A Systematic Approach on the Dynamic Modelling of Reactive Distillation Processes with Potential Liquid Phase Splitting. Building-up the improved PHSP simulation model. II

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As shown in the first part of our work [1], this paper deals with the presence of a three-phase regime (vapour-liquid-liquid) on the reactive distillation (RD) column stages due to a liquid liquid phase splitting (PHSP) between aqueous and organic phases. Special attention has to be paid on this subject, because detecting the three phase regime can lead to different operating and design strategies for RD columns. In this second part of the paper, the authors present in detail their original modeling approach which detects the existence of phase splitting in RD columns. Its hybrid software implementation is composed from a classical model (pseudo-homogeneous, previously presented) in connection with a robust phase splitting algorithm (based on the homotopy-continuation method), performed at each simulation step. By using the proposed model instead of the classical one (with no phases separation – NPHSP), important improvements in terms of simulated system behaviour and results accuracy are obtained.

Keywords: reactive distillation; phase splitting; nonlinear model; continuation

The first part of this paper emphasized the importance and advantages of the combined approach between reaction and separation by distillation through the reactive distillation (RD) processes: efficiency (with respect to conventional process design) and low costs (from design to normal operation) [2-6]. But their nonlinear dynamic behaviour can be a serious obstacle when trying to implement such a technology in real plants [7-9]. This is why significant dynamic simulation studies have to be performed in order to understand the process and take all benefits that RD may provide.

To build-up a realistic simulation tool, a relevant mathematical model is strongly needed. At this point, any suitable model must take into account the potential liquid-liquid phase splitting on RD column stages, because this is the only way to obtain a pertinent behavioral description of such a complex system [9, 10]. Because the classical NPHSP mathematical model was already subject of the first part, here we present only its extension to our originally robust PHSP form. As previously mentioned, this work intends to be a guideline on how a classical model (with no phase splitting) can be transformed into the more realistic one (phase-splitting-based). This is the reason why all required steps will be adequately detailed and extensively commented from our own perspective.

The mathematical PHSP model for reactive distillation processes

Because there are many situations when the classical approach in RD modeling is not satisfactory, an extension of the NPHSP model to a new form, which takes into account the potential liquid-liquid splitting (PHSP) on the column trays, is strongly required.

In our works, the phase splitting algorithm is separately approached, being externally performed in a separate software procedure which is called by the main code at each simulation step [2, 7-9]. Practically, the main code solves a model relatively close to the "classical" one (without phase splitting) – in terms of global compositions – and calls the external routine in order to get the right information about the two liquid phases compositions. The external routine reads its inputs from main code (global compositions on trays, temperatures and the needed parameters to perform the phase splitting algorithm) and replies with data mainly about phases compositions and ratios [2, 7-9]. The great advantage of using this mechanism is that it provides a relative independency between those two models (RD column model and phase splitting algorithm), which allows changing one without affecting the other when the same data exchange protocol is respected [10].

Figure 1 shows an alternative diagram for the reactive distillation column. We call it "alternative" because it tries to emphasize some imposed characteristics for the new built model, which are not present (or are present in a different manner) in the classical model.
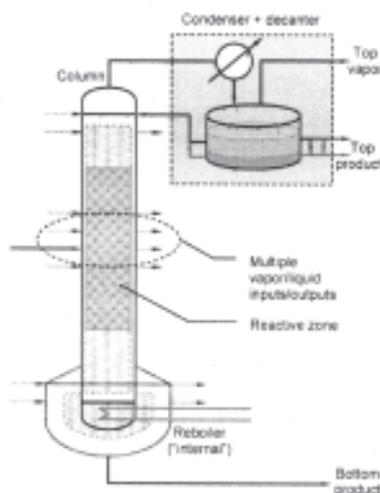

Fig. 1. Alternative representation for a reactive distillation column [8]

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From top to bottom, a slightly changed structure at the top can be observed. First, the decanter now contains two liquid phases, an "organic" one and an "aqueous" one. Second, different reflux and top products may be chosen: pure phase 1, pure phase 2 or a mixture between them. As a conclusion, the model for the combined system condenser + decanter is slightly different from the previous one, especially because it reflects the new way to calculate streams compositions. Another change is that there is a more flexible policy in placing external feeds/sidedraws: now it is possible to handle these material streams everywhere, including the column bottom (even to feed the column through reboiler!). One exception applies, the condenser being unapproachable in this manner. A more important change is at the column bottom: we propose to combine the model for continuous distillation with batch distillation. This allows switching between those two cases via some model structural parameters. It implies the modeling of variable holdup in the reboiler (which is regarded now as an "internal" one), with an appropriate strategy for the structural exchange between continuous and batch reactive distillation.

