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Reactive distillation modelling and sensitivity analysis based on NEQ Model

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Abstract

Firstly, a non-equilibrium model (or NEQ model) has implemented for multi component reactive separation processes. The mass transfer description is based on the Maxwell Stefan approach and the hydrodynamics on the film theory model. We have excluded other restrictive assumptions. The code calculation is implemented in the simulation software **P**ro**S**im Plus™. Secondly, an experimental packed reactive distillation pilot has been developed in order to obtain experimental. The experiments were performed for homogeneously catalysed esterification of acid acetic and methanol into methyl acetate and water. Five runs have been performed for which the inlet flow rate and compositions, as well as the concentration in catalyst are modified. For each run, the simulation results are in good agreement with the vapour composition and the liquid temperature profile, without any parameter adjustment.

Finally, a sensitive analysis of the NEQ model parameters has been done. It seems for the various physical parameters (e.g. the liquid and vapour film thickness, the liquid hold-up and the interfacial area), that the interfacial area is the most sensitive. For the other parameters, their sensitivity depends where the reaction and the mass transfer resistance take place. Moreover, a step discretisation analysis in regard to the axial co-ordinates shows that the type of flow inside the column could be compared to a plug flow. In addition, the need of taking into account the reaction contribution in the diffusional layers is clearly shown.

Keywords: modelling, simulation, reactive distillation, Non Equilibrium model, experimental validation, sensitivity analysis.

1. Introduction

Nowadays, simulation and design of reactive distillation are usually carried out using the non equilibrium stage model (NEQ model). Recent works have exposed the limitations of conventional equilibrium stage model (EQ model) for final design, due to the difficulties of calculation efficiencies (Lee and Dudukovic (1998), Baur et al. (2000), Taylor and Krishna (1993), and Wesselingh (1997)). NEQ models are widely developed in literature (Noeres et al. (2003), Higler et al. (1999), Pagani et al. (2001), Lee and Dudukovic (1998), Taylor and Krishna (2000), Yu et al.(1997)). Experimental validation of NEQ model has also been carried out (Noeres et al. (2003), Kenig et al. (2001), Gorak A. and Hoffmann A. (2001), Pagani et al. (2001), Higler et al. (1999)). However, the authors do not go into all details of the operating conditions.

Thus, a NEQ model has previously implemented in order to simulate a non ideal mutlicomponent reactive separation processes (Rouzineau et al. (2001,2003)).

Moreover, to validate the model, an experimental pilot plant has been developed in which a production of methyl acetate catalysed by sulphuric acid has been performed. Through these articles, the NEQ model seems a good tool for simulation, design and optimisation of reactive distillation.

Nevertheless, this model needs more parameters than EQ model due to the column internal description. The quality of the NEQ model results depend on these new parameters, generally evaluated by correlation. Consequently, a sensitivity analysis of these parameters must be carried out to ascertain the key parameters.

The first part of this article summarise the NEQ model implementation and experimental validation. The second part concerns parameters sensitivity study.

1. Non equilibrium model

1.1 Non equilibrium equation

The non equilibrium model (NEQ) is presented in details in previous papers (Rouzineau et al. (2001,2003)). The 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. 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 interface equations link the two phases. Physical equilibrium is assumed at the vapour liquid interface for each component. To compute heat and mass transfer through the diffusion layer considered in the film theory, the balance equations are written in steady state, taking into account the reactions. The fluid is considered as an n component reactive non ideal mixture. For mass transfer, the Maxwell Stefan diffusion law is used. 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 used. No assumption is made on the type or the number of reactions, thus they can be controlled by kinetics or instantaneously equilibrium. For the heat transfer, the *Dufour* and *Soret* effects are neglected and the diffusion heat rate is evaluated by *Fourier*'s law.

1.2 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. 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.

1.3 Experimental validation

An experimental pilot has been developed to have comparison with simulation results papers (Rouzineau et al. 2003)). 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. 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. 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. Five experiments have been realised by changing the flow rates and compositions of the feed, as well as the concentration of catalyst, in order to modify the rate of reaction.Calculation were made for the above systems with our non equilibrium model. 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 (see figure 2).

2. Sensitivity analysis

2.1 Methodology

In first, the values resulting from simulation in agreement with experimental values are taken as reference value. The reference value, named $X_{ref,j}$ is thus a vector which can be containing the liquid and vapour mass fractions of each component as well as the liquid and vapour temperatures, for each NEQ stage j .

Secondly, four simulations are carried out with a parameter variation of +10, 20, 30 and 50 % respectively. So, a given parameter θ is modified $\theta_{new}= \theta +\varepsilon*\theta$ with ε = 10, 20, 30 and 50 %. All other parameters are kept constant. The simulation leads to a new value of vector $X_{var,j}$. Finally, the deviation generated by the new parameter θ_{new} is calculated as an average values along the column:$\Delta X= \Sigma|X_{var,j}- X_{ref,j}|/N$ with N : NEQ stage number and j=1,N.

