Optimization parameters of the reactive separations with very fast chemical reaction

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Abstract

The goal of this work was to create a non-equilibrium mathematical model of a reactive distillation (RD) column with a fast homogeneous reaction and to adjust it in order some strong and robust solvers could be used. When modeling vapor-liquid contact, used film theory can be based either on the simple Fick's law or on Maxwell-Stefan approach. Steady state modeling leads to a system of both nonlinear algebraic equations (NAE) and second-order nonlinear differential equations with boundary condition given in two points (BVP). Within every iteration of the outer loop (solving NAE's), internal loop of BVP's had to be solved using a solver with automatically adjusted discretization grid for the spatial variable. Modified Hatta number has been introduced and was evaluated at each reactive stage of the column. The proposed algorithm proved to be a steady and robust tool. Effects of changing feed positions, feeds' ratio, number of trays in the column, and reflux ratio have been observed.

Introduction

Mathematical modeling of such complex systems requires many assumptions and proper simplification. It is inevitable to keep the model as simple as possible and as precise as possible on contrary. If a very fast homogeneously catalyzed chemical reaction occurs in the liquid phase, there have to be described phenomena of both mass transfer and chemical reaction. In this case, the Fick's law is more suitable to use and a so-called reaction-diffusion equation can be easily derived.

The majority of papers is dealing with heterogeneously catalytic reactive distillation and strongly advise using Maxwell-Stefan approach (Smejkal 2000; Taylor 2000; Smejkal 2002; Noeres 2003). Krishna and Wesselingh (Krishna 1997) and Frank et al. (Frank 1995) described simultaneous mass transfer and reaction. Numerical problems arise as reported when a fast chemical reaction takes place. In this paper, no such thing occurred because of using simple Fick's law.

Lower precision of the Fick's law compared to the MS approach can be overcome in the case of column performance optimization or safety analysis when the column parameters and performance conditions are changed in a wide range.

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Mathematical model

The presented mathematical model of reactive column is valid under following assumptions: ideal behavior of the gas phase, non-ideal behavior of the liquid phase, thermodynamic equilibrium only at the V-L interface, film theory applied, constant overall pressure in the system, steady state, all phases have the same temperature and reaction takes place only in the liquid phase. Mathematical model consists of these parts: bulk liquid phases material and enthalpy balances, liquid film balances, condenser and reboiler material and enthalpy balances.

Film model equations

A heterogeneously catalyzed reaction takes place also in the liquid film resulting in a simultaneous process of mass transfer by means of diffusion and chemical reaction. To describe such process, the diffusion can be modeled by either Fick's law or Maxwell-Stefan approach. The first mentioned is simple enough to combine it with a chemical reaction resulting into a so-called reaction-diffusion equation (1). This is not possible when following the second mentioned approach, the Maxwell-Stefan's one.

$$D_{\ell,i}\left(\frac{d^2 c_{f,i}}{dz^2}\right) = -\sum_{j=1}^{N_R} \nu_{i,j}\dot{\xi}_{V,z,j} \qquad (1)$$

With boundary conditions given in two points:

$$\begin{aligned} z &= 0 \qquad c_{f,i} = c^*_{f,i} \\ z &= \delta \qquad c_{f,i} = c_{\ell,i} \end{aligned} \qquad (2)$$

Bulk phases balances

Material balance of the i-th component in the liquid phase on the e-th tray:

$$\dot{F}_e^L x_{i,e,F}^L + \dot{L}_{e-1} x_{i,e-1} + V_{R,e}\sum_{j=1}^{N_R} \nu_{i,j}\dot{\xi}_{V,j} + V_{R,e} a_\nu \left(\dot{N}_i\right)_{z=\delta} - \dot{L}_e x_{i,e} = 0 \qquad (3)$$

Material balance of the i-th component in the gas phase on the e-th tray:

$$\dot{F}_e^G y_{i,e,F}^G + \dot{V}_{e+1} y_{i,e+1} - V_{R,e} a_\nu \left(\dot{N}_i\right)_{z=0} - \dot{V}_e y_{i,e} = 0 \qquad (4)$$

Overall enthalpy balance of e-th tray:

$$\dot{F}_e^G h_{F,e}^G + \dot{F}_e^L h_{F,e}^L + \dot{Q}_{R,e} + \dot{Q}_{d,e} + \dot{V}_{e+1} h_{V,e+1} + \dot{L}_{e-1} h_{L,e-1} - \dot{V}_e h_{V,e} - \dot{L}_e h_{L,e} = 0 \qquad (5)$$