For the new model, the following assumptions are considered:
- the column has NSTAGE theoretical stages, including the assembly condenser + decanter and the reboiler;
- the liquid (molar) holdup on all trays and decanter is constant (while at the bottom it is variable), the vapor holdup on trays being neglected;
- the energy balance is not taken into account – so the vapour flow is constant from stage to stage (only feeds and/or sidedraws could change these flowrates);
- the vapour and liquid phases on each tray are in equilibrium;
- the reaction takes place only in liquid phases, where there is a perfect mixture between reactants and catalyst; Furthermore, the catalyst has the same concentration in both liquid phases (uniform distribution between them);
- akinetic expression for the reaction rate R is known;
- the combined system condenser + decanter is operated at the boiling point.

The column top ("tray" 1)
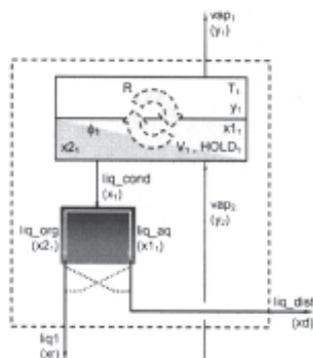In figure 2, a schematic representation for the column top (condenser + decanter) is detailed.

Fig. 2. Schematic representation for the column top – new approach

The two-phase regime is represented by a different filled surface for the liquid. In this case, there is one common stream, the condensed liquid (liq_cond), which is then separated in decanter in two other streams: organic (liq_org) and aqueous (liq_aq). There are cases when emergent streams are not these "pure" liq_org and liq_aq (a mixture between them is possible), so the figure indicates this fact through "dotted mixing lines", which suggest that liq1 (reflux) and liq_dist (considering this as

the only distillate) may have different compositions, xr respectively xd.

In this case, the mathematical model consists in the following equations.

Component material balance:

$$HOLD_1 \frac{dx_{i,1}}{dt} = vap_2 \cdot y_{i,2} - liq\_cond \cdot x_{i,1} - vap_1 \cdot y_{i,1} +$$
$$+ \nu_i \cdot \left[(1 - \Phi_1) \cdot R(x1_{1,1},...,x1_{NC,1}) + \Phi_1 \cdot R(x2_{1,1},...,x2_{NC,1})\right] \cdot V_1 \quad i = 1,...,NC \tag{1}$$

As presented in [8], we consider a global reaction rate R, which is the linear combination between the reaction rate in phase 1 and the reaction rate in phase 2, taking into account the phases ratio. If the liquid phase splitting does not occur, then the compositions in both phases are equal and the reaction ratios are identical. As a remark, such a linear expression $\left[(1 - \Phi_1) \cdot R(x1_{1,1},...,x1_{NC,1}) + \Phi_1 \cdot R(x2_{1,1},...,x2_{NC,1})\right]$ may be a little simplified when an equal catalyst distribution in both liquid phases is considered [6, 8].

Summation condition for global liquid phase compositions:

$$\sum_{j=1}^{NC} x_{j,1} = 1 \tag{2}$$

Compositions in liquid phase 1:

$$a_{x1} \frac{dx1_{1,i}}{dt} = -x1_{1,i} + x1_{1,i}^{PSA} \quad i = 1,...,NC \tag{3}$$

The value $x1_{1,i}^{PSA}$ is obtained through the external subroutine implementing the phase splitting algorithm, as previously mentioned. By using such a model, any simulation engine may often encounter serious difficulties when some large magnitude changes occur in $x1_{1,i}^{PSA}$ value. Usually, the integration (simulation) step cannot be properly adjusted, since there is no strong control over the external procedure. A robust solution we have found is represented by a low pass filter. The time constant a_{x1} should be regarded as a fine tuning parameter for the model and has to be carefully chosen, according to the system intrinsic dynamic behaviour. The same principle extends to equations describing the compositions in the second liquid phase and, respectively, the phase ratio. After many simulation tests, the authors have found that values somewhere around 100…1000 times less than the minimum system time constant are satisfactory.

