

# DYNAMIC SIMULATION OF REACTIVE DISTILLATION PROCESSES WITH LIQUID-LIQUID PHASE SPLITTING

Gabriel Rădulescu<sup>1</sup>, Jignesh Gangadwala<sup>2</sup>, Achim Kienle<sup>2,3</sup>  
Frank Steyer<sup>2</sup>, Kai Sundmacher<sup>2,4</sup>

<sup>1</sup> Control Engineering and Computers Department  
Petroleum – Gas University of Ploiești, Romania  
E-mail: gabriel.radulescu@mail.upg-ploiesti.ro

<sup>2</sup> Max-Planck-Institut für Dynamik komplexer technischer Systeme,  
Magdeburg, Germany

<sup>3</sup> Lehrstuhl für Automatisierungstechnik und Modellbildung  
Otto-von-Guericke-Universität Magdeburg, Germany

<sup>4</sup> Lehrstuhl für Systemverfahrenstechnik  
Otto-von-Guericke-Universität Magdeburg

**Abstract:** This paper presents a modern modeling approach for reactive distillation processes with potential phase splitting. It is based on a classical model (pseudo-homogeneous) in connection with a robust and reliable phase splitting algorithm (through homotopy-continuation method), performed at each simulation step. Model validation stage and a simple case-study (by applying the new approach to a reactive distillation column for waste water treatment) are also presented. All simulation scenarios revealed a good agreement between simulation results and the real system behavior, much better than using a classical pseudo-homogeneous mathematical model.  
*Copyright © 2006 IFAC*

**Keywords:** phase splitting, homotopy continuation, reactive distillation, modeling and dynamic simulation.

## 1. INTRODUCTION

As previously known, the reactive distillation (RD) process integrates chemical reaction and separation by distillation in a single processing unit. This structural approach has a big economical advantage over the conventional process designs, where reaction and separation are carried out in different processing units (Gangadwala, *et al.*, 2003; Sundmacher and Kienle, 2002; Singh, *et al.*, 2005).

However, one important disadvantage must be revealed: due to the strong interaction between reaction and separation, RD processes can sometimes show an intricate nonlinear dynamic behavior. Phenomena such as steady state multiplicities, self sustained nonlinear oscillations and bi-stability are only a few particular issues when dealing with the RD processes. Naturally, a

profound understanding of these phenomena as well as their reliable prediction is not only of scientific interest, but also a necessary prerequisite for improved process design and industrial control (Gangadwala, *et al.*, 2004; Grüner, *et al.*, 2003; Luyben, *et al.*, 2004; Sundmacher and Kienle, 2002).

At present, for our group of specialists at The Max-Planck Institute for the Dynamics of Complex Technical Systems, Magdeburg (Germany) and The Petroleum-Gas University, Ploiești (Romania), the current focus is on processes with potential phase splitting of the liquid phase. For this purpose, a dynamic model with potential phase splitting of the liquid phase was implemented and tested on different RD column structures – this work intending to show in a “spotlight” this approach in reactive distillation modeling and dynamic simulation.

Theoretical aspects regarding the mathematical model formulation are briefly emphasized and then, after the model validation, some results for butyl-acetate system are presented.

As remark, this paper has no comprehensive character, assuming the reader is used to deal with (reactive) distillation models, but being an outline on this modern modeling approach, which describes in an improved manner the real system behavior.

## 2. MODEL SUMMARY

In this work, the case of a classic RD column, as depicted in fig. 1, is taken into account.

For maximum model flexibility, the column is considered having multiple vapor/liquid feeds and/or sidedraws on trays. At top, the vapor is condensed and then the resulting liquid is accumulated in decanter – a part of the top product(s) being returned as external reflux – while at bottom an internal reboiler is present. The reactive zone may be located anywhere inside the column (supposing the catalyst load can be freely specified on each stage).

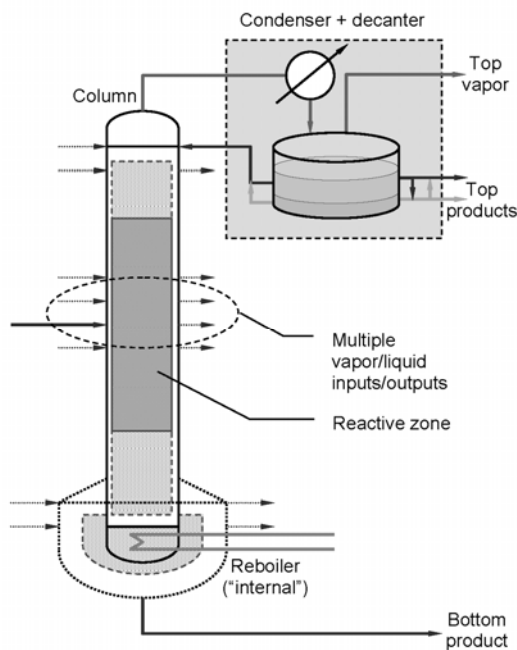


Fig. 1. Schematic representation for the RD column.

The classical approach treats the RD process as a pseudo-homogeneous system, where no phase splitting occurs in the liquid phase (Sundmacher and Kienle, 2002; Taylor and Krishna, 2000). But there are some cases when this classical approach in RD modeling – which does not take into

account a potential liquid phase splitting – is not satisfactory. For instance, high purity products can be obtained by using a “smart” and adaptive reflux policy exploiting the miscibility gap appearance at the condenser and in the upper part of the column (a typical example being the production of butyl acetate). Also, for some systems, significant differences between states in pseudo-homogeneous regime (no liquid phase splitting) and heterogeneous regime (with phase splitting) can be revealed (Bausa and Marquardt, 2000; Brüggemann, *et al.*, 2004). As consequence, an appropriate model has to be used in order to better reflect the real system behavior.