Where the heat produced by chemical reactions on the e-th tray can be written:

$$\dot{Q}_{R,e} = V_{R,e}\sum_{j=1}^{N_R}\left(-\Delta_R H_j\right)\dot{\xi}_{V,j,e} + V_{R,e} a_{\nu,e}\sum_{j=1}^{N_R}\int_0^{\delta}\left(-\Delta_R H_j\right)\dot{\xi}_{V,j,e}\,dz \qquad (6)$$

Vapor-liquid equilibrium of i-th component on e-th tray:

$$P_{total} y_{i,e}^{*} = P_{i,e}^{\circ} x_{i,e}^{*} \gamma_{i,e} \tag{7}$$

Total condenser

If the reflux ratio is defined as:

$$\mathbb{R} = \frac{\dot{L}_{LD}}{\dot{L}_{D}} \tag{8}$$

then material balance of i-th component is in form:

$$\dot{V} y_{i} = \dot{L}_{D} \left(\mathbb{R} + 1 \right) x_{D,i} \tag{9}$$

where

$$y_{i} = x_{D,i} \tag{10}$$

The condenser enthalpy balance:

$$\dot{V} h_{V} - \dot{Q}_{cond} - \dot{L}_{D} \left(\mathbb{R} + 1 \right) h_{LD} = 0 \tag{11}$$

Reboiler model

The reboiler was considered equilibrium, because all the components enter it in the liquid phase. Thus, the chemical reaction takes place predominantly in the bulk liquid.
Material balance of i-th component:

$$\dot{F}_{reb}^{L} x_{i,reb,F}^{L} + \dot{F}_{reb}^{G} y_{i,reb,F}^{G} + \dot{L}_{reb-1} x_{i,reb-1} + V_{R,reb} \sum_{j=1}^{N_R} \nu_{i,j} \dot{\xi}_{V,j} - \dot{L}_{reb} x_{i,reb} - \dot{V}_{reb} y_{i,reb} = 0 \tag{12}$$

Enthalpy balance of the reboiler:

$$\dot{F}_{reb}^{G} h_{F,reb}^{G} + \dot{F}_{reb}^{L} h_{F,reb}^{L} + \dot{Q}_{R,reb} + \dot{Q}_{d,reb} + \dot{L}_{reb-1} h_{L,reb-1} - \dot{V}_{reb} h_{V,reb} - \dot{L}_{reb} h_{L,reb} = 0 \tag{13}$$

Thermodynamic equilibrium equations remain the same as for the tray (7).

Algorithm of solution

Mathematical model of a reactive-distillation column in a steady state then consists of two sub-models:

- Ordinary second-order differential equations (1) describing reaction and diffusion in the liquid film with boundary conditions defined in two points (liquid film boundaries)
- System of non-linear algebraic equations (NAE) governing from enthalpy balances (5) and all components' material balances in bulk liquid (3) and gas phase (4),

summation equations, thermodynamic equilibrium (7) and model of condenser (9) and (11).

The whole integral system of NAE could be solved by an appropriate solver. In this case, the algorithm proposed by Ferraris et al. (Ferraris 1986) was used. Inside each iteration of the NAE solution, on each tray, a system of ODE (BVP) had to be solved using actual bulk concentrations as BCs, providing mass fluxes at the vapor-liquid interface and liquid film-bulk liquid interface, which are necessary for completing and solving material balances in bulk phases. This algorithm is schematically depicted in Fig.1.

For very fast chemical reactions, the concentration profile of a component along the liquid film could be very steep (Carrá 1987) and appropriate discretization along the film coordinate has to be applied to calculate the space derivations of the dependent variables (concentrations) numerically. For this reason, the algorithm proposed by (Pereyra 1978) and implemented in the IMSL Math library was chosen. This algorithm automatically generates a non-uniform calculation grid for the space variable. This leads to avoiding numerical problems with very fast chemical reactions between reactants entering the liquid film from the vapour phase with reactants present in the liquid phase.

