

MODELLING OF REACTIVE DISTILLATION – PROPYLENE OXIDE PRODUCTION

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Abstract

Selectivity and equilibrium of chemical reactions can be significantly influenced by the distillation of one or more products from the reaction mixture. Simultaneous reaction and separation of the desired product is very important in the case of consecutive reactions. Simulation of the reactor for propylene oxide (POX) synthesis from propylenechlorohydrine (PCH) and calcium hydroxide is presented in the paper. The main reaction is very fast, followed by hydrolysis of POX in a basic solution into propylene glycol (PGLY). To eliminate the PGLY production, POX is stripped by steam from the reaction mixture. Using the developed model, the optimal design and working performance of the reactor are presented. The role of chemical reaction kinetics is discussed.

Key words: reactive distillation, propylene oxide production, mathematical model

Introduction

The present conceptual design of any chemical process results in a flow-sheet which contains a reactor and a separation unit. As a separation unit is often used a distillation column, because of its effectivity and performance. The aim is to decrease the operational costs, improve equipment performance... These goals can be achieved by combining mentioned units to one device via reactive distillation. This method offers following advantages ^[1]:

- murgence of reaction and separation units into one implies reduction of the capital costs,
- chemical reaction equilibrium limitation can be overcome,
- less heat consumption, due to exothermic reaction heat utilisation,
- selectivity can be improved. Removing products from the reaction mixture can suppress side reactions,
- reduced catalyst requirements for the same degree of conversion,
- avoidance of azeotropes. Conditions in the reactive distillation (RD) column can allow the azeotropes to be “reacted away” in a single vessel,
- safer process running. The reaction heat is withdrawn by liquid vaporisation.

These advantages were known long time ago. Reactive distillation phenomena include a complex system of non-linear equations. Due to this fact, an extensive research was limited by computational power of PC's. The occurrence of chemical reaction on stages makes behaviour of RD columns different to conventional columns. Following that, short-cut estimation methods (e.g. Fenske-Underwood-Gilliland) with their assumptions cannot be applied. To obtain RD column parameters, the whole system of equations (material balances, enthalpy balances.) has to be

solved. The aim of this paper is to show our used model and a way of balancing which can lead to relevant results. As an example, the production of propylene oxide from propylene chlorohydrine is discussed.

Mathematical model

We consider a multistage rectification column illustrated in Fig. 1, where the following parameters are known: number of stages (m), range of the reactive section bounded with the upper (n_{TOP}) and lower (n_{BTM}) reactive stage, characteristics of the feed, reflux ratio in case of a total condenser, condensation temperature (T_0) in a partial condenser if used, volume of liquid on each stage and in the reboiler.

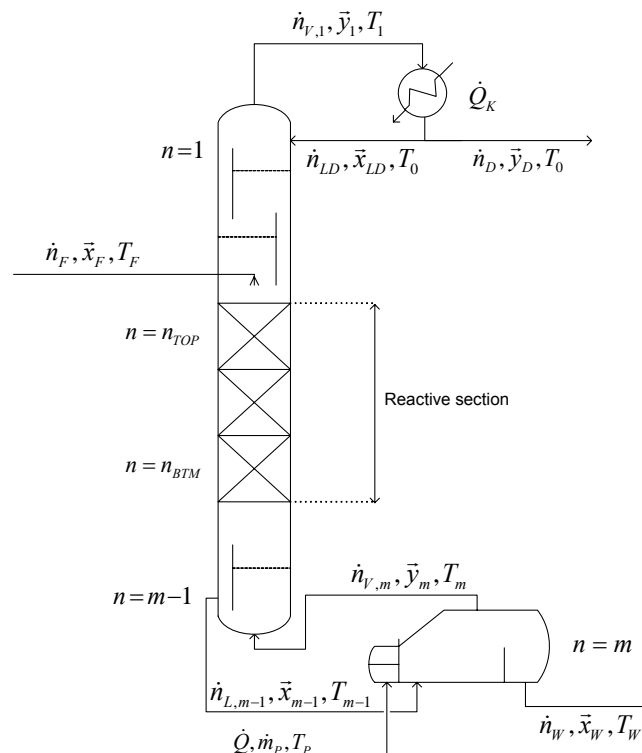


Fig.1: Scheme of RD column

We started the column balancing by dividing it into two major parts. First part was a column balance, which includes range of stages from reboiler ($n=m$) to the top of the column ($n=1$). On each stage material, enthalpy and equilibrium equations were calculated. In another way a condenser was balanced. In dependence on its functionality (total, partial condenser), adequate equations were estimated.