### 2.1. The new model structure

As written in the open literature, although extremely beneficial for the process itself, the appearance of a second liquid phase (more precisely: taking it into account as a possibility) makes the dynamic simulation of the (reactive) distillation column a much more difficult task (Bausa and Marquardt, 2000; Brüggemann, *et al.*, 2004; Steyer, *et al.*, 2005). The main problems are the phase state rapid, robust and reliable determination on each tray during the simulation horizon, the compositions calculation (in both phases for the trays in heterogeneous regime), phases ratio determination, managing in the same time the switches in the process model (when changes in the phase state on some trays occur).

In order to override the last problem – model switching – which brings more obstacles for the dynamic simulation, the authors of this work found a robust approach, considering that always there are two liquid phases and, when the system leaves the heterogeneous regime, these two phases become identical (having the same compositions). This way, there is no need to change the number of model equations (as some other authors revealed) when the system crosses the boundary between the homogeneous and heterogeneous region (Brüggemann, *et al.*, 2004).

In this work, in order to improve the simulation robustness, a structural modeling approach was adopted, considering here two sections:

- *the main model*, relatively close to the “classical” RD model (without phase splitting), which calculates at each step the global composition in liquid ( $x$ ) and vapor ( $y$ ) phases, temperature ( $T$ ), internal liquid (liq) and vapor (vap) streams flowrates, for all distillation stages (column trays and condenser + decanter);

- the phase splitting algorithm, externally carried out in a separate procedure, called by the main model at each integration step, for all distillation stages; this algorithm gets from the main model the global compositions ( $x$ ) and temperatures ( $T$ ), together with some other parameters, giving back both liquid phases compositions ( $x_1$  and  $x_2$ ) and ratios ( $\Phi$ ).

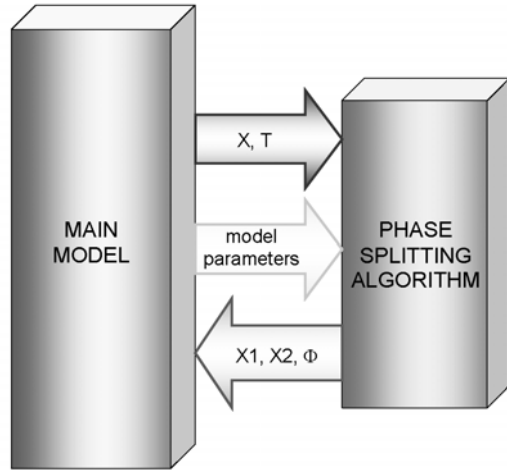


Fig. 2. The structural modeling approach for RD processes with potential liquid phase splitting.

This new model structure can be seen in fig. 2. Regarding the software implementation, an appropriate simulation environment has to be used, allowing this particular structural connection between the main model and a separate (independent) procedure. Due to its high performances, flexibility and robustness, the author's choice is DIVA – Dynamische Simulation Verfahrenstechnischer Anlagen (Mangold, *et al.*, 2000), working coupled with an external FORTRAN routine which run the phase splitting algorithm.

## 2.2. Modeling principles

### A. Main model

In order to have a robust and pertinent dimensional model, some basic simplifying assumptions need to be formulated – and taken into account when writing the model equations. But, as the authors implemented the model in several different forms (i.e. continuous and batch distillation, homogeneously and heterogeneously catalyzed process, with or without energy balance and so on), two assumption categories, *general* and *specific*, can be identified. While the particular assumptions need to be presented for each specific case, the general ones are always valid – and so here they are:

1. All column trays (also the decanter) have constant liquid holdups.
2. The vapor holdup on trays is neglected.
3. The vapor and liquid phases are in equilibrium.
4. The reaction takes place only in liquid phases.
5. A kinetic expression for the reaction rate ( $R$ ) is known.

As example, the simple case of  $k^{\text{th}}$  regular tray inside the column (as shown in fig. 3), for a homogeneously catalyzed process, with perfectly mixed reactants and catalyst, without considering the energy balance, is here presented. The regular equations are:

Component material balance:

$$\text{HOLD}_k \frac{dx_{i,k}}{dt} = \text{liq}_{k-1} \cdot x_{i,k-1} + \text{vap}_{k+1} \cdot y_{i,k+1} - \text{liq}_k \cdot x_{i,k} - \text{vap}_k \cdot y_{i,k} + \text{flzu}_k \cdot z\text{flzu}_{i,k} + \text{fgzu}_k \cdot z\text{fgzu}_{i,k} - \text{flab}_k \cdot x_{i,k} - \text{fgab}_k \cdot y_{i,k} + v_i \cdot [(1 - \Phi_k) \cdot R(x_{1,k}, \dots, x_{1,NC,k}) + \Phi_k \cdot R(x_{2,1,k}, \dots, x_{2,NC,k})] \cdot V_k \quad i=1, \dots, NC - 1. \quad (1)$$

It can be seen that a global reaction rate  $R$  is considered, as 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 remark, such a linear expression  $[(1 - \Phi_k) \cdot R(x_{1,k}, \dots, x_{1,NC,k}) + \Phi_k \cdot R(x_{2,1,k}, \dots, x_{2,NC,k})]$  may be simplified when an equal catalyst distribution in both liquid phases is considered.