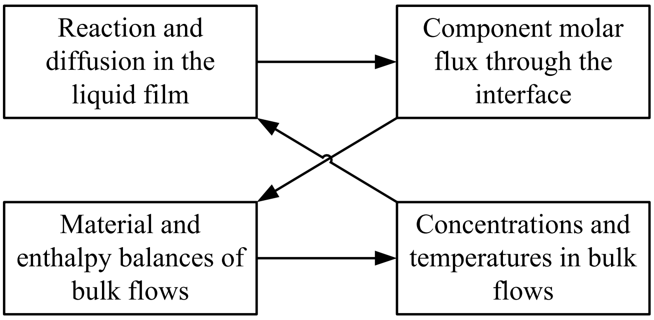

Figure 1 Mathematical model solution structure using film model

Case study

The presented mathematical model and proposed algorithm of solution have been tested using the following reaction system

$$A + B \rightarrow R + S \qquad \text{(R1)}$$

$$R + S \rightarrow A + B \qquad \text{(R2)}$$

with corresponding reaction rates expressions:

$$\dot{\xi}_{V1} = k_{V1} c_A c_B \qquad (14)$$

and

$$\dot{\xi}_{V2} = k_{V2} c_R c_S \qquad (15)$$

proceeding in a bubble-cap tray column, characteristics of which (number of trays, reflux ratio, reboiler heat duty, etc.) are briefly described in Table 2.

Physical and chemical properties were modeled as for the system of acetic acid estherification with ethanol (A = acetic acid, B = ethanol, R = ethyl acetate, S = water) and they were taken from the HYSYS database and (Reid 1987). To calculate activity coefficients in the liquid phase, the WILSON equation was chosen. Kinetic parameters were varied in the simulations to show the effect of very fast reaction rate on column behavior. Temperature dependence of the reaction rate is defined by the Arrhenius equation (See Table 1). In all simulations, the pre-exponential factor of reaction (R2) was constant. The pre-exponential factor of reaction (R1) was varied from $5,28\times10^{-8}$ to $5,28\times10^{-2}$ (m^3 mol^{-1} s^{-1}). Values of the specific interface area were calculated from the correlations for bubble-cap tray column as published by Trambouze and Euzen (Trambouze 2002). Values of the liquid and vapour film thicknesses were estimated in accordance with Taylor and Krishna (Taylor 1993) (for the liquid film 0.01-0.1mm). Multicomponent Wilke-Chang (liquid phase) and Fuller (gas phase) equations (Reid 1987) were used to calculate the diffusion coefficients. Mass transfer coefficients in respective phases were then obtained using convention as

$$k = \frac{D}{\delta} \tag{16}$$

Table 1: Selected kinetic parameters

N_I	4
N_R	2
$\Delta_R H_1$ (J mol^{-1})	-4000
$\Delta_R H_2$ (J mol^{-1})	4000
E_{A1} (J mol^{-1})	5000
E_{A2} (J mol^{-1})	5000
$k_{V\infty1}$ (m^3 mol^{-1} s^{-1})	$5,28\times10^{-8} - 5,28\times10^{-2}$
$k_{V\infty2}$ (m^3 mol^{-1} s^{-1})	$1,35\times10^{-8}$

Table 2: Column characteristics

a_v (m^2 m^{-3})	150 - 300
d_c (m)	0,6
N_{ET}	20
ET_L	5
ET_G	15
h_{liquid} (m)	0,05
P_{total} (Pa)	101325
$\dot{Q}_d$ (J s^{-1})	$1,25\times10^5$
$\mathbb{R}$	5
T_{cond} (K)	330,5
$V_{reboiler}$ (m^3)	1

Results and discussion

The goal of this paper was to investigate behaviour of an RD column with fast chemical reaction proceeding in the liquid phase. Therefore a modified Hatta number was introduced and defined as:

$$Ha_e^2 = \frac{\dot{\xi}_{V1,e} D_{\ell,B}}{k_\ell^2 c_{B,e}} \tag{17}$$

It is being used only as an indicator of the reaction-diffusion circumstances in the liquid film and evaluated on each tray with respect to the actual conditions unlike the original Hatta number.

Before proceeding on with further simulations, the built non-equilibrium algorithm was compared to the equilibrium one. In this case, the reaction rate was set to the low values because of EQ's inability to converge at the higher values. From both figures (Figure 2, Figure 3), it can be stated, that a good agreement between EQ and NEQ results was achieved. The feeds' specifications can be seen in Table 3.