Assumptions and simplifications

From the mathematical point of view, RD column represents a system of strong non-linear equations. Equations used to describe physical and chemical properties of the studied process should be chosen carefully. By every added equation we obtain more precisely described system, however problems with finding its solution can occur. In our case following assumptions are considered:

- pressure drop in the column is neglected
- zero mixing enthalpies of streams

- ideal behaviour of the vapour phase (process running at atmospheric pressure)
- chemical reaction occurs only in the liquid phase
- steady state
- ideal mixing on each stage
-

Vapour-liquid equilibrium

Specifying the general condition of vapour-liquid equilibrium (given by equality of compound fugacities in each phase) in terms of mentioned assumptions for the n -th stage we obtain:

$$P \cdot y_{n,i} = P_{n,i}^o \cdot x_{n,i} \cdot \gamma_{n,i} \tag{1}$$

where P is system pressure, $\gamma_{n,i}$ – activity coefficient of the i -th component in the liquid solution. The vapour pressure of pure species $P_{n,i}^o$ was estimated by Antoine’s equation:

$$\ln P_{n,i}^o = \left[A_{a,i} + \frac{B_{a,i}}{C_{a,i} + T_n} + D_{a,i} \cdot \log T_n + E_{a,i} \cdot T_n^{F_{a,i}} \right] \tag{2}$$

where $A_{a,i}, B_{a,i}, C_{a,i}, D_{a,i}, E_{a,i}, F_{a,i}$ are Antoine’s equation constants of the species i . For the calculation of activity coefficients of each i component on the n -th stage $\gamma_{n,i}$ Wilson’s model for multicomponent mixture was used:

$$\ln \gamma_{n,i} = - \ln \left(\sum_{j=1}^{N_i} x_{n,i} \cdot \Lambda_{ij} \right) + 1 - \frac{\sum_{k=1}^{N_i} x_{n,k} \cdot \Lambda_{ki}}{\sum_{j=1}^{N_i} x_{n,j} \cdot \Lambda_{kj}} \tag{3}$$

$$\Lambda_{ij} = \frac{V_j^{(l)}}{V_i^{(l)}} \exp \left(- \frac{(\lambda_{ij} - \lambda_{ii})}{RT_n} \right) \quad , \quad \Lambda_{ii} = \Lambda_{jj} = 1 \tag{4}$$

$$\lambda_{ij} - \lambda_{ii} = A_{ij} + B_{ij} \cdot T_n \tag{5}$$

Coefficients A_{ij}, B_{ij} can be based on the experimental vapour-liquid equilibrium data of binary systems. Our individual pairs A_{ij}, B_{ij} were obtained from HYSYS program database, where B_{ij} coefficients were equal to zero. Unknown pairs were computed by contributory methods. By including Murphee’s stage efficiency E_y^M equation (1) changes into:

$$y_{n,i} = E_y^M \frac{P_{n,i}^o \gamma_{n,i}}{P} \cdot x_{n,i} - (1 - E_y^M) \cdot y_{n+1,i} \tag{6}$$

Material balances

For a better interpretation, Fig.2 schematically expresses directions and meaning of the assumed streams on the n -th stage for the i -th component.

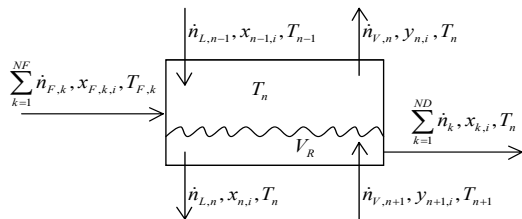


Fig. 2: Scheme of one stage

In steady state we can for the n -th stage and the i -th component write material balance (MB):

$$\sum_{k=1}^{NF} \dot{n}_{F,k} \cdot x_{F,i} + \dot{n}_{L,n-1} \cdot x_{n-1,i} + \dot{n}_{V,n+1} \cdot y_{n+1,i} + z_{n,i} \cdot V_R - \sum_{k=1}^{ND} \dot{n}_{k,n} \cdot x_{n,i} - \dot{n}_{L,n} \cdot x_{n,i} - \dot{n}_{V,n} \cdot y_{n,i} = 0 \quad (7)$$

and the overall balance relation (see Fig.3):

$$\sum_{NS=1}^n \sum_{k=1}^{NF} \dot{n}_{F,k,NS} + \dot{n}_{V,n+1} + \sum_{NS=1}^n V_{R,NS} \sum_{i=1}^{Ni} z_{NS,i} - \sum_{NS=1}^n \sum_{k=1}^{ND} \dot{n}_{k,n,NS} - \dot{n}_{L,n} - \dot{n}_D = 0 \quad (8)$$

where NF is the number of feeds, ND is the number of drains, term $\sum_{i=1}^{Ni} z_{NS,i}$ represents reaction source in a unit volume at the current stage NS . This can be evaluated by the following equation:

$$z_{n,i} = \sum_{j=1}^{Nr} \dot{\xi}_{V,n,j} \cdot v_{j,i} \quad (9)$$

where $\dot{\xi}_{V,n,j}$ is the reaction rate of the j -th reaction on the n -th stage related to the volume of reaction mixture V_R ; $v_{j,i}$ represents the stoichiometric coefficient of component i in reaction j .