2.2 Physical Parameter

The sensitivity analysis concerns the liquid film thickness (el), vapour film thickness (ev), interfacial area (ae), liquid hold-up (holdup), thermal heat loss (Q). The results are represented in figure 1.

Observation

An error of plus or minus 10 to 50 % in the liquid film thickness "el" does not implies a significant change of the results and those remain in the experimental error of the mass fraction. The sensitivity is more significant on the temperatures but remains small: only a variation of 50 % generates an average deviation greater than 1 degree. The vapour film thickness "ev" is more sensitive than "el". A variation of 50 % exceed the measurement error of the experimental values. The interfacial area "ae" is the most sensitive parameter for mass fractions. A variation of only 30 % involves a deviation of 0.017 on the vapour mass fraction. 10 to 30 % hold up variations do not significantly modifies the results. Therefore, the liquid hold up is not sensitive in this example. The thermal heat loss "Q" is the less sensitive parameter.

Interpretation

In our example, the resistance of the vapor mass transfer is important, so the vapour film thickness is a sensitive. A small variation in the vapour film thickness modifies the quantity of methanol transferred in the liquid phase, which must react with the acetic acid. Logically, the conversion ratio will be modified.

The liquid film thickness and the liquid hold-up are not sensitive parameters. Indeed, the reaction takes place principally in the liquid film in the vicinity of the interface. So, the liquid film thickness variation does not change the reaction conversion ratio. Not much reaction occurs in the bulk, so the liquid hold up variation has not a significant

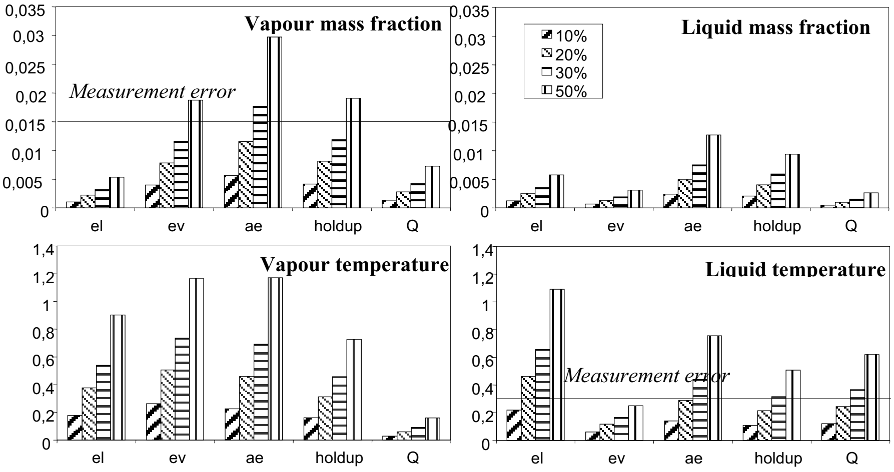

Figure 1 :Sensitivity analysis of physical parameter

impact on the reaction conversion. The location of the reaction has been confirmed by Hatta number evaluation, a value greater than 10 has been obtained for each experiments. An other proof of the reaction location has been obtained via a new simulation of the reference experiment without taking into account the reaction in the diffusional layers. The profiles are compared with the experimental and simulated results with reaction in the film, as shown in figure 2. It is clear that the results are different, so the reaction meanly takes place in the liquid film. Moreover, this example shows the importance in the model development of taking into account the reaction in the diffusional film. Furthermore, the faster the reaction is, the greater the gap between these two cases is important.

In order to achieve a sensitivity analysis in the case of slow reaction (located in the bulk) a simulation is carried out with a fictive example: on one hand, the kinetic constant is decreased to a small Hatta number (Ha<3), so the reaction occurs only in the bulk; and on the other hand the liquid hold-up is increase to have the same conversion and the same profile as the reference value. A novel sensitivity study is done in the same way. The results are presented in figure 3 (white bars in this figure are the previous sensitivity analysis). In this new situation the liquid film thickness and the liquid hold-up become more sensitive. For the others parameters (ev, ae, Q), there are no change.