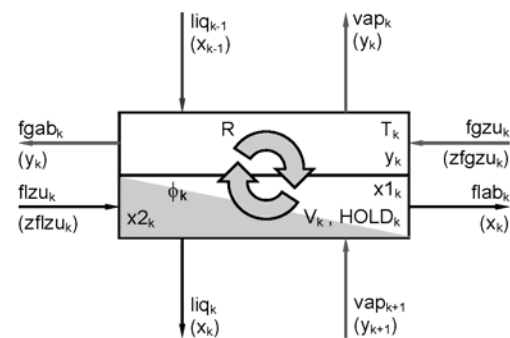


Fig. 3. The  $k^{\text{th}}$  tray inside RD column.

Summation condition for global liquid phase compositions:

$$\sum_{j=1}^{NC} x_{j,k} = 1. \quad (2)$$

Compositions in liquid phase 1 (externally calculated):

$$x_{1,i,k} = x_{1,i,k}^{PSA}, i=1, \dots, NC. \quad (3)$$

In this equation,  $x_{1,i,k}^{PSA}$  represents the phase 1 composition, externally determined with the “Phase Splitting Algorithm”. The same annotation, PSA, is attached for compositions in liquid phase 2 and phase ratio, also given by the same procedure:

Compositions in liquid phase 2 (externally calculated):

$$x_{2,i,k} = x_{2,i,k}^{PSA}, i=1, \dots, NC. \quad (4)$$

Phase ratio (externally calculated):

$$\Phi_k = \Phi_k^{PSA}. \quad (5)$$

Phase equilibrium:

$$y_{i,k} \cdot p = \eta \cdot psp_i \cdot \gamma_{1,i,k} \cdot x_{1,i,k}, i=1, \dots, NC. \quad (6)$$

As remark, although two liquid phases are present and the vapor phase have to be in equilibrium with both of them, the liquid phase 1 is in equilibrium with liquid phase 2 and so only one equation for the phase equilibrium is needed.

Summation condition for vapor phase compositions:

$$\sum_{j=1}^{NC} y_{j,k} = 1. \quad (7)$$

Total material balance for the liquid phase:

$$\begin{aligned} 0 = & liq_{k-1} - liq_k + flzu_k - flab_k + \\ & + \sum_{i=1}^{NC} [v_j \cdot [(1 - \Phi_k) \cdot R(x_{1,i,k}, \dots, x_{1,NC,k}) + \\ & + \Phi_k \cdot R(x_{2,i,k}, \dots, x_{2,NC,k})] \cdot V_k]. \end{aligned} \quad (8)$$

Total material balance for the vapor phase:

$$vap_k = vap_{k+1}. \quad (9)$$

The models for the column top (condenser + decanter) and bottom (including the reboiler) are also based on the “core” equations above, with usual changes (available in the literature) describing these slightly modified structures.

## B. Phase splitting algorithm

As mentioned before, the phase splitting algorithm is performed in a separate routine, as depicted in fig. 2. To be more explicit, that means it runs almost independently, checking at each step the state of all distillation stages and returning to the main model the phases compositions and ratios. Of course, before

running, it takes some mandatory information from the main model, including overall compositions, stages temperatures and other needed parameters (i.e. for the vapor-liquid-liquid equilibrium calculation, also some algorithm “tuning parameters” – as starting points for the internal continuation algorithm, for instance – and so on).

The authors used in this work a phase splitting algorithm originally presented by Bausa and Marquardt (2000), in the improved form proposed by Steyer, *et al.* (2005). It is a hybrid method using a-priori knowledge of phase diagram properties in order to tune-up the computational algorithm. The flash calculation is decomposed in two steps: a *preprocessing* step and the *computational* one.

In the first step, all heterogeneous regions of the system’s phase diagram at the specified pressure and boiling temperature are divided into convex regions and, for each region, one reference state inside it,  $(x^{START}, x_1^{START}, x_2^{START}, y^{START}, \Phi^{START}, p^{START}, T^{START})$ , is stored – denoting here the overall composition, compositions in both liquid phases, vapor composition, phases ratio, pressure and temperature. Typically, this analyzing procedure may be carried out only once, before simulations and more, since the phase diagrams are investigated in an early phase of the process design, the information on the heterogeneous region(s) existence may be directly provided by user (at least for mixture with up to four components).

In the next step, the difficult problem is solved by homotopy (meaning the search of non-trivial two-phase solution,  $x_1, x_2$  and  $\Phi$ , at some desired global composition  $x$ ) by starting from a simple problem (the solution at a binary mixing gap with the composition  $x^{START}$  where the compositions of the two phases,  $x_1^{START}$  and  $x_2^{START}$ , and phase ratio  $\Phi^{START}$  are known). By parametrizing the overall composition  $\bar{x}$  with a continuation parameter  $\lambda$ , it can be changed from the starting composition  $x^{START}$  to the composition  $x$ , for which the phase splitting behavior has to be checked,

$$\bar{x}_i = \lambda \cdot x_i + (1 - \lambda) \cdot x_i^{START} = \bar{x}_i(\lambda), i=1, \dots, NC. \quad (10)$$

$\lambda$  is changed from 0 to 1 when the continuation is performed. It can be observed that  $\bar{x}_i(0) = x_i^{START}$  and  $\bar{x}_i(1) = x_i$ .

On its turn, the homotopy continuation algorithm is based on a repetitive two-step process. First one, the *correction step*, solves the following equations:

Mass balances (as constraints):

$$x1_i \cdot (1 - \Phi) + x2_i \cdot \Phi = \bar{x}_i(\lambda), i=1, \dots, NC, \quad (11)$$

Activity difference equations (as necessary conditions):

$$x1_i \cdot \gamma1_i - x2_i \cdot \gamma2_i = 0, i=1, \dots, NC, \quad (12)$$

and

The summation equation (as constraint):

$$1 - \sum_{i=1}^{NC} x1_i = 0 \quad (\text{or } 1 - \sum_{i=1}^{NC} x2_i = 0). \quad (13)$$

The above equations are written for the global composition  $\bar{x}$  at a particular value for  $\lambda$ . A remark regarding the annotations: no tray index "k" is provided, in order to increase the readability.