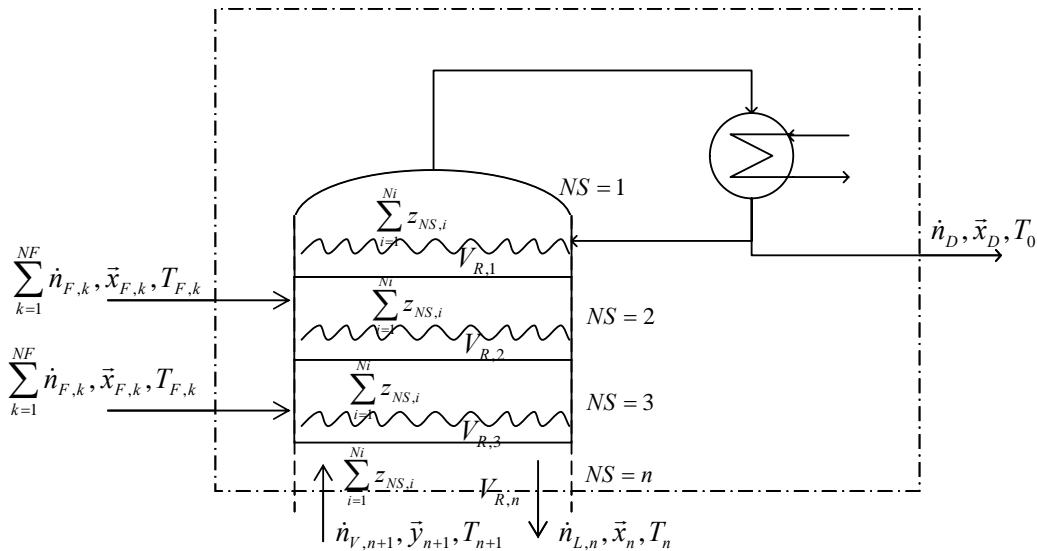


Fig. 3: Balancing scheme for the overall material balance of the n -th stage

Equation (7) is valid for the first stage of the column in a modified form. For the balance of component i , the following substitution is applied:

$$\dot{n}_{L,n-1} \cdot x_{n-1,i} = \dot{n}_{LD} \cdot x_{LD,i} \quad (10)$$

Aspects about methods of estimations of $\dot{n}_{LD} \cdot x_{LD}$ are discussed bellow (see condenser balances). Another specific stage is the last stage. It contains one stream less than the general stage. The material balance on each stage is supplemented by the definition equation:

$$1 - \sum_{i=1}^{Ni} x_{n,i} = 0 \quad (11)$$

Enthalpy balances

Similar to material balancing practice enthalpy balancing was applied for the column. Each stage has been separately balanced, covering its special settings (e.g. reboiler, first stage...). As the reference state the liquid state has been declared at the reference temperature. According to this fact, the enthalpies of particular streams were calculated as follows:

Molar enthalpy of the liquid flow on the n -th stage:

$$H_{L,n} = \sum_{i=1}^{Ni} x_{n,i} \cdot H_{L,n,i}^o \quad (12)$$

where the molar enthalpy of pure liquid component i $H_{L,n,i}^o$ is given by the relation:

$$H_{L,n,i}^o = \int_{T_{ref}}^{T_n} Cp_{L,i} dT \quad (13)$$

Developing $Cp_{L,i}$ to polynomial series and consequently applying an integration, we obtain:

$$H_{L,n,i}^o = A_{L,i} \cdot (T_n - T_{ref}) + B_{L,i} \cdot \frac{(T_n^2 - T_{ref}^2)}{2} + C_{L,i} \cdot \frac{(T_n^3 - T_{ref}^3)}{3} + D_{L,i} \cdot \frac{(T_n^4 - T_{ref}^4)}{4} \quad (14)$$

For the vapour stream enthalpy on n -th stage:

$$H_{V,n} = \sum_{i=1}^{Ni} y_{n,i} \cdot H_{V,n,i}^o \quad (15)$$

and finally for the i -th pure component vapour enthalpy holds:

$$H_{V,n,i}^o = \Delta_{vap} H_i^o + A_{V,i} \cdot (T_n - T_{ref}) + B_{V,i} \cdot \frac{(T_n^2 - T_{ref}^2)}{2} + C_{V,i} \cdot \frac{(T_n^3 - T_{ref}^3)}{3} + D_{V,i} \cdot \frac{(T_n^4 - T_{ref}^4)}{4} \quad (16)$$

where $A_{X,i}, B_{X,i}, C_{X,i}, D_{X,i}$ for $X = L, V$ are constants used for the molar heat capacity evaluation. The subscript X indicates the state and $\Delta_{vap} H_i^o$ is the heat of evaporation of pure component i at reference temperature. With assumption of the existence of a reaction only in liquid phase, the relation for the reaction enthalpy has the following form:

$$\Delta_r H_j(T_n) = \Delta_r H_j(T_{ref}) + \int_{T_{ref}}^{T_n} \sum_{i=1}^{Ni} \nu_{j,i} \cdot Cp_{L,i} dT, \quad (17)$$

which is an inter-step to the overall reaction heat $\dot{Q}_{r,n}$ on the n -th stage:

$$\dot{Q}_{r,n} = \sum_{j=1}^{Nr} (-\Delta_r H_j(T_n)) \cdot \dot{\xi}_{V,n,j} \quad (18)$$