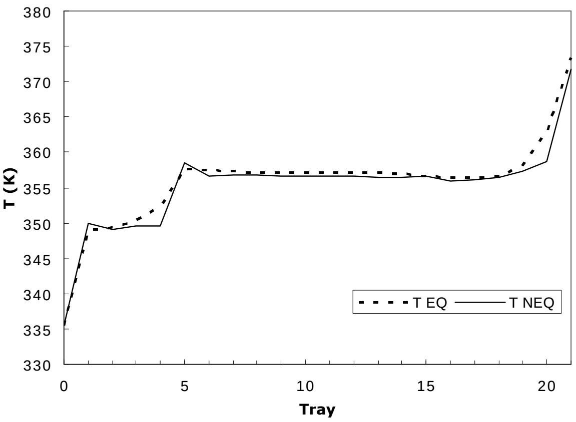

Figure 2 Algorithm benchmark with EQ – Temperature profiles at the lowest pre-exponential factor ($k_{V1\infty}=5.28\times10^{-8}$ m^3 mol^{-1} s^{-1})

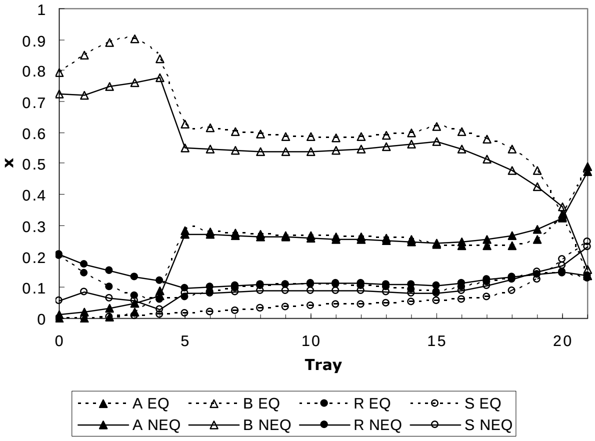

Figure 3 Molar fractions in the bulk liquid at the lowest pre-exponential factor ($k_{V1\infty}=5.28\times10^{-8}$ m^3 mol^{-1} s^{-1})

Table 3: Parameters of feeds

	T (K)	Phase	$\dot{F}$ (mol s^{-1})	x_A	x_B	x_R	x_S
1	330.15	liquid	1.111	0.98	-	-	0.02
2	352.15	gaseous	1.111	-	0.98	-	0.02

The first big advantage of using reaction-diffusion equation is the possibility of utilization of a solver, which uses non-uniform discretization method of the space variable. This leads to a more effective tool and saving computational time. The non-uniform discretization can be good seen in the Figure 4 and Figure 5, where the concentration profiles in the liquid film at the highest reaction rate is depicted. In the areas with no strong influence of the chemical reaction, the profiles are flat and no dense computational grid is needed. In the areas, where the profiles are bent and the influence of chemical reaction is comparable with that of diffusion, the discretization grid becomes denser.

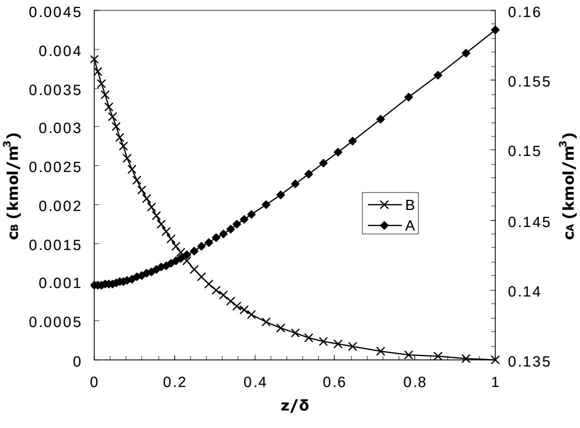

Figure 4 Concentration profiles of the reactants in the liquid film on the the 14th tray ($k_{V1\infty}=5.28\times10^{-2}$ m^3 mol^{-1} s^{-1})