Compositions in liquid phase 2:

$$a_{x2} \frac{dx2_{1,i}}{dt} = -x2_{1,i} + x2_{1,i}^{PSA} \quad i = 1,...,NC \tag{4}$$

Phase ratio:

$$a_{\Phi} \frac{d\Phi_1}{dt} = -\Phi_1 + \Phi_{1,i}^{PSA} \tag{5}$$

Phase equilibrium:

$$y_{i,1} \cdot p = \eta \cdot psp_i \cdot \gamma 1_{i,1} \cdot x_{i,1} \quad i = 1,...,NC \tag{6}$$

Summation condition for vapor phase compositions:

$$\sum_{j=1}^{NC} y_{j,1} = 1 \tag{7}$$

Total material balance:

$$0 = -liq\_cond + vap_2 - vap_1 +$$
$$+ \sum_{j=1}^{NC} \left[\nu_j \cdot \left[(1 - \Phi_1) \cdot R(x1_{1,1},...,x1_{NC,1}) + \Phi_1 \cdot R(x2_{1,1},...,x2_{NC,1})\right] \cdot V_1\right] \tag{8}$$

Decanter equations:

$$liq\_org = \Phi_1 \cdot liq\_cond$$
$$liq\_aq = liq\_cond - liq\_org$$
$$liq\_dist = liq\_cond - liq_1 \qquad (9)$$

Free variables:

$$vap_1 = \ldots user\ given \ldots \ (liq_1 = \ldots user\ given \ldots) \qquad (10)$$

As in the case of the classical approach, these two variables may be freely specified by the user, but not simultaneously (because they are both part of the total material balance equation).

Top product and reflux composition:

$$xr_i = \ldots given\ after\ re\text{-}mixing\ organic\ and\ aqueous\ phases\ldots$$
$$i = 1,\ldots,NC)$$
$$xd_1 = \ldots given\ after\ re\text{-}mixing\ organic\ and\ aqueous\ phases\ldots$$
$$i = 1,\ldots,NC) \qquad (11)$$

For maximum flexibility, the model must be able to permit various reflux policies. For example, the reflux may be chosen as follows:
- a global reflux, having the global $x_{i,1}$ composition, when its maximum flowrate is limited to the condensed liquid flowrate, liq_cond;
- pure phase 1 reflux, having $x1_{i,1}$ composition, when its maximum flowrate liq_1 is limited to the phase 1 (supposed aqueous) liquid flowrate, liq_aq;
- pure phase 2 reflux, having $x2_{i,1}$ composition, when its maximum flowrate liq_1 is limited to the phase 2 (supposed organic) liquid flowrate, liq_org;
- mainly phase 1 reflux, when its maximum flowrate liq_1 is limited to liq_cond; it has $x1_{i,1}$ composition because liq_1 is set by the user as $liq_1 < liq\_aq$, or a different composition if liq_1 is set greater than liq_aq (when $liq_1 >$ liq_aq, the reflux contains some organic phase too);
- mainly phase 2 reflux, when its maximum flowrate liq_1 is limited to liq_cond; it has $x2_{i,1}$ composition because liq_1 is set by the user as $liq_1 < liq\_org$, or a different composition if liq_1 is set greater than liq_org (when $liq_1 >$ liq_org, the reflux contains some aqueous phase too).

The regular stage (tray "k")
As shown in figure 3, the schematic representation for the tray indicates only one major change, by taking into account the liquid phase splitting. The model is as follows:
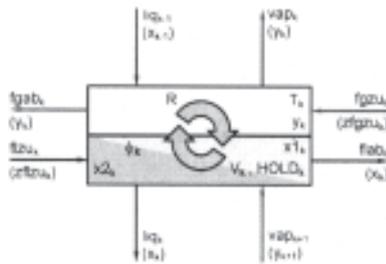
Fig. 3. Schematic representation for a regular stage – new approach [8]

Component material balance:

$$HOLD_k \frac{dx_{i,k}}{dt} = liq_{k-1} \cdot x_{i,k-1} + vap_{k+1} \cdot y_{i,k+1} - liq_k \cdot x_{i,k} - vap_k \cdot y_{i,k} +$$
$$+ flzu_k \cdot zflzu_{i,k} + fgzu_k \cdot zfgzu_{i,k} - flab_k \cdot x_k - fgab_k \cdot y_k +$$
$$+ \nu_i \cdot \left[(1-\Phi_k) \cdot R(x1_{1,k},\ldots,x1_{NC,k}) + \Phi_k \cdot R(x2_{1,k},\ldots,x2_{NC,k}) \right] \cdot V_k$$
$$i = 1,\ldots,NC-1 \qquad (12)$$

Summation condition for global liquid phase composition:

$$\sum_{j=1}^{NC} x_{j,k} = 1 \qquad (13)$$

Compositions in liquid phase 1:

$$a_{x1} \frac{dx1_{k,i}}{dt} = -x1_{k,i} + x1_{k,i}^{PSA}$$
$$i = 1,\ldots,NC \qquad (14)$$

Compositions in liquid phase 2:

$$a_{x2} \frac{dx2_{k,i}}{dt} = -x2_{k,i} + x2_{k,i}^{PSA} \qquad i = 1,\ldots,NC \qquad (15)$$