Similar as for material balances, the form of the balancing equation for the current stage depends on its configuration respective position in the column. In general case this equation can be written in the form:

$$\dot{Q}_{r,n} \cdot V_{R,n} - \dot{n}_{V,n} \cdot H_{V,n} - \dot{n}_{L,n} \cdot H_{L,n} + \dot{n}_{V,n+1} \cdot H_{V,n+1} + \dot{n}_{L,n-1} \cdot H_{L,n-1} + \sum_{k=1}^{NF} \dot{n}_{F,k,n} \cdot H_{F,k,n} - \sum_{k=1}^{ND} \dot{n}_{L,k,n} \cdot H_{L,k,n} = 0 \quad (19)$$

A modification of equation (19) for the first stage includes the following substitution:

$$\dot{n}_{L,n-1} \cdot H_{L,n-1} = \dot{n}_{LD} \cdot H_{LD}$$

Assessment of column's last stage (reboiler) involves removing the term $\dot{n}_{V,n+1} \cdot H_{V,n+1}$ from equation (19).

Condenser balances

As we have been mentioned before, two types of condenser are assumed. Each of them has its own specification, e.g. number of unknown parameters, model conception, etc. In the next section we will discuss about both these cases.

In case of a partial condenser, this is considered to act like another equilibrium stage. As a matter of fact, the outgoing gas and the liquid phase have an equilibrium composition given by the known composition of the inlet stream $\dot{n}_{V,1} \cdot \bar{y}_1$ and by temperature and pressure conditions in the condenser. Therefore, by setting up the condenser temperature, we can determine the composition and indirectly the rate of outgoing streams. Despite the mentioned, we treat the composition and flow rates as unknown parameters, because they cannot be expressed implicitly. To obtain their values, a system of non-linear equations has to be solved. These extra equations were added to the whole column balancing relations and estimated as the entire "package". Briefly, the used equations are summarised below.

Material balance of the species i :

$$\dot{n}_{V,1} \cdot y_{1,i} - \dot{n}_D \cdot y_{D,i} - \dot{n}_{LD} \cdot x_{LD,i} = 0 \quad (20)$$

Equilibrium condition for the i -th component:

$$y_{D,i} - \frac{P_{0,i}^o \cdot \gamma_{0,i}}{P} \cdot x_{LD,i} = 0 \quad (21)$$

Summation equation:

$$\sum_{i=1}^{N_i} y_{D,i} - \sum_{i=1}^{N_i} x_{LD,i} = 0 \quad (22)$$

And finally, for the enthalpy balance holds:

$$\dot{n}_{V,1} \cdot H_{V,1} - \dot{n}_D \cdot H_D - \dot{n}_{LD} \cdot H_{LD} - \dot{n}_{LD} \cdot \Delta_{vap} H_0 - \dot{n}_{V,1} \cdot C p_{V,0} = 0, \quad (23)$$

where two last terms represent heat removed in the condenser; the inlet vapour stream cooled from the temperature T_1 to T_0 ($\dot{n}_{V,1} \cdot C p_{V,0}$) and consequently condensation of exactly that part of the vapour stream, which is being returned to the column via reflux ($\dot{n}_{LD} \cdot \Delta_{vap} H_0$) at the condensation temperature T_0 .

A different situation occurs with total condenser engagement. We assume that the whole inlet vapour stream is being condensed. As a consequence of that, there is no change of composition encountered. Written into a formula for the i -th component, we obtain:

$$y_{1,i} = x_{LD,i} \quad (24)$$

Establishing the reflux ratio definition:

$$\dot{n}_{LD} = \dot{n}_{V,1} \cdot \frac{R_X}{R_X + 1} \quad (25)$$

means, that only one parameter is unknown. It is the temperature T_0 in the condenser. We assume that the condensate is taken away at the boiling temperature of the mixture. The value can be obtained by a standard technique, solving the following equation:

$$1 - \sum_{i=1}^{N_i} y_{D,i} = 0 \quad (26)$$

where the value of $y_{D,i}$ was obtained from equation (21).

Solving method

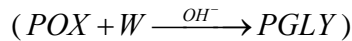
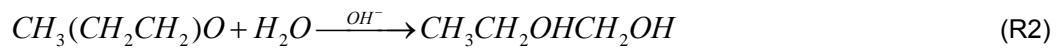
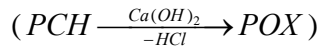
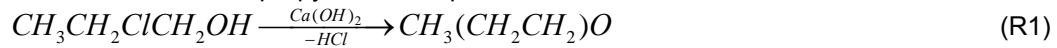
Model equations (1) – (26) represent a system of non-linear algebraic equations, which were solved using the Newton-Raphson method with numerical evaluation of the Jacobian matrix and with defined constrains for all variables.

Model system

Propylene oxide synthesis has been chosen as a model system. It is a typical problem of a consecutive reaction, taking place in the liquid phase, for which reactive distillation is advantageous. By stripping propylene oxide from the solution, the production of the consecutive side product, ethylene glycol, can be minimized.