In the second step (*predictor step*), a solution  $\theta$  to equations (11), (12) and (13) for a new value of  $\lambda$  is estimated using

$$\theta_{m,s+1} = \theta_{m,s} + \Delta\theta_m = \theta_{m,s} + \frac{d\theta_m}{d\lambda} \Delta\lambda, \quad m=1, \dots, 2NC+1, \quad (14)$$

$\theta_m$  denoting an element of the solution vector. For Bausa and Marquardt,  $\theta$  contains  $2NC$  mole fractions ( $x1$  and  $x2$ ) and one phases ratio ( $\Phi$ ).

The algorithm works by alternating prediction and correction steps while increasing  $\lambda$  from 0 to 1, effectively moving along the binodal surface in an effort to reach the desired  $x$  composition. During continuation, depending on where the studied composition  $x$  is located, three scenarios are possible, as shown in fig. 4.

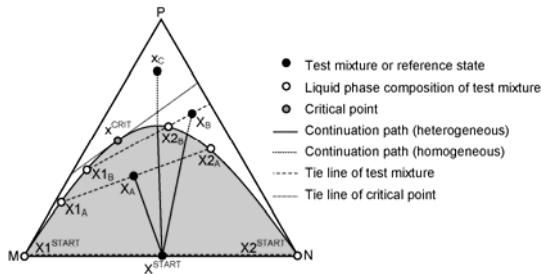


Fig. 4. Example of phase diagram for a ternary (M–N–P) system.

First, the test mixture with composition  $x_A$  resides in the heterogeneous region (vapor-liquid-liquid equilibrium, VLLE) and splits into the liquid phases  $x1_A$  and  $x2_A$ . Obviously, to calculate these

compositions, the continuation algorithm has to be performed only in the heterogeneous region.

The second scenario refers to test mixture  $x_B$ , located in the homogeneous regime (vapor-liquid-liquid equilibrium, VLE), but still located below the tangent to the critical point  $x_{CRIT}$  of the miscibility gap. The first part of the continuation algorithm is performed in the heterogeneous regime, while the last part crosses the homogeneous region. Even in this case it is still possible to find a solution  $x1_B$  and  $x2_B$ , but the phase ratio  $\Phi$  is greater than 1 (which has no physical meaning).

The last case corresponds to the test mixture  $x_C$ , located in the homogeneous region, above the tangent to the critical point. In this case, no valid solution (with physical meaning)  $x1_C$  and  $x2_C$  is found by continuation and, like in the previous case, the algorithm's answer is "no phase splitting occurs".

In systems with multiple binary pairs that exhibit phase splitting, multiple starting points have to be used in order to reach the correct solution (Bausa and Marquardt, 2000). This is due to the fact that the straight line according to equation (10) connecting the starting point  $x^{START}$  with the desired composition  $x$  might cross over a region of one-phase behavior between the two-phase starting and ending points. As Bausa and Marquardt show in their paper, this approach is very successful in finding the correct solution very quickly, with a high reliability.

However, their original implementation has a big drawback: the solution vector  $\theta$  has  $2NC+1$  components (even if the system degree of freedom is  $NC!$ ), increasing this way the computational time for the solver (equation 14). This is why a modified method, developed by Steyer, Flockerzi and Sundmacher, was used. The method's principle is to parametrize the solution vector  $\theta$  by introducing so-called phase partitioning coefficients, reducing the system order to  $NC$ , as the quoted authors proved in their work (Steyer, *et al.*, 2005).

The correction step is based on Newton-type iteration, where the following equation system has to be solved:

$$\theta_{s+1} = \theta_s - J^{-1}(f(\theta_s)) \cdot f(\theta_s). \quad (15)$$

In this equation,  $J$  denotes the Jacobian matrix of the remaining equation system (after model reduction), denoted here as  $f$ . To avoid inverting the Jacobian matrix, the equivalent linear equation system has to be solved. Also, for a fast

and reliable solution, the authors suggest that Jacobian should be computed analytically since the equation system is highly non-linear due to the activity coefficient model used to calculate  $\gamma_i$  (Steyer, *et al.*, 2005).

### 3. MODEL VALIDATION

In order to take the benefits of the new model, a compulsory stage had to be fulfilled, denoting here the model validation.

Due to the lack of comprehensive experimental data, the authors decided to validate their model by reproducing the results of Brüggemann, *et al.* (2004). Their study is focused on batch distillation process simulation in heterogeneous regime, taking as example the laboratory column for butanol esterification to butyl acetate, previously presented by Venimadhavan, *et al.* (1999).

Taking into account the existence of several low-boiling azeotropes, in such a column the butyl acetate cannot be directly recovered as the product. However, it is shown that high-purity butyl acetate could be obtained by using a clever reflux policy that exploits the appearance of a miscibility gap at the condenser and in the upper part of the column. Studying the column behavior, the quoted authors followed three operating strategies, for which they present an important amount of results:

**a)** ternary non-reactive distillation (loading the column still pot with a mixture of 40% water, 20% butanol and 40% butyl acetate, with no catalyst load), at a constant reflux ratio (0.9);

**b)** reactive distillation (filling the still pot with a binary mixture of 51% butanol and 49% acetic acid), homogeneously catalyzed with sulfuric acid, at a constant reflux ratio (0.9);

**c)** reactive distillation (filling the still pot with a binary mixture of 51% butanol and 49% acetic acid), homogeneously catalyzed with sulfuric acid, at a variable-adaptive reflux ratio (0.9 and 0.99).

