1

Modelling reactive separations with very fast chemical reactions

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Abstract

The goal to be reached in this paper is to develop an effective tool for mathematical modelling of reactive distillation column including very fast chemical reactions. Concerning mass transfer near the vapour-liquid interphase, film theory was used with Fick's equation describing diffusion. It is suitable when a fast chemical reaction takes place in the film layer. Using Fick's equation leads to a system of reaction-diffusion equations in the liquid film that is standard boundary value problem.

Hatta number is being evaluated at each stage. Big differences occur between stage-values when a fast reaction sets in. Therefore a tool was used that can set a grid with non-uniform density leading to a huge savings of computational time.

Keywords

Reactive, separation, distillation, absorption, fast reaction, film model, mathematical model

1. Introduction

Mathematical modelling became inevitable part of process control, design, optimization and safety analyses. Mathematical modelling of reactive separations comes along with their implementation into technologies.

Two main approaches can appear modelling reactive distillation unit: non-equilibrium or a simpler equilibrium model. Non-equilibrium model is presented by a film theory. In non-equilibrium model, reaction can take place either in the bulk liquid or also in the liquid film, if the system is homogeneously catalysed. Reaction and diffusion in the film is described by Fick's equation resulting into a so-called reaction-diffusion equation.

2. Problem Statement, background

Keeping model as simple as possible and despite as precise as it gets leads to following assumptions:
- reaction only in liquid phase, both in bulk and film,
- constant pressure, no pressure drop along the column,
- total equilibrium condenser, equilibrium reboiler,
- ideal behaviour of gas phase, non-ideal liquid phase,
- vapour-liquid equilibrium only at the V-L interphase,
- all phases on the stage have the same temperature,
- steady state.

In non-equilibrium model, reaction is supposed to take place also in the liquid film. If the reaction is extremely fast, the film plays much more important role. To describe mass transfer in the film, a reaction-diffusion equation for each component rises. Model of the steady-state RD column then consists of nonlinear algebraic equations (NAE) describing each component's material balances and enthalpy balances of each tray; and first-order ordinary differential equations with boundary condition given in two points (BVP) describing reaction and diffusion in the liquid film.

3. Paper approach

3.1. Methodology

Mathematical model of the reactive-distillation column in steady-state operation consists of a system of strongly nonlinear algebraic equations describing bulk flows. Used solver BUNLSI [1] was imported to solve these balance equations with possibility of setting constraints on variables by user. Liquid film is described by the reaction-diffusion equation being a boundary value problem. To solve such system DBVPFD solver from IMSL Math library was used [2].

A source code in FORTRAN[©] was built to simulate this system. The algorithm is based on the two cycle loop. In the outer, balance equations are solved, the inner (reaction-diffusion equations) is called in each loop to

calculate the mass flux values to and from the liquid film, completing the balance equations (Fig.1).

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┌─────────────────────────┐        ┌─────────────────────────┐
│ Reaction and diffusion in│───────▶│  Mass flux through the  │
│  the film - FILM MODEL  │    ╲ ╱  │      interface          │
└─────────────────────────┘     ╳   └─────────────────────────┘
┌─────────────────────────┐    ╱ ╲  ┌─────────────────────────┐
│  Material and enthalpy  │───────▶│   Concentrations and    │
│ balances in the bulk flows│       │ temperatures in bulk flows│
└─────────────────────────┘        └─────────────────────────┘
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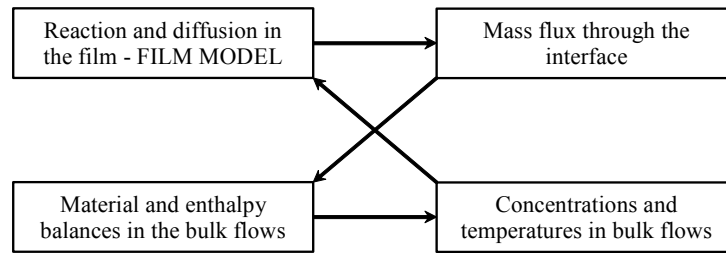
Figure 1. Scheme of algorithm structure

Built program is standalone, no further software is needed for solution. It is able to converge even with badly estimated starting values of the model variables. Estimation of the concentration profiles in the liquid film is being performed by the program, using given boundary conditions.