Kinetics of chemical reactions

The reaction scheme for the propylene oxide production can be written as follows:



The reaction rate can be expressed by the following expressions [2]:

$$\dot{\xi}_{V1} = k_{V1} \cdot C_{PCH} \quad (27)$$

$$\dot{\xi}_{V2} = k_{V2} \cdot C_{POX} \cdot C_{OH^-} \quad (28)$$

As a source of OH^- ions, $Ca(OH)_2$ is usually used. Because of its small solubility in water, the concentration of OH^- ions is constant and depends only on temperature [2]:

$$C_{OH^-} = 0.13 - 3.01 \times 10^{-4} T \quad (29)$$

The temperature dependence of the reaction rate constants k_{V1}, k_{V2} can be expressed by equation:

$$k_{V,j} = k_{V\infty,j} \cdot \exp\left(\frac{-E_j}{R.T}\right) \quad j = 1, 2 \quad (30)$$

The values of kinetic parameters $k_{V\infty,j}$ and E_j, j for both reactions (R1) and (R2) are summarized in Table 1. For reaction (R1) two values from two different sources were found, [2], [3].

Table 1: Kinetic parameters of the assumed reactions

Reaction	$k_{V\infty}$		E [kJ kmol ⁻¹]	References	$\Delta_r H(25^\circ C)$
(R1)	3.394×10^{24}	s ⁻¹	187131	[3]	-27520 kJ kmol ⁻¹
(R1)	3.02×10^9	s ⁻¹	66402.6	[2]	
(R2)	2.68×10^8	m ³ mol ⁻¹ s ⁻¹	68048.1	[2]	-83920 kJ kmol ⁻¹

Material balance

A water solution of propylene chlorohydrine is mixed with a water suspension of $Ca(OH)_2$ and fed into the column (with an excess of $Ca(OH)_2$ with respect to PCH). Because of a lack available data for $Ca(OH)_2$ and $CaCl_2$ influence on V – L equilibrium and physical and chemical properties of the liquid solution, these compounds were neglected (together with other organic compounds like DCP , which are side products from the PCH synthesis). We assumed in the column only four compounds: PCH , POX , $PGLY$ and W . As a heating medium, saturated steam at a temperature of 158.8°C was used. This was fed directly into last stage – reboiler. The composition of feed streams into the column is reported in Table 2. The parameters for V – L equilibrium described by Wilson's equation and physical properties of vapour and liquid solutions were taken from the literature,^{[4], [5]}.

Table 2: Parameters of the feed streams into the column

Feed characteristics			x_F mol.%			
Number of feed	Feed stage	Feed temperature	PCH	POX	$PGLY$	W
1 (raw material)	variable	90°C	0.096	0	0	0.9904
2 (steam)	25	158.8°C	0	0	0	1.0

Table 3: Parameters of the reactive distillation column

Fixed column parameters		Variable column parameters	
Number of stages	25	Position of the feed stage	5;10;18
Volume of the reboiler	5 m^3	Number of the reactive stages	20;15;7
Diameter of the column	1.8 m	Mass flow of the steam	$2.5 - 16\text{ t h}^{-1}$
Height of the stage	0.3 m	Kinetics data performed by	nchz ^[3]
Liquid height in the stage	0.08 m		mdli ^[2]
Temperature in the condenser	80°C		

Results and discussion

There is a lot of parameters, influencing the behaviour of the RD column, mainly the number of column stages, position of the feed stage (and consequently the number of reactive stages), volume of the reboiler, steam temperature and flow rate, temperature in the condenser, diameter of the column, volume of the liquid on the stage, etc. Therefore, in this paper, we fixed some of them, as listed in Table 3. In the following pictures and discussions, the kinetic parameters of reaction (R1) are taken from^[3].

Simulation of the column

In Fig. 4 are given the concentration profiles of all assumed compounds in the vapour phase (25 column stages, with 20 reactive stages including reboiler). From the feed stage the POX fraction is increasing, what is induced by a drop of temperature in the partial condenser $T_0=80^\circ\text{C}$. At given temperature, 57 mol% of POX in the distillate was obtained.

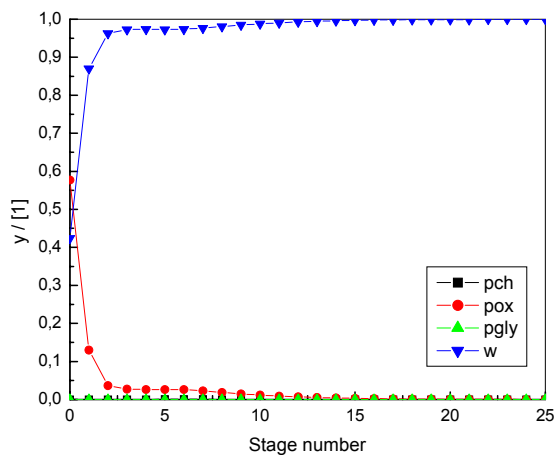


Fig. 4: Molar compositions over the RD column. The feed stage is the fifth stage.