In order to reproduce those scenarios, the model presented in this work was adapted for a 33 stage batch column, including the condenser + decanter

and the still pot (with internal reboiler). The holdup on each tray is 0.001kmol, the combined holdup of the condenser and decanter is 0.01kmol and the initial holdup of the still pot is 2kmol. Also, a constant vapor flowrate of 2kmol/h from the reboiler is considered. The thermodynamic data (the UNIQUAC model is used for  $\gamma_i$  calculation) were taken from DECHEMA database, as a consistency condition with Brüggemann's work – even if the binary interaction coefficients from there do not correctly describe the mixture behavior (Brüggemann, *et al.*, 2004). In the same time, specific simplifying assumptions were used:

1. No energy balance is considered, leading to a constant vapor flow from stage to stage.
2. There is an uniform liquid catalyst distribution between liquid phases.

Fig. 5 presents the schematic representation of the considered batch distillation column. The simulation results are further depicted in fig. 6, 7, 8 and 9 (due to the lack of space, only the first two scenarios are here covered).

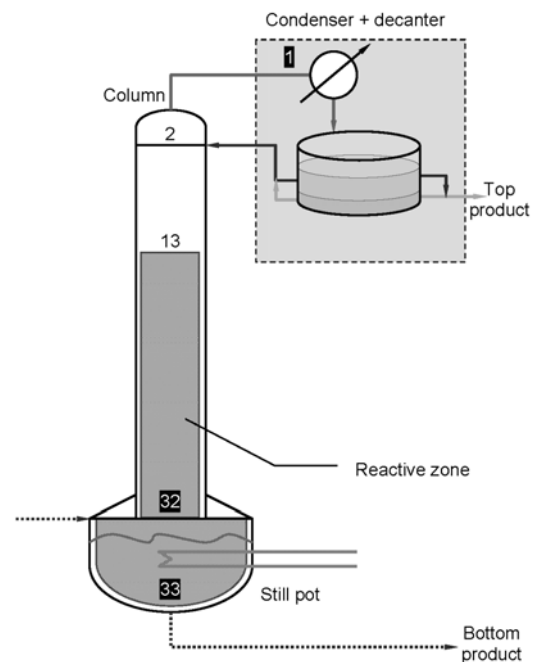


Fig. 5. Batch RD column used for validation.

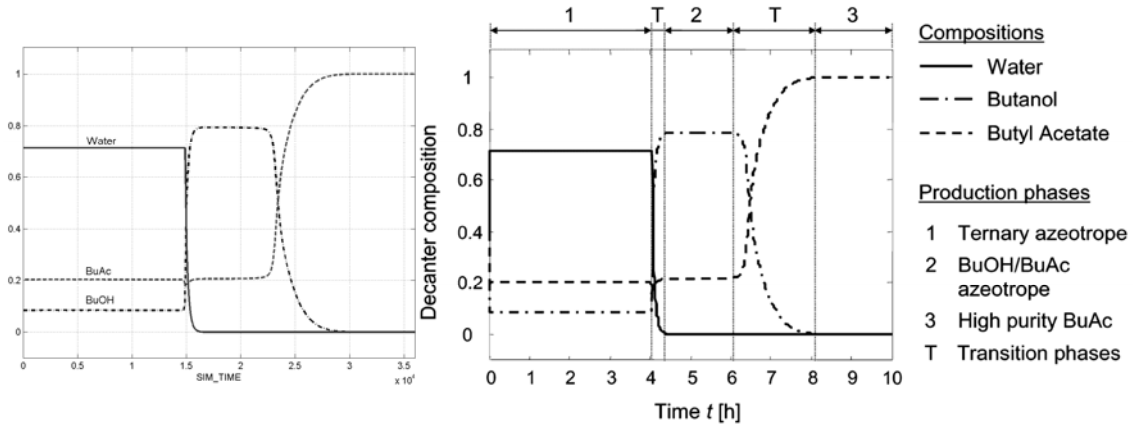


Fig. 6. Comparison between our model results (left) and literature results (right), for the first scenario – global composition in decanter. On the left, the simulation time SIM\_TIME is expressed in  $[\text{sec} \times 10^4]$ , on the right, t is in [hours]. The right hand side picture is taken from Brüggemann, *et al.* (2004).

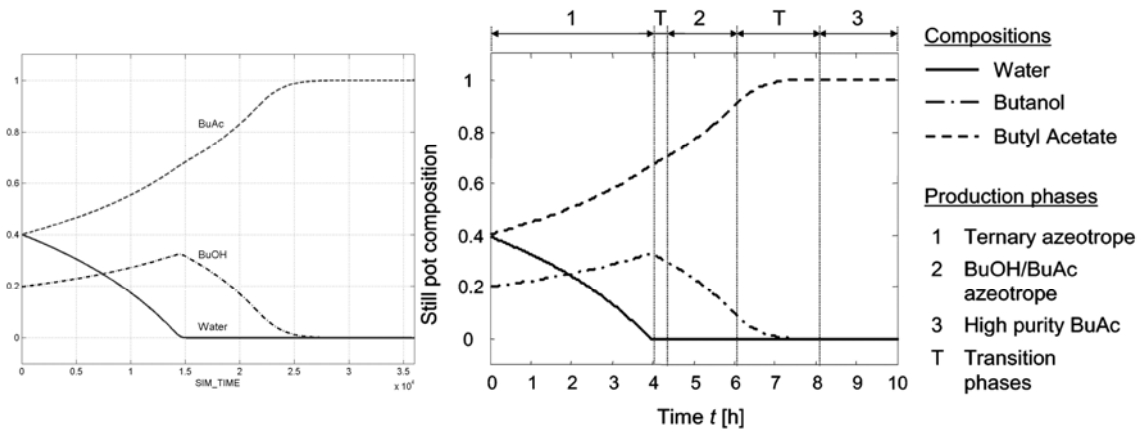


Fig. 7. Comparison between our model results (left) and literature results (right), for the first scenario – global composition in still pot. On the left, the simulation time SIM\_TIME is expressed in  $[\text{sec} \times 10^4]$ , on the right, t is in [hours]. The right hand side picture is taken from Brüggemann, *et al.* (2004).