3.2. Case study

Studied system consists of four components taking part in a reverse chemical reaction (1):

$$A + B \leftrightarrow R + S \tag{1}$$

The physical and chemical data were set as for system of acetic acid esterification with ethanol [3], [4] with respect to following naming: *A*-acetic acid, *B*-ethanol, *R*-ethyl acetate and *S*-water. The reaction rate was gradually significantly increased to test the program and its ability to describe the film layer. Parameters characterizing mass transfer were taken from [5]. Modelled system was represented by a reactive distillation tray column with a total condenser. The reactant *A* was fed in liquid phase and the reactant *B* in gaseous phase, respective feed compositions can be seen in the Table 1. Number of trays (including reboiler) is set to 20, the liquid feed enters the column on the 5th tray and the gaseous one on the 13th (numbered from the top).

Table 1. Composition and molar flows of feeds

Tray	Feed	Molar flow (mol s^{-1})	Component molar fraction		
			A	*B*	*S*
5	liquid	1.944	0.7	-	0.3
13	gaseous	1.389	-	0.2	0.8

3.3. Results & discussions

The goal of the work was to study concentration profiles in the column, driving forces of the mass transfer, flows along the column and concentration profiles in the film. The observation criterion was either the number of final grid points in the liquid film or the *modified Hatta number* (2) reflecting the actual conditions on respective trays.

$$Ha_e^2 = \frac{\dot{\xi}_{V1,e} D_{\ell,B}}{k_\ell^2 c_{B,e}} \tag{2}$$

In which the *e* subscript represents the actual tray, $\dot{\xi}_{V1,e}$ actual direct reaction rate, $D_{\ell,B}$ a diffusion coefficient of the reactant *B* in the liquid, k_ℓ liquid-side mass transfer coefficient and $c_{B,e}$ molar concentration of the reactant *B* in the bulk liquid.

In the case, when direct reaction rate was significantly increased, the EQ model was unable to describe the behavior of the column. The processes running under such conditions are very close to those of reactive absorption. The first strong feature of built program is the non-uniformity of the calculation-grid density. Number of the grid points is controlled by the program and varies from tray to tray (Fig. 2), what makes the calculation faster and more effective. Modified Hatta number (Fig. 2) enables to see the different reaction and diffusion circumstances in the liquid film along the column. In the middle of the column, where the reaction and diffusion process in the film is most intensive the Hatta criterion rises significantly.
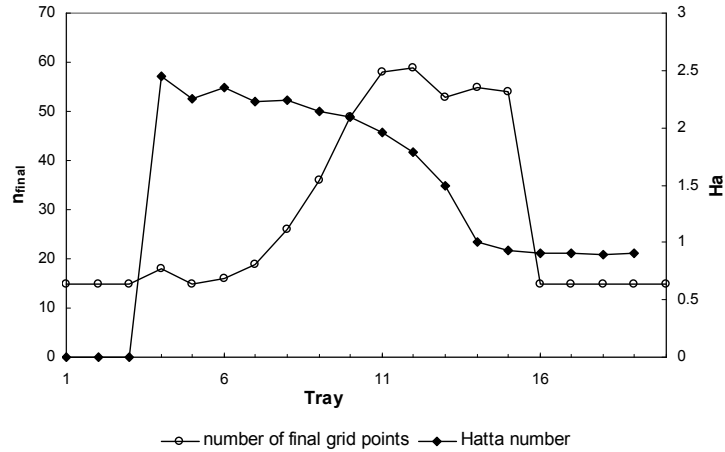