In designing the column with a maximal yield of *POX* and minimizing the *PGLY* production, two problems for solving must be solved:

- by increasing the number of reactive stages, we can minimize the concentration of *PCH* in the reboiler (there are severe ecological limits for organic chlorine released from the reboiler). On the other hand, a lot of reactive stages favour the hydrolysis of *POX* into *PGLY*.
- The hydrolysis of *POX* could be avoided by increasing the flow rate of the stripping steam. High steam flow rate reduces the production of *PGLY* and the concentration of *POX* and *PCH* in the reboiler, on the other hand, it needs a condenser, in which a huge amount of heat has to be removed to obtain a distillate with desired composition.

The above mentioned conclusions are demonstrated in Figs. 5, 6, 7. In Fig. 5 the plot of the production of *POX* vs. flow rate of fed steam into the reboiler is drawn. The parameter is the number of reactive stages is drawn. For a low steam flow rate, the influence of number of the reactive stages on *POX* production is not great. However the yield of *PGLY* is considerably higher for a higher number of reactive stages. A high steam flow rate influenced the *POX* production with a higher number of reactive stages. This fact can be explained by a short residence time of *POX* on the reactive stages. For a low number of reactive stages, *POX* is not quantitatively stripped from the liquid phase and is passed to the reboiler, where its residence time is high because of the reboiler volume, and its hydrolysis can proceed to high degree (see Fig. 7).

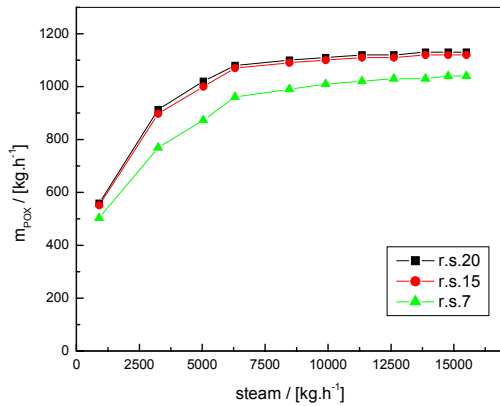


Fig. 5: Mass flow rate of *POX* from the condenser vs. flow rate of steam fed into the reboiler. Parameter of the curves is the number of reactive stages. 20,15,7

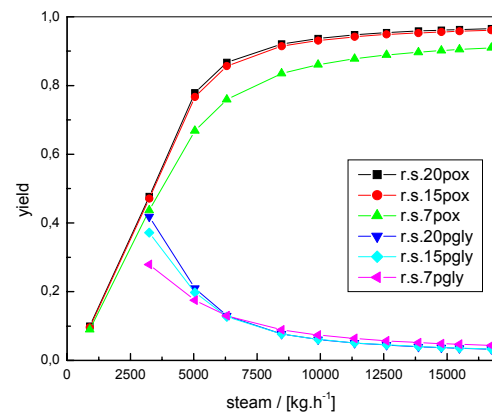


Fig. 6: Yield of *POX* and *PGLY* as a function of the number of reactive stages and the amount of steam fed into the reboiler

The optimal design of the column therefore requires an economic analysis balancing the price of *POX*, price of the used steam and cooling water in the condenser, taking into account also the ecological constrains (for *PCH* and *PGLY* concentrations in the waste stream from the reboiler, which is passed to the waste water treatment plant).

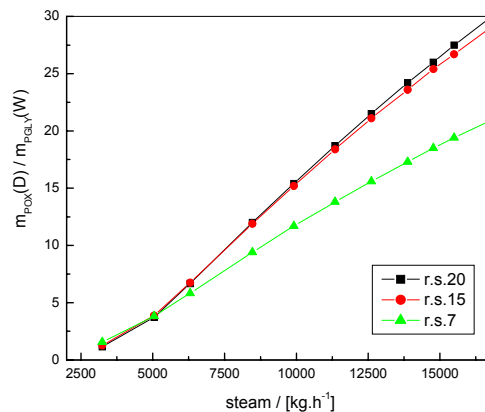


Fig. 7: The amount of *POX* [kg h^{-1}] produced compared to 1 kg h^{-1} of *PGLY* as a function of steam flow rate and the number of reactive stages.

Influence of kinetic parameters on the column simulation

For simulation of RD column for *POX* synthesis two rate constants of reaction (R1) were used:

- rate constants estimated from the experimental data obtained in a laboratory scale batch reactor, measured in NCHZ, Inc., Nováky, Slovakia,^[3]
- rate constant taken from the work of Carra et al.,^[2]

In Table 1 are summarized the values of the pre-exponential factors and activation energies. A comparison of the reaction rate constant of reaction (R1) at a temperature of 100°C , using parameters from^[3] and^[2] shows that reaction rate constant using data from^[2] is approximately 70 times higher than that from data evaluated in^[3]. Therefore, in this part of work some simulations have been done to demonstrate the importance of appropriate kinetic data for RD column design and optimization.