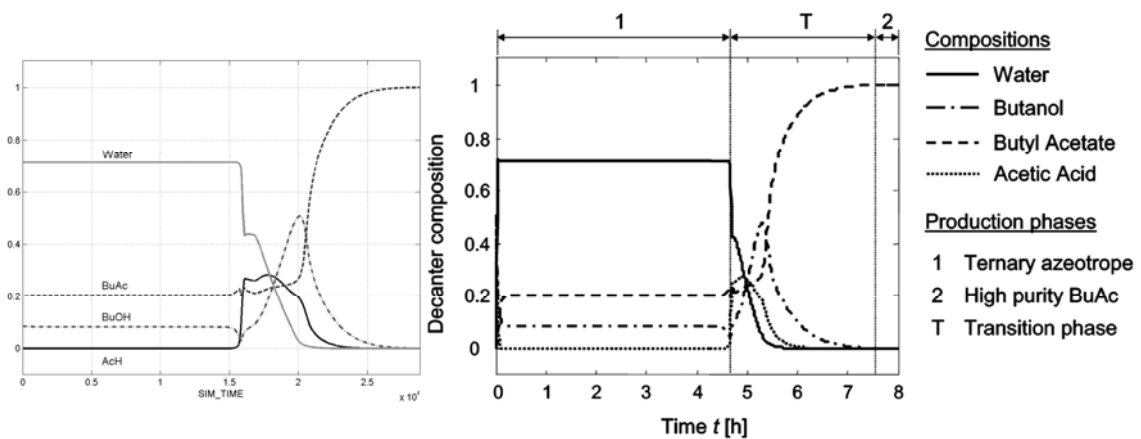


Fig. 8. Comparison between our model results (left) and literature results (right), for the second scenario – global composition in decanter. On the left, the simulation time SIM\_TIME is expressed in  $[\text{sec} \times 10^4]$ , on the right, t is in [hours]. The right hand side picture is taken from Brüggemann, *et al.* (2004).

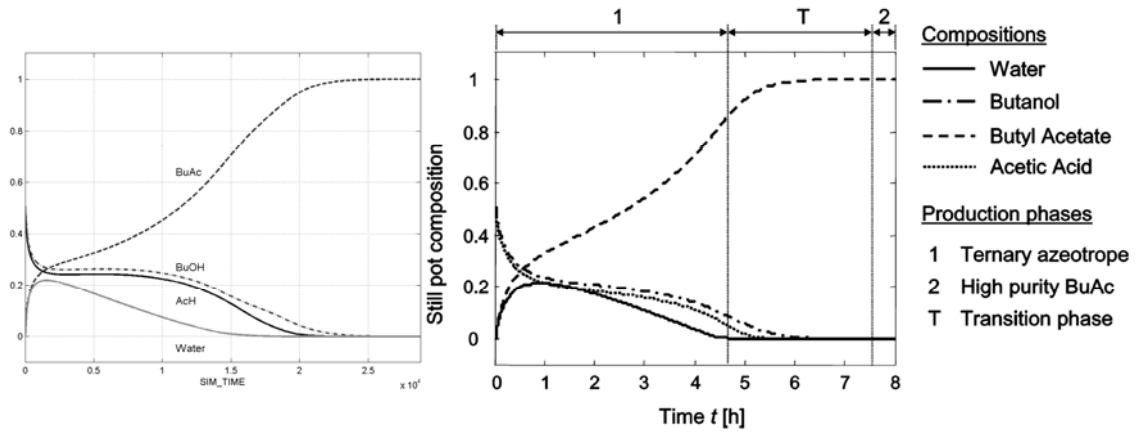


Fig. 9. Comparison between our model results (left) and literature results (right), for the second scenario – global composition in still pot. On the left, the simulation time SIM\_TIME is expressed in [sec × 10<sup>4</sup>], on the right, t is in [hours]. The right hand side picture is taken from Brüggemann, *et al.* (2004).

After a close analysis, the authors concluded there is a very good agreement between our diagrams and those from the original Brüggemann’s paper, both for decanter and still pot, not only qualitatively-quantitatively, but also as timing, so the modeling approach in this work may be considered as valid and has to be put into value and tested for some other applications.

#### 4. A SHORT CASE-STUDY. RESULTS

At present, many studies have their focus on waste utilities treatment, especially for those associated with industrial plants. Significant emphasis is put on the recovery of dilute acetic acid from water, due to the inherent process difficulty and high environmental impact.

It is well known that acetic acid cannot be easily separated from water by conventional distillation or extraction. As consequence, alternative techniques were found, one of these being the reactive distillation. In this last case, the acetic acid recovery is done through esterification (with n-butanol, for example), where a value-added ester (butyl acetate) is formed and – if the process is carefully operated – almost pure water can be withdrawn.