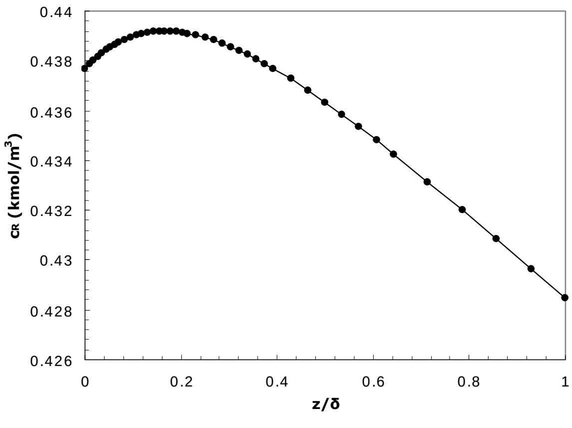

Figure 5 Concentration profile of the product in the liquid film on the the 14th tray ($k_{V1\infty}=5.28\times10^{-2}$ m^3 mol^{-1} s^{-1})

The first issue of RD column optimization was the liquid versus gaseous feeds' ratio. It has been changed in a range from 0.35 to 2.5. The optimal regime in the column from this point of view seems to be operation at the lower reboiler temperature. The excess of high boiling point component causes the rise of the temperature in the reboiler and increases reboiler duty costs.

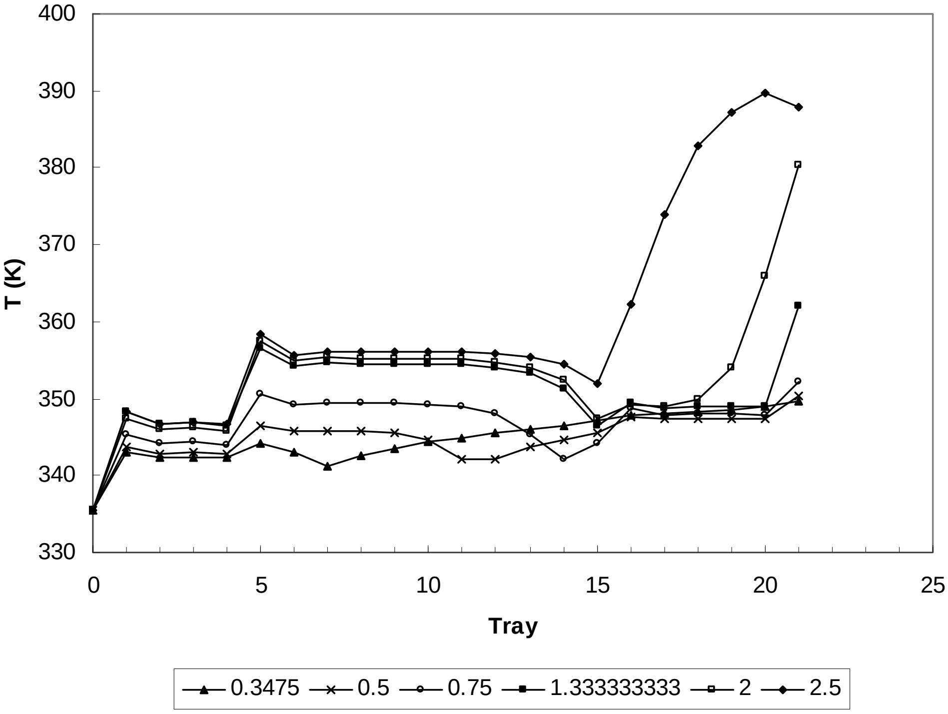

Figure 6 Temperature profiles in the column for various feeds‘ ratio

Final number of the computational grid points is higher at the upper feed’s position when it is in lack, the liquid film plays important role here, because of the intensive reaction-diffusion interactions. The same can be stated for the lower part of the column in case of excess of the top-feed component.

Another parameter influencing the column operation is reflux ratio. It has been changed between 2 and 18. The higher the reflux ratio, the better concentration of product in the distillate proved to be. On the other hand, the operation costs are rising also. The changing reflux ratio but doesn’t push the reactive-diffusion area represented by the Hatta values, what can be seen in the Figure 7.

Further parameter was position of the respective feeds. There are many possible ways how to deal with this issue. The feeds can be either coupled to be fed on one tray or separated into two various feed points. Due to the fact, that the products form an azeotrope, the influence of changing position on distillate composition was negligible. The temperature profiles remained almost the same except for the peaks caused by the feed, which were moving. Final number of the grid points was also moving with the feeds. Concentration and molar flow profiles are quite flat when feeds enter the same tray anywhere in the column. Separate feeds proved to be more effective leading to a little higher product concentration in the distillate and better contact between reactants what can be seen in the figures Figure 8 - Figure 11.