In Figs. 8 and 9 the production of *POX* and *PGLY* is compared using different kinetic data for reaction (R1) as a function of the steam flow rate and position of the feed stage. Because the predicted reaction using the data from^[3] is very low (with respect to data from^[2]), dehydrochlorination of *PCH* is not sufficient in a low number of reactive stages, and the important part of *PCH* is flowing into the reboiler (see Fig. 10). Even a high steam flow rate is unable to strip *POX* from the liquid and its hydrolysis in the reboiler yields a high production of *PGLY*. By increasing number of reactive stages (from 5 to 15) the production of *POX* is increased with a higher selectivity, but it is still lower than in the case of a reaction proceeding with a higher rate (using data from^[3]) in all the range of the assumed steam flow rate (c.f. Figs. 9 and 11).

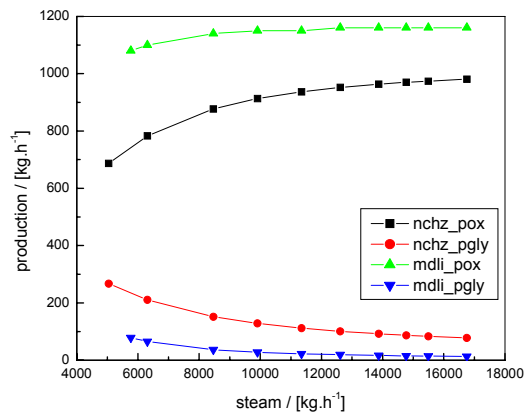


Fig. 8: Production of *POX* and *PGLY* vs steam flow rate by using two sets of kinetic data. The number of stages is 20, the number of feed stage is 15.

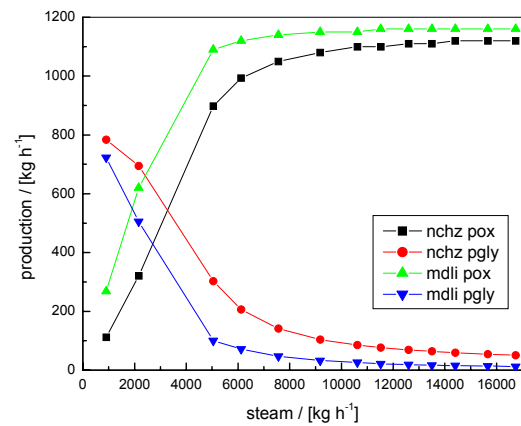


Fig. 9: Production of *POX* and *PGLY* vs steam flow rate by using two sets of kinetic data. The number of stages is 20, the number of feed stage is 5.

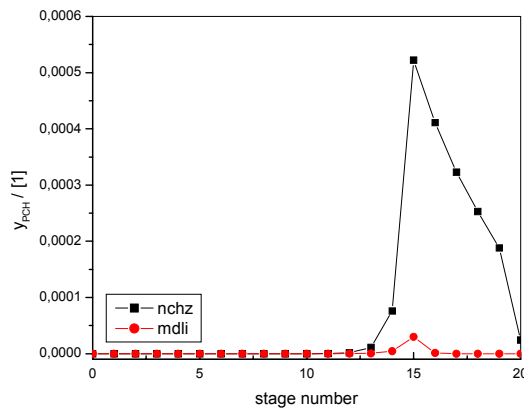


Fig. 10: Comparison of the concentration profiles of *PCH* in the column obtained using two different reaction rate constants for simulation. The number of stages is 20, the number of feed stage is 15 (5 reactive stages)

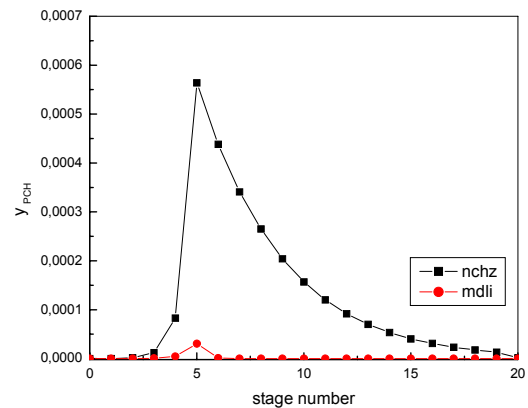


Fig. 11: Comparison of the concentration profiles of *PCH* in the column obtained using two different reaction rate constants for simulation. The number of stages is 20, the number of feed stage is 5 (15 reactive stages)

Conclusion

The steady state mathematical model of a reactive distillation column and its FORTRAN code were developed. The possible use of such model is demonstrated for the example of propylene oxide synthesis. This example was chosen as a typical process with consecutive reactions, where the desired product could be converted into a side, undesirable product.

In this paper the presented model and robust algorithm of model equations solution represent an useful tool for simulation and design of the reactive distillation column size and optimal performance conditions.

The ability of the model to simulate the RD column behaviour depends also on the appropriate values of the model parameters. The main effort has to be paid to parameters of the multicomponent vapour – liquid equilibrium model, and kinetic parameters. The importance of the first group of parameters is discussed in numerous papers in the literature, c.f.^[1]. In this paper we focused our attention to the second group of parameters, i.e., kinetic parameters. By simulating the RD column with two different values of the reaction rate constant of the principal chemical reaction (R1), different results have been obtained, both in the selectivity and the yield of the process.