Recent experimental studies of Saha, *et al.* (2000) revealed that, depending on their RD column design, the acetic acid conversion could be somewhere between 32% and 58%. Considering that a more convenient value could be obtained, the authors of this work led their own research, identifying some alternative process structures where a conversion of up to 99% could be achieved.

Because these design studies will be the subject of a separate work, only some of our team results are here presented, in order to illustrate how the new RD modeling approach can offer a more precise image on the real process behavior than the classical approach.

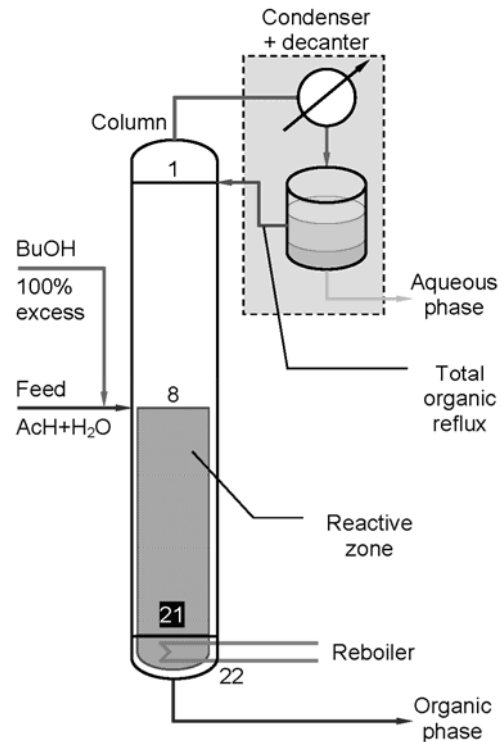


Fig. 10. RD process for acetic acid recovery from waste water.

Fig. 10 shows one of the original alternative designs proposed by the authors of this paper. It is a 22-trays RD column, where at top the organic



phase (separated in decanter after condensation) is totally refluxed, while the aqueous phase is withdrawn; in this case, the organic phase constitutes the bottom product.

The column is fed with unpurified water and excess of butanol (such as the mole ratio AcH:BuOH is 1:2) on the 8<sup>th</sup> tray, right above the reactive zone. The total feed flowrate is 0.00675 kmol/h, liquid holdup is  $2 \times 10^{-4} \text{ m}^3$  (per stage); the catalyst has a load of 0.0024 kg on each tray in the reactive zone.

Accordingly, the mathematical model was configured taking into account some new specific assumptions:

1. The liquid holdup on column bottom is constant.
2. The energy balance is taken into account.
3. The process is heterogeneously catalyzed.

Many simulations were performed in order to design and test this structure behavior. As overview, an acetic acid conversion of 99% was achieved, which represent a big improvement if one makes a comparison with other results announced in literature so far.

By using the proposed modeling approach, with potential phase splitting calculation, very useful information about this configuration was obtained. The column operates in 3-phase regime at decanter level and also around the feed tray, leading to different composition profiles when the process is simulated with classical model (pseudo-homogeneous approach) and the new one (including phase stability test). As example, fig. 11 and 12 shows the butyl acetate and water concentration along the column (in both cases).

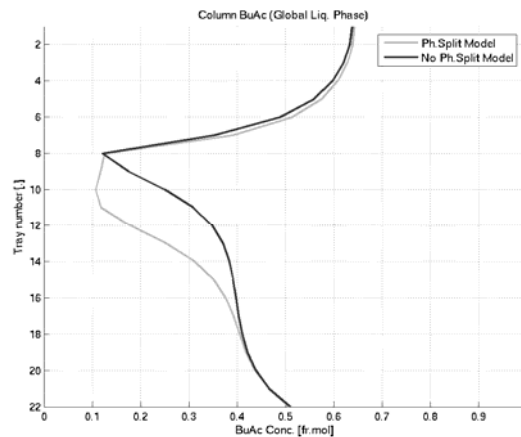


Fig. 11. Comparison between butyl acetate concentration profile when simulating the column with “phase split” model (light gray line) vs. “no phase split” model (dark gray line).

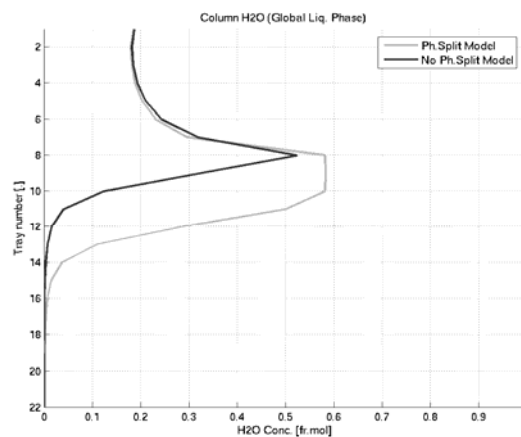


Fig. 12. Comparison between water concentration profile when simulating the column with “phase split” model (light gray line) vs. “no phase split” model (dark gray line).

As remark, it can be seen that a severe drift between concentration profiles is present in the reactive zone, exactly located in the region situated in heterogeneous (liquid-liquid splitting) regime. Obviously, in this particular case one can say that by using the classical modeling approach the results accuracy is seriously affected, while the new model gives a better image on process intimacy, leading to more precise results.

Dynamic simulation tests revealed also a very interesting feature of this configuration: a high sensitivity to disturbances (especially in feed flowrate and composition), due to traveling wave phenomena (Grüner and Kienle, 2004). For

instance, a 5% only increase in feed flowrate (deviation from the nominal operating point) leads to a serious drop in acetic acid conversion (from 99% to 38%, see fig. 13), while the system moves toward a new steady state with totally different composition profiles in the reactive zone. As it can be seen in fig. 14 and 15, the non-reactive zone above the feed tray remains unaffected. Also, fig. 16 shows how the 3-phase regime extends from a small region around the feed tray to about 75% of the reactive zone, without any effect in the upper part of the column.