Due to the high reaction rate and the mentioned azeotrope, the number of trays and reboiler capacity didn’t have any greater influence on column operation and product concentration.

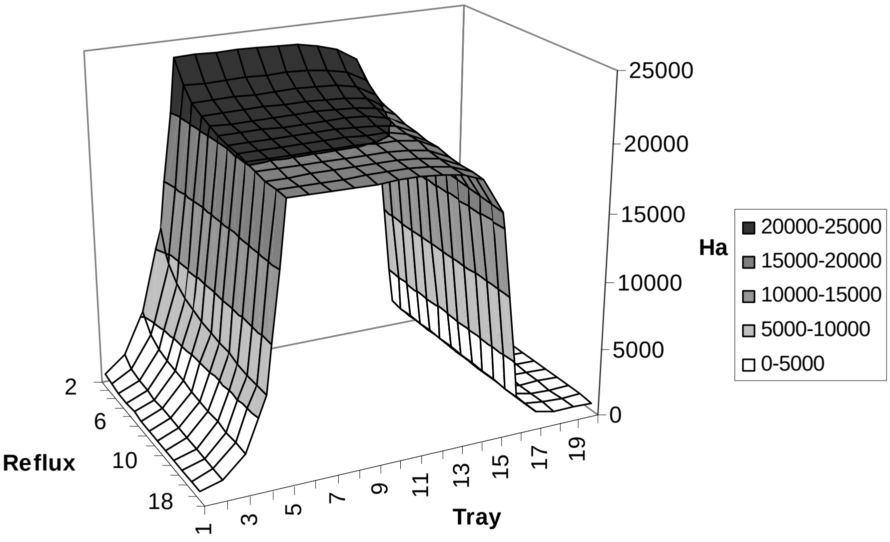

Figure 7 Hatta number values along the column for changing reflux ratio

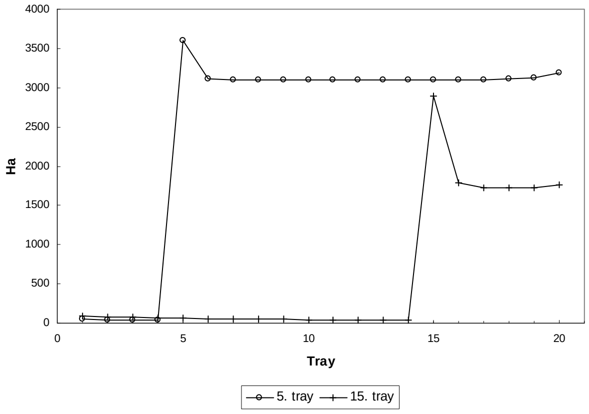

Figure 8 Hatta number values for types of feeding on one tray

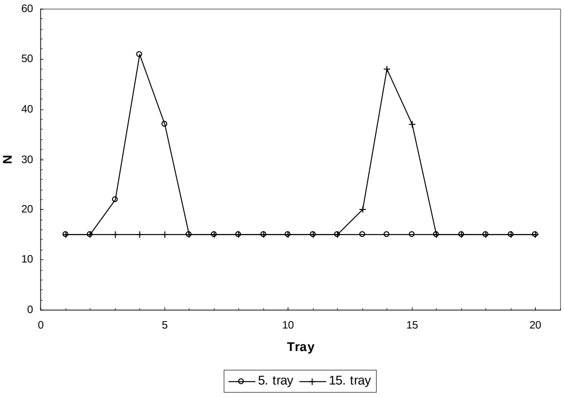

Figure 9 Final number of the grid points for two types of feeding on one tray

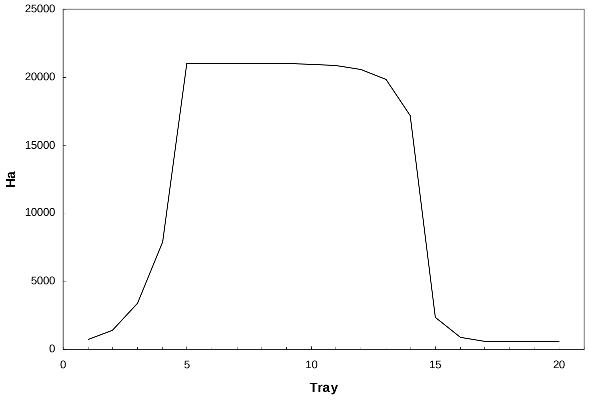

Figure 10 Hatta number values for separate feeds

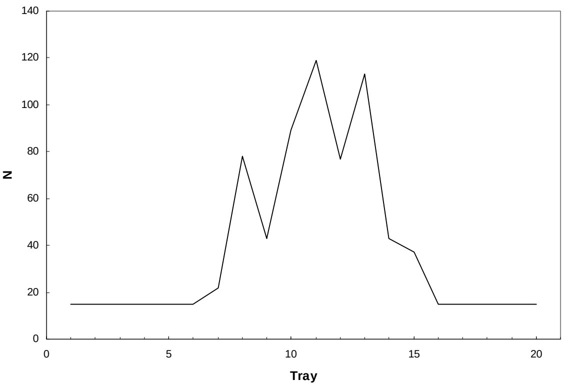

Figure 11 Final number of the grid points for separate feeds

Conclusion

Two main goals were to be reached in this paper. First, creating steady-state non-equilibrium mathematical model of an RD column and second, simulation of various parameters influence on the column operation. Mass transfer and reaction in the liquid film were described by the reaction-diffusion equation derived from the Fick's law. Modified Hatta number was introduced to observe the reaction-diffusion conditions in the column. The developed algorithm was first tested considering the normal conditions (low reaction rate, thin liquid film) and the results were compared to those of the EQ model. A good agreement can be stated. In the next step, the reaction rate was increased to simulate a regime limited by the diffusion in the liquid film. Mathematical model with proper solvers proved to be robust and stable. In the second part, influence of changing feeds' position and ratio, reflux ratio, reboiler capacity and number of trays was observed. High reaction rate and formation of azeotrope at certain circumstances were working as a buffer in some simulations, so the results are not as intended.