Phase ratio:

$$a_\Phi \frac{d\Phi_k}{dt} = -\Phi_k + \Phi_{k,i}^{PSA} \qquad (16)$$

Phase equilibrium:

$$y_{i,k} \cdot p = \eta \cdot psp_i \cdot \gamma1_{i,k} \cdot x_{i,k} \qquad i = 1,\ldots,NC \qquad (17)$$

Summation condition for vapour phase compositions:

$$\sum_{j=1}^{NC} y_{j,k} = 1 \qquad (18)$$

Total material balance for the liquid phase:

$$0 = liq_{k-1} - liq_k + flzu_k - flab_k +$$
$$+ \sum_{j=1}^{NC} \left[\nu_j \cdot \left[(1-\Phi_k) \cdot R(x1_{1,k},\ldots,x1_{NC,k}) + \Phi_k \cdot R(x2_{1,k},\ldots,x2_{NC,k}) \right] \cdot V_k \right] \qquad (19)$$

Total material balance for the liquid phase:

$$vap_k = vap_{k+1} \qquad (20)$$

The column bottom ("tray" NSTAGE)
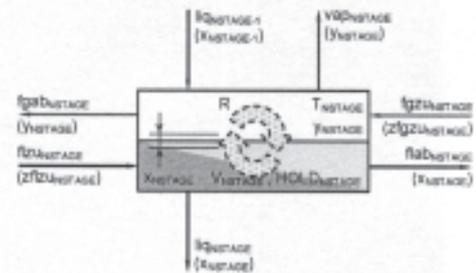Figure 4 depicts a schematic representation for the column bottom (the reboiler).

Fig. 4. Schematic representation for the column bottom – new approach

Component material balance:

$$HOLD_{NSTAGE} \frac{dx_{i,NSTAGE}}{dt} = liq_{NSTAGE-1} \cdot x_{i,NSTAGE-1} -$$
$$- liq_{NSTAGE} \cdot x_{i,NSTAGE} - vap_{NSTAGE} \cdot y_{i,NSTAGE} +$$
$$+ flzu_{NSTAGE} \cdot zflzu_{i,NSTAGE} + fgzu_{NSTAGE} \cdot zfgzu_{i,NSTAGE} -$$
$$- flab_{NSTAGE} \cdot x_{NSTAGE} - fgab_{NSTAGE} \cdot y_{NSTAGE} +$$
$$+ \nu_i \cdot \left[(1-\Phi_{NSTAGE}) \cdot R(x1_{1,NSTAGE},\ldots,x1_{NC,NSTAGE}) + \right.$$
$$+ \Phi_{NSTAGE} \cdot R(x2_{1,NSTAGE},\ldots,x2_{NC,NSTAGE}) \left] \cdot V_k - \right.$$
$$- x_{i,NSTAGE} \cdot RHS\_TMB_{NSTAGE} \qquad i = 1,\ldots,NC-1$$
$$(21)$$

Summation condition for global liquid phase composition:

$$\sum_{j=1}^{NC} x_{j,NSTAGE} = 1 \qquad (22)$$

Compositions in liquid phase 1:

Compositions in liquid phase 1:

$$a_{x1} \frac{dx1_{NSTAGE,i}}{dt} = -x1_{NSTAGE,i} + x1_{NSTAGE,i}^{PSA}$$

$$i = 1,...,NC \qquad (23)$$

Compositions in liquid phase 2:

$$a_{x2} \frac{dx2_{NSTAGE,i}}{dt} = -x2_{NSTAGE,i} + x2_{NSTAGE,i}^{PSA}$$

$$i = 1,...,NC \qquad (24)$$

Phase ratio:

$$a_{\Phi} \frac{d\Phi_{NSTAGE}}{dt} = -\Phi_{NSTAGE} + \Phi_{NSTAGE,i}^{PSA} \qquad (25)$$

Phase equilibrium:

$$y_{i,NSTAGE} \cdot p = \eta \cdot psp_i \cdot \gamma1_{i,NSTAGE} \cdot x_{i,NSTAGE}$$

$$i = 1,...,NC \qquad (26)$$

Summation condition:

$$\sum_{j=1}^{NC} y_{j,NSTAGE} = 1 \qquad (27)$$

Total material balance for the liquid phase:

$$\frac{dHOLD_{NSTAGE}}{dt} = liq_{NSTAGE-1} - liq_{NSTAGE} - vap_{NSTAGE} + flzu_{NSTAGE} + fgzu_{NSTAGE} +$$

$$+ \sum_{j=1}^{NC} [\nu_i \cdot [(1-\Phi_{NSTAGE}) \cdot R(x1_{1,NSTAGE},...,x1_{NC,NSTAGE}) +$$

$$+ \Phi_{NSTAGE} \cdot R(x2_{1,NSTAGE},...,x2_{NC,NSTAGE})] \cdot V_k] = RHS\_TMB_{NSTAGE} \qquad (28)$$