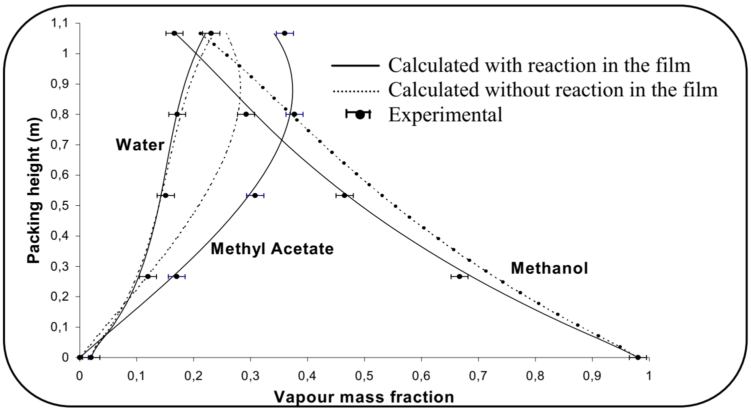

figure 2 : Composition profile with and without reaction in the film

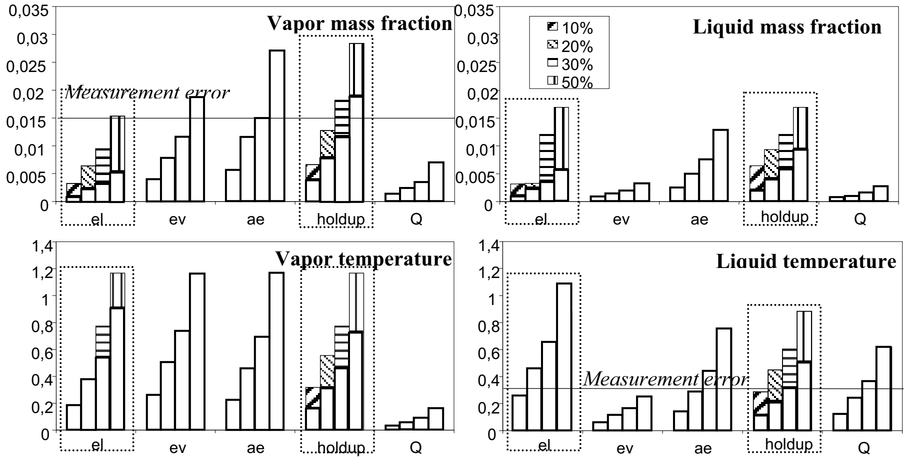

figure 3 :Sensitivity analysis of physical parameter with reaction in the bulk

2.3 Numerical parameters

In the case of packing column, a discretisation in regard to the axial co-ordinates has been carried out. When the number of steps exceeds 30 segments (figure 4), the simulation results are in agreement with experimental value and for higher value no noticeable change in the vapour mass profiles occurs. The same result is observed with the liquid temperature profile. So, with 30 steps (for an 1 meter column), the results are in agreement with the experimental values and this discretisation offers a good compromise between time calculation and the desired precision.

Moreover, this kind of results leads to the conclusion that the flow pattern looks like a plug flow. Let us underline that a discretisation analysis is regarded to normal (film thickness) co-ordinates is not necessary. Indeed the film model equations are solved by a integration based on the Gear method extended by Petzold L. R.(1982) to DAE systems. With this numerical tool the integration step and method order are automatically adjusted. If discretisation procedures are used for solving this system, then a sensitivity analysis on the number of discretisation steps in regards to the radial coordinates is needed (Kucka L. et al. (2003), Schneider R. et al. (2003), Higler A. et al. (1999b)).

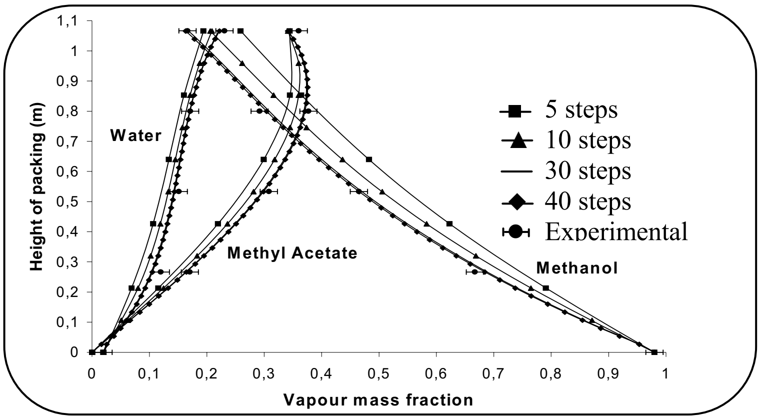

figure 4 : Vapour composition profile with different number of steps

3. Conclusion

A non equilibrium model has been implemented for multi-component reactive separation techniques. To validate the model, an experimental pilot has been developed. The results of steady state simulation are in good agreement with the experimental data. The sensitivity parameter of NEQ model depends where the reaction takes place. If the reaction is very fast and take place in the vicinity of the interface, the liquid film thickness and the liquid hold-up are not significant parameter. So, the vapour film thickness becomes the most significant parameter, after the interfacial area which remains in all case the most sensitive parameter. Only variation of 50 % on physical parameter gives more significant deviation on the simulation results. But this kind of parameters is evaluated by correlation and can involve this large error. It is therefore necessary to pay great attention to the choice of the correlation for the physical parameters and more importantly for the interfacial area.

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