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List of symbols

a_v	Specific interfacial area	$m^2\ m^{-3}$
c	Molar concentration	$mol\ m^{-3}$
D_ℓ	Effective liquid diffusion coefficient	$m^2\ s^{-1}$
d_c	Column diameter	m
e	Index of tray	
E_A	Reaction activation energy	$J\ mol^{-1}$
ET_L	Number of the tray where the liquid feed enters	
ET_G	Number of the tray where the gaseous feed enters	
$\dot{F}$	Feed molar flow	$mol\ s^{-1}$
Ha	Hatta number	
h	Molar enthalpy of a stream	$J\ mol^{-1}$
h_{liquid}	Liquid level on a tray	m
$\Delta_R H$	Reaction enthalpy	$J\ mol^{-1}$
k_G	Mass transfer coefficient in gas phase	$mol\ s^{-1}\ kg^{-1}\ m^{-1}$
k_ℓ	Mass transfer coefficient in liquid phase	$m\ s^{-1}$
k_V	Reaction rate constant	
$k_{V\infty}$	Pre-exponential factor	
$\dot{L}$	Molar flow of the liquid	$mol\ s^{-1}$
$\dot{N}$	Specific molar flow	$mol\ m^{-2}\ s^{-1}$
N_{ET}	Number of trays in the column	
N_I	Number of components	

N_R	Number of reactions	
P°	Pure component saturated vapours’ pressure	Pa
P_i	Partial pressure of the i-th component	Pa
P_{total}	Total pressure in the system	Pa
$\dot{Q}_R$	Reaction heat	J s^{-1}
$\dot{Q}_d$	Heat input	J s^{-1}
$\mathbb{R}$	Reflux ratio	
T	Temperature	K
$\dot{V}$	Gas molar flow	mol s^{-1}
V_R	Reaction mixture volume on a tray	m^3
x	Liquid molar fraction	
y	Gas molar fraction	
z	Distance in the film	m

Greek symbols

γ	Activity coefficient	
δ	Film thickness	m
ν	Stoichiometric coefficient	
$\dot{\xi}_V$	Reaction rate	mol m^{-3} s^{-1}

Superscripts

$*$	Interface
$\circ$	Pure component
G	Gas phase
L	Liquid phase
T	Actual temperature

Subscripts

$cond$	Condenser
D	Distillate
e	Index of tray
f	Liquid film
F	Feed
i	Index of component
j	Index of reaction
ℓ	Liquid phase
L	Liquid stream
LD	Liquid reflux stream
reb	Reboiler
V	Vapor stream
z	Position in the liquid film

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