_i	Molar concentration constituent i (mol/m ³)
c_t	Total concentration total (mol/m ³)
D_{im}	Diffusion coefficient of component i in mixture m (m ² /s)
D_{ij}	Maxwell Stephan diffusion coefficient binaries i - j (m ² /s)
N_i	Molar flux constituent i (mol/m ² /s)
N_t	Molar flux molar total (mol/m ² /s)
n	Number of constituents
x_i	Molar fraction constituent i
z	Space reference (m)
γ_i	Activity coefficient constituent i

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