Figure 2. Hatta number and final number of grid points in the column

The most spectacular process of diffusion and reaction takes place on the feed trays (Fig. 3). The curves sketched represent the overall driving force

of the mass transfer of respective components; the positive part of diagram generally represents direction from gas to liquid phase, the negative part from liquid to gaseous phase.
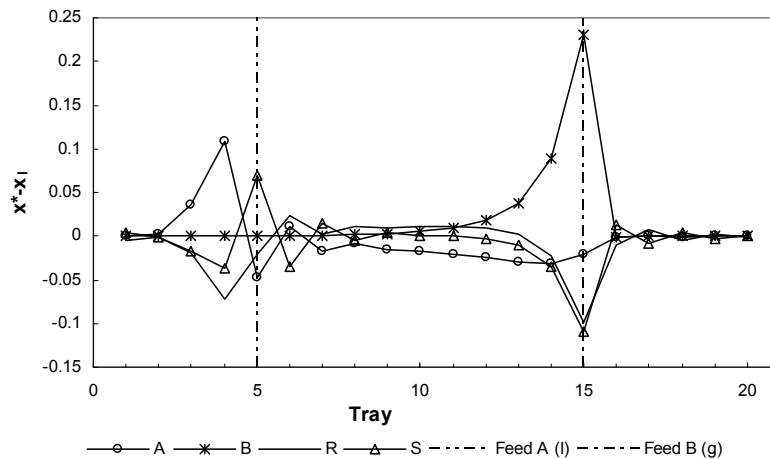

Figure 3. A liquid-side mass transfer driving force (x^* represents concentration at the interphase, x_l is concentration in the bulk liquid)
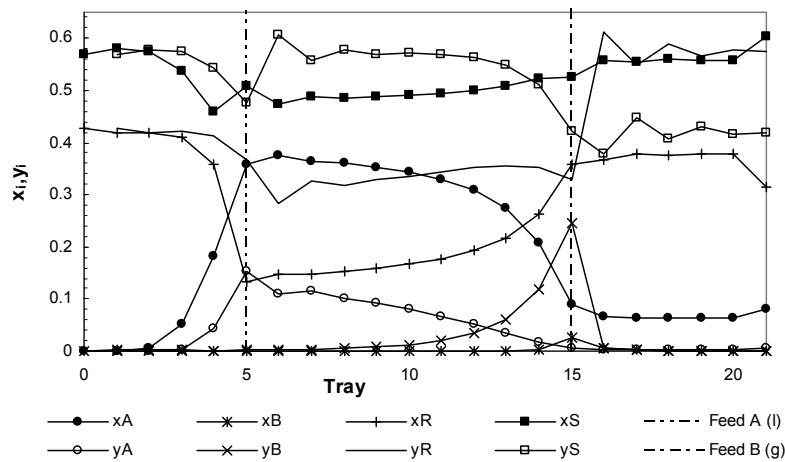

Figure 4. Concentration profiles in the bulk phases along the column (x represent component molar fraction in the liquid phase, y is component molar fraction in the gas)

Almost zero concentration of reactant *B* (Fig. 4) in bulk liquid indicates that most of it takes place in the reaction in liquid film. Despite of it, concentration

of the liquid-fed reactant *A* still falls downwards proving again hypothesis of reaction taking place in the film in preference.

4. Conclusions

The goal of this paper was to present a program that would be able to simulate processes of reactive distillation and absorption with extremely fast chemical reactions. Two models were chosen – equilibrium and non-equilibrium. In the other one, Fick's equation was used to describe reaction and diffusion in the liquid film. The column containing up to 20 trays with total condenser had been simulated. Built program proved to be both steady and robust tool for calculation in such systems. Starting values of concentration profiles in the film are set by the program alone. Program is able to converge even with bad estimation of the starting parameters. The most useful feature is the utilization of this tool for both reactive distillation and absorption.

Acknowledgements

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