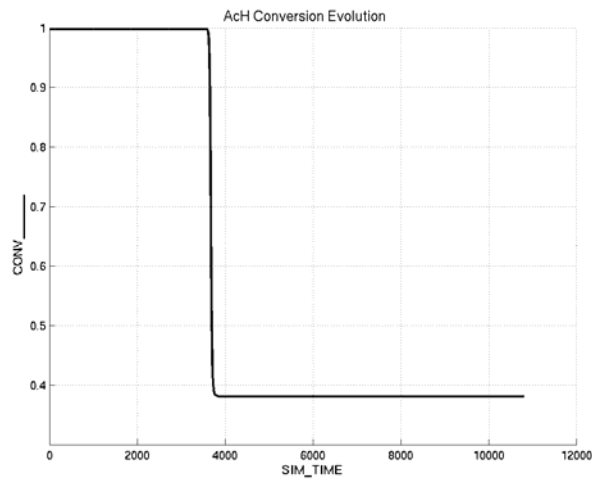


Fig. 13. The evolution of acetic acid conversion, subject to a 5% increase in feed flowrate, after 3600 sec. since the simulation start. SIM\_TIME is expressed in [sec].

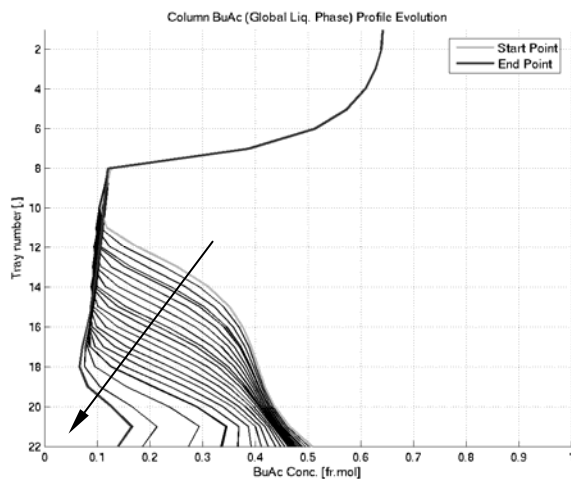


Fig. 14. The butyl acetate profile evolution, after a 5% increase in feed flowrate.

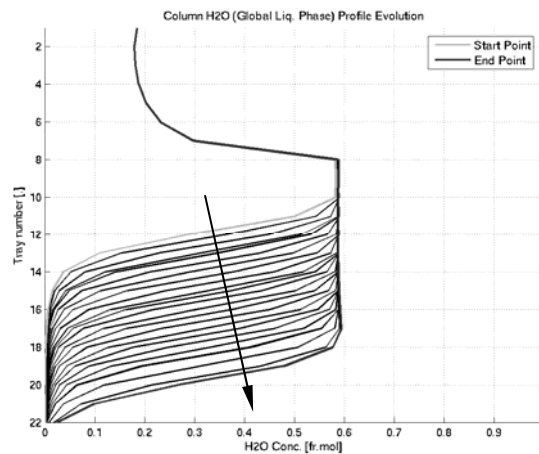


Fig. 15. The water profile evolution after a 5% increase in feed flowrate.

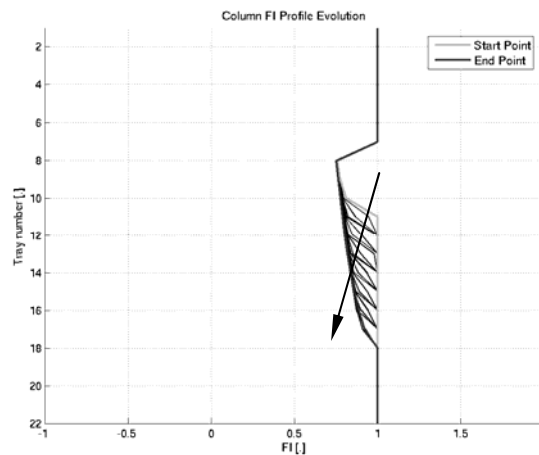


Fig. 16. The  $\Phi$  ("FI") profile evolution after a 5% increase in feed flowrate.

As a general remark, all other simulation scenarios – not included here – confirmed the robustness and reliability of this modeling approach, as well as the most important fact: by including the phase splitting calculation, the model describes in an improved manner the real system behavior, comparing it with the classical pseudo-homogeneous approach results.

## 5. CONCLUSIONS

This work presented the new features characterizing a modern modeling approach for RD processes, which include phase splitting calculation. By adapting a rapid, robust and reliable algorithm based on homotopy-continuation method, the new model implementation was first validated and then put into value for a specific application (waste water treatment). A good agreement between computer data and real system behavior can be expected by using the proposed model, so it should be used

when precise RD simulation results have to be obtained.

## NOMENCLATURE

HOLD	molar liquid holdup on tray
J	Jacobian matrix
NC	number of components
R	reaction ratio
T	temperature
V	volumetric liquid holdup on tray
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
liq	internal liquid molar flowrate
p	pressure
psp	saturation pressure in the vapor phase
vap	internal vapor molar flowrate
x	mole fraction, liquid (global)

x1	mole fraction, liquid (phase 1)
x2	mole fraction, liquid (phase 2)
y	mole fraction, vapor phase
zflzu	mole fraction in external liquid feed
zfgzu	mole fraction in external vapor feed

## Greek letters

$\Phi$	phases ratio
$\gamma_1$	activity coefficient (