Equation for liq_{NSTAGE} (with different for continuous and batch distillation):

$$RHS\_TMB_{NSTAGE} = 0 \quad \text{(cont. case)} \quad \text{or} \quad liq_{NSTAGE} = 0 \text{ (batch case)} \qquad (29)$$

Free variable:

$$vap_{NSTAGE} = ...user\ defined...$$

$$i = 1,...,NC \qquad (30)$$

Notes on the phase splitting algorithm

To illustrate how the phase splitting algorithm works, we will extensively refer to (and quote from) the open literature, with emphasis on [10, 11]. Also, for more specific aspects and comments on the algorithm, the reader may consult our paper [9].

First, the phase splitting algorithm, as previously mentioned, is performed separate from the main model, in a dedicated software routine. To be more specific, this routine runs almost independently, at each simulation (integration) step, checking the state of all distillation stages and returning (especially) the phases compositions and ratio to the main model. Before running, the algorithm also takes some mandatory information from the main model, for instance the overall compositions, the stages temperatures, the needed parameters for the vapour-liquid(-liquid) equilibrium calculation and algorithm "tuning parameters" (i.e. starting points for the internal continuation algorithm) [9]. Second, we need to emphasize that Marquardt's method is a hybrid one, meaning it uses a-priori knowledge of phase diagram properties in order to tune the computational algorithm [2]. The flash calculation is decomposed in two steps: a "pre-processing" step and the "computational" one.

In the first step, all heterogeneous regions of the system at the specified pressure and boiling temperature are divided into convex regions and, for each region, one reference state inside it, $[x^{START}, x1^{START}, x2^{START}, y^{START}, \Phi^{START}, p^{START}, T^{START}]$ is stored. The state variables are: the overall composition, compositions in both liquid phases, vapour composition, phase ratio, pressure and temperature. Typically, this pre-processing procedure is required only once, before simulations. In the literature it is stated that, because the phase diagrams are involved only during the process design, the information on the heterogeneous region existence may be directly provided by user (at least for mixture with up to four components) [2, 9, 10].

In the next step, the homotopy method is used to solve a difficult problem by starting from a simple problem to which a solution is already known [10, 12-15]. In our case, the hard part is the search for the non-trivial two-phase solution (the two phases compositions and ratio) for an arbitrary overall composition x, while for the simple problem we know the solution for a binary mixing gap having the composition x^{START}. By parameterizing the overall composition x with a continuation parameter λ, the overall composition can be changed from the starting composition to the composition for which the phase splitting behaviour has to be checked:

$$\bar{x}_i = \lambda \cdot x_i + (1-\lambda) \cdot x_i^{START} = \bar{x}_i(\lambda). \qquad (31)$$

λ is the continuation parameter and its value is changed from 0 to 1 when the continuation is performed. It can be observed that:

$$\bar{x}_i(0) = x_i^{START} \text{ and } \bar{x}_i(1) = x_i \qquad (32)$$

The homotopy continuation algorithm is based on another repetitive two-step process. The "correction step" involves the following equations [9,10]:
Mass balances (as constraints):

$$x1_i \cdot (1-\Phi) + x2_i \cdot \Phi = \bar{x}_i(\lambda) \qquad i = 1,...,NC \qquad (33)$$

Activity difference equations (as necessary conditions):

$$x1_i \cdot \gamma1_i - x2_i \cdot \gamma2_i = 0 \qquad i = 1,...,NC \qquad (34)$$

and
The summation equation (as constraint)

$$1 - \sum_{i=1}^{NC} x1_i = 0 \quad (\text{or } 1 - \sum_{i=1}^{NC} x2_i = 0). \qquad (35)$$

The equations (31)...(35) involve the overall composition x at a particular λ value. All the annotations are the same (with an exception: the tray index "*k*" is intentionally omitted for a better equations understanding).