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List of symbols

$A_a, B_a, C_a, D_a, E_a, F_a$	constants of Antoine's equation	
A_{ij}, B_{ij}	binary coefficients in Wilson's activity model	
A_L, B_L, C_L, \dots	constants of polynomial series used for the molar heat capacity of the liquid phase computation; the unit depends on the form of the polynomial	
A_V, B_V, C_V, \dots	constants of polynomial series used for the molar heat capacity of the vapour phase computation; the unit depends on the form of the polynomial	
C	molar concentration	mol.m^{-3}
C_{pL}	liquid molar heat capacity	$\text{J.mol}^{-1}.\text{K}^{-1}$
C_{pV}	vapour molar heat capacity	$\text{J.mol}^{-1}.\text{K}^{-1}$
E	activation energy of chemical reaction	J.mol^{-1}
E_y^M	Murphee's stage efficiency	
H_L	molar enthalpy of the liquid stream	J.mol^{-1}
H_{LD}	molar enthalpy of the liquid reflux stream	J.mol^{-1}
H_L^o	molar enthalpy of the pure liquid material	J.mol^{-1}
H_V	molar enthalpy of vapour stream	J.mol^{-1}
H_V^o	molar enthalpy of pure vapour material	J.mol^{-1}
$\Delta_r H$	reaction enthalpy	J.mol^{-1}
$\Delta_{vap} H^o$	heat of vaporisation of pure material	J.mol^{-1}
k_V	reaction rate constant in the reaction volume unit; dimension depends on the form of the reaction rate equation	
k_{Voo}	pre-exponential factor; dimension depends on the form of the reaction rate equation	
m	last stage (reboiler)	
\dot{m}_P	steam mass flow rate	kg.h^{-1}
n	number of the stage	
\dot{n}	molar flow rate	mol.s^{-1}
N_{TOP}	number of the first reactive stage	
N_{BTM}	number of the last reactive stage	
N_i	number of species	
N_r	number of reactions	
P	pressure	Pa
P^o	vapour pressure of pure component	Pa
\dot{Q}_K	heat removed in the condenser	J.s^{-1}
\dot{Q}_r	heat released by chemical reactions	$\text{J.s}^{-1}.\text{m}^{-3}$

R	gas constant	$\text{J.mol}^{-1}.\text{K}^{-1}$
R_X	reflux ratio	
T	thermodynamics temperature	K
$V_i^{(l)}$	molar volume of the i -th liquid component	$\text{m}^3.\text{mol}^{-1}$
V_R	reaction mixture volume	m^{-3}
x	molar ratio in the liquid phase	
y	molar ratio in the vapour phase	
z	chemical reaction source	$\text{mol.s}^{-1}.\text{m}^{-3}$
• Greek letters		
γ	activity coefficient in the liquid phase	
λ_{ij}	energy of interaction of the i -th with the j -th component	
A_{ij}	Wilson's parameter	
$\nu_{j,i}$	stoichiometric coefficient of the i -th component in the j -th reaction	
$\dot{\xi}_V$	chemical reaction rate in the volume unit	$\text{mol.s}^{-1}.\text{m}^{-3}$
• Subscripts		
0	indication of condenser	
$1,2, \dots$	number of stage	
D	distillate	
F	feed	
i	component labelling	
j	reaction labelling res. identification of the second component in Wilson's model	
L	liquid phase	
LD	reflux	
m	last stage (reboiler)	
n	current number of stage	
NS	number of stage	
V	vapour phase	
W	distillation rest	
• Superscripts		
g	gas phase	
l	liquid phase	
ND	number of drains	
NF	number of feeds on the stage	
Ni	number of compounds	
Nr	number of chemical reactions	
o	pure material	
• List of abbreviations		
DCP	dichloropropane	$\text{ClCH}_2\text{ClCH}_2\text{CH}_3$
PCH	propylene chlorohydrine	$\text{CH}_3\text{CHClCH}_2\text{OH}$
$PGLY$	propylene glycol	$\text{CH}_3\text{CH}_2\text{OHCH}_2\text{OH}$
POX	propylene oxide	$\text{CH}_3(\text{CH}_2\text{CH}_2)\text{O}$
RD	reactive distillation	
W	water	H_2O

References

- [1] Taylor R., Krishna R., Modelling reactive distillation, Chemical Engineering Science, 55, (2000), 5183-5229
- [2] Carrá, S., Santacesaria, E., Morbidelli, M., Cavalli, L., Synthesis of propylene oxide from propylene chlorohydrins – 1. Kinetics aspects of the process, Chemical Engineering Science, 34, (1979), 1123-1132
- [3] Markoš, J., Jelemenský, L., Kotora, M., Technical report of the Contract No.47/04 for NCHZ, Inc., 2004
- [4] Reid, R.,C., Prausnitz, J., M., Poling, R., E., The Properties of Gases and Liquids, McGraw – Hill Book Comp., New York, 1989
- [5] Šoóš, M., Graczová, E., Markoš, J., Molnár, A., Steltenpohl, P., Design and simulation of a distillation column for separation of dichloropropane from a multicomponent mixture, Chemical Engineering and Processing, 2003, 42, 273 – 284