In the second step ("predictor step"), an estimate of the solution to equations (33), (34) and (35) for a new value of λ is estimated using [10]:

$$\theta_{i,s+1} = \theta_{i,s} + \Delta\theta_i = \theta_{i,s} + \frac{d\theta_i}{d\lambda} \Delta\lambda. \qquad (36)$$

In this equation, θ_i denotes an element of the solution vector. In the case studied by Bausa and Marquardt [11], this solution vector contains 2NC mole fractions (*x1* and *x2*) and the ratio Φ. According to them, the computation of the gradient with respect to λ can either be done analytically or numerically. The algorithm continuously alternates the prediction and correction steps while λ increases from 0 to 1 (trying this way to reach the desired composition, *x*) [11]. In systems with multiple binary pairs

leading to phase splitting phenomenon, multiple starting compositions must be used in order to obtain the correct solution. In the quoted author's view, this is due to the fact that the trajectory which connects x^{START} with x, described by (31), might intersect a region of one-phase behaviour between the two-phase starting and ending points [11]. As Bausa and Marquardt show in their paper, this approach is very successful in finding the correct solution very quickly and with a high reliability [11].

However, in our view, Bausa's and Marquardt's original implementation has a big drawback: although the system has only NC degrees of freedom, the solution vector θ has 2NC+1 components! In this way, the computational time significantly increases. This is why we decided to use a slightly modified method, developed by Steyer, Flockerzi and Sundmacher and extensively presented in their quoted paper [10]. In order to reduce the number of equations and variables to the number of degrees of freedom, this method introduces the so-called "phase partitioning coefficients" which becomes the elements of the parameterized (solution) vector θ:

$$\theta_i = \frac{n1_i}{n1_i + n2_i} \quad . \tag{37}$$

Here, $n1_i$ and $n2_i$ denote the molar amounts of the "i" component in the phase 1 and 2, respectively. In this case, the θ_i represents the fraction of component i being present in phase 1. Each θ_i is limited to the range from 0 to 1. If these fractions are known for all substances involved as well as the overall composition, the phases' mole fractions are given by [10]:

$$x1_i = \frac{\theta_i \cdot n_i^{TOTAL}}{\sum_{j=1}^{NC}(\theta_j \cdot n_j^{TOTAL})}, \quad x2_i = \frac{(1-\theta_i) \cdot n_i^{TOTAL}}{\sum_{j=1}^{NC}(\theta_j \cdot n_j^{TOTAL})}. \tag{38}$$

Steyer, Flockerzi and Sundmacher reveal the advantage of this approach: when restating the equations in these new variables, the mass balances (33) and summation equations (35) are always fulfilled, reducing the system to NC activity difference equations (34) with the remaining NC θ_i variables [10].

As the same authors show, the correction step is based on Newton-type iteration. During this iteration, the following equation system has to be solved:

$$\theta_{s+1} = \theta_s - J^{-1}(f(\theta_s)) \cdot f(\theta_s). \tag{39}$$

In this equation, J is the Jacobian matrix of the restated system based on equation (34), denoted here as f. To avoid having to invert the Jacobian matrix, the equivalent linear equation system must be solved [9, 10]. In equation (39), the Jacobian matrix has to be differentiated with respect to θ instead of x. For a fast and reliable solution, the Jacobian should be computed analytically since the equation system is highly non-linear. According to Steyer, Flockerzi and Sundmacher, having in mind the rather complex nature of the equations used to compute γ_i – as, e.g. the NRTL (or UNIQUAC) equation – the derivation of the analytical Jacobian matrices with respect to θ_i would be a lengthy process which may lead to errors. For this reason, the following transformation was applied [10]:

$$\frac{\partial \gamma_i}{\partial \theta_j} = \gamma_i \frac{\partial \ln(\gamma_i)}{\partial \theta_j} = \gamma_i \sum_{k=1}^{NC} \frac{\partial \ln(\gamma_i)}{\partial x_k} \cdot \sum_{l=1}^{NC-1} \frac{\partial x_k}{\partial x_l} \cdot \frac{\partial x_l}{\partial \theta_j}. \tag{40}$$

The change in the derivative to the logarithmic form was done because many activity coefficient models compute this logarithm directly. The step of differentiating x_k with respect to x_l has to be introduced because of the constraint $\sum_{k=1}^{NC} x_k = 1$. The $l=1,...,NC-1$ independent mole fractions are denoted as x_l.

Results and discussions

In order to use the model above, based on the presented simplifying assumptions, the first (and compulsory!) step was to validate it. Such a procedure is detailed in our previous work [2], where we considered a homogeneously catalyzed RD column also used by Brüggemann, Oldenburg, Zhang and Marquardt in their studies [16]. We have shown that the phase splitting algorithm (in the form adapted by Steyer, Flockerzi and Sundmacher) unambiguously detects the liquid-liquid splitting phenomenon. Regarding the heterogeneously catalyzed RD processes, our model cannot be "classically" validated in the phase splitting regime because alternative literature data are not available. However, even in this case, as shown in [8], there are serious reasons making us believe that our modeling approach is more than appropriate at least for the following qualitative-quantitative investigations. Moreover, all dynamic studies we have already performed are in good agreement with both the objective data at our disposal and similar research results announced in the open literature [2, 7-9].

As we have mentioned before, by omitting the potential liquid-liquid separation, the RD model can lead to erroneous responses when it is used for dynamic simulations. In order to prove this statement we decided to make an experiment, by investigating a hypothetic transient regime which may appear when, for a particular RD process, the mathematical model changes from PHSP form (with phase splitting detection) to NPHSP form (with no phase splitting taken into account).

For this case study we configured our model for an RD column used for acetic acid (AcH) recovery from waste water through esterification with n-butanol (BuOH). In this case a value-added ester (butyl acetate BuAc) is formed and, if the process is adequately operated, almost pure water can be withdrawn [2].

This 22-trays RD column (with the standard structure in figure 1) accepts a totally refluxed organic phase (separated in decanter after condensation) so that the top product is the aqueous phase. As expected, the organic phase constitutes the bottom product. By taking into account the same experimental frame as in our work [2], the column feed on tray number 8 is a mixture of unpurified water (with AcH) and butanol (in excess, the mole ratio AcH:BuOH being 1:2). The total feed flowrate is 0.00675 kmol/h and the liquid holdup is 2×10^{-4} m^3 (considered constant on each stage). The reactive zone (heterogeneous type) is located below the 8th tray, considering a catalyst load of 0.0024 kg per tray.

For this chemical system it is known that binary pairs of BuOH-water and BuAc-water exhibit miscibility gaps and, in this situation, liquid-liquid phase splitting phenomenon can appear when a particular concentration of water, BuOH and/or BuAc is met [9]. Moreover, because a large amount of water feeds the column, it is expected that on trays located near the feed position these miscibility conditions are fulfilled and, consequently, the liquid will split into two liquid phases (as depicted in fig. 5).

As a consequence of the phase splitting phenomenon, the components activities on the implied trays severely differ from those calculated by using the NPHSP model, this also leading to significant differences in reaction rates calculated with PHSP and NPHSP models.
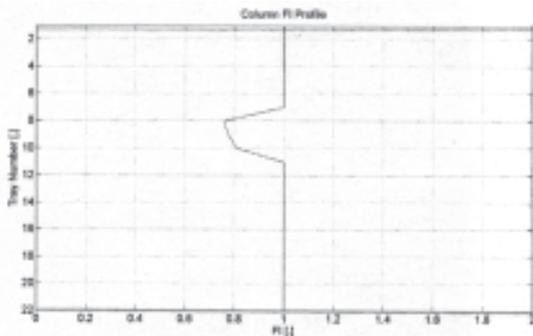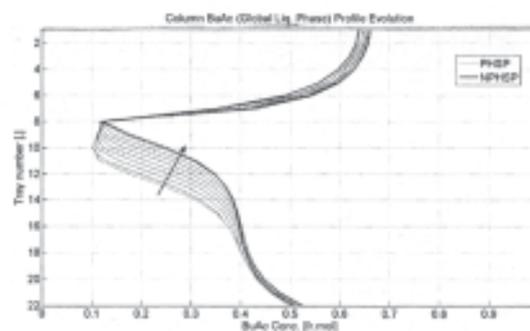
Fig. 5. Φ(FI) profile along the column.

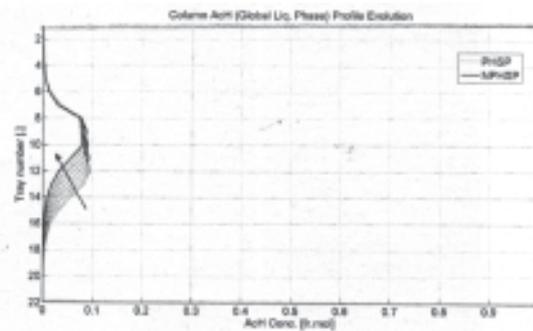Fig. 8. BuAc profile evolution (from PHSP to NPHSP)

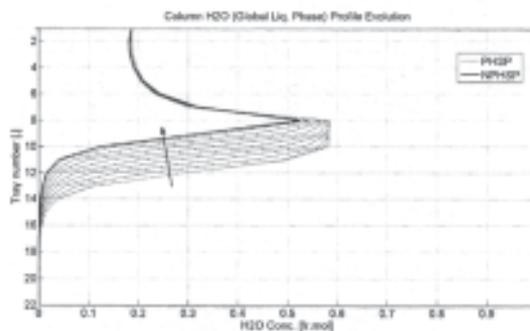Fig. 6. AcH profile evolution (from PHSP to NPHSP)

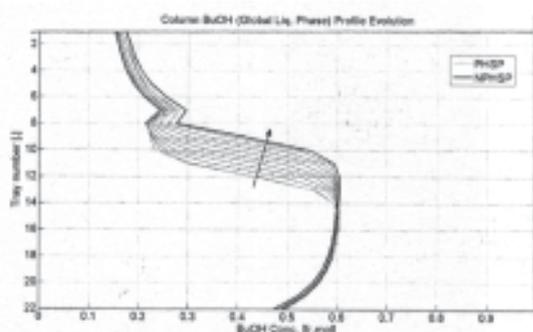Fig. 9. Water profile evolution (from PHSP to NPHSP)
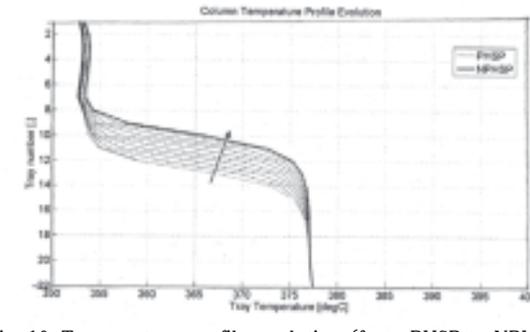

Fig. 7. BuOH profile evolution (from PHSP to NPHSP)

Fig. 10. Temperature profile evolution (from PHSP to NPHSP)

Our proposed "dynamic experiment" assumes that, initially, the system (in steady state regime) is described by the PHSP model. Then, by keeping constant all incident and emergent streams flowrates (as well as the feed composition) the model switches to its NPHSP form. A transient regime appears until a new steady state is reached.

By analyzing the column parameters evolutions, severe drifts between the initial and final steady states and their associated profiles can be observed, especially near the lower part of the column (below the feed tray). Figures 6-9 depict these evolutions in terms of AcH, BuOH, BuAc and water mole fractions in the global liquid phase, respectively.

The arrows indicate how the profiles move from the initial state (PHSP model – light gray line) to the final state (NPHSP model – dark gray line). We can observe that the NPHSP model wrongfully predicts these compositions below the feed position (tray 8), the most critical point being somewhere around tray 12. Here, for instance, AcH mole fraction drops from 0.1 (PHSP) to 0.04 (NPHSP), BuOH increases from 0.43 (PHSP) to 0.6 (NPHSP), BuAc increases from 0.17 (PHSP) to 0.34 (NPHSP) while water dramatically drops from 0.3 (PHSP) to 0.02 (NPHSP).

As shown in figure 10, the temperature profile also changes in the lower part of the column. On the same tray 12, for instance, we notice a serious error of +17 ^{0}C

between the values returned by the PHSP and NPHSP model, respectively.

By summarizing the observations above, we can say that, in this particular case, by using the classical modeling approach (NPHSP) the results' accuracy is seriously affected, while our new model (PHSP) gives a better image on process intimacy, leading to more precise results.

Of course, one can say that such a remark only applies if a particular RD system operates very close to the liquid-liquid phase splitting regime. This is true, but we can also state that it is very hard to precisely predict when such a complex system meets the conditions to enter this regime.

Conclusions

The intrinsic RD complexity, its various operating strategies (and also some unexpected disturbances) may easily lead the process to a hard-predictable state where the phase splitting occurs. In this respect, we strongly believe that it is always better to use the proposed PHSP model, as an important prerequisite in obtaining accurate simulation results.

Nomenclature
a - time constant
f - function vector to be solved to 0
fgab - vapor sidedraw molar flowrate
fgzu - external vapor feed molar flowrate
flab - liquid sidedraw molar flowrate
flzu - external liquid feed molar flowrate
HOLD- molar liquid holdup on tray
J - Jacobian matrix
liq - internal liquid molar flowrate
NC - number of components
p - pressure
psp - saturation pressure in the vapour phase
R - reaction ratio
T - temperature
vap - internal vapor molar flowrate
V - volumetric liquid holdup on tray
x - mole fraction, liquid (global)
*x*1 - mole fraction, liquid (phase 1)
*x*2 - mole fraction, liquid (phase 2)
y - mole fraction, vapor phase
zflzu - mole fraction in external liquid feed
zfgzu- mole fraction in external vapour feed

Greek letters
γ1 - activity coefficient (phase 1)
γ2 - activity coefficient (phase 2)
η - tray efficiency
θ - solution vector
λ - continuation parameter
ν - stoichiometric coefficient
Φ - phases ratio

Superscripts
CRIT - critical point of the miscibility gap
PSA - *P*hase *S*plitting *A*lgorithm
START - reference state

Subscripts
i - component indices
k - tray number
m - variable indices (for solution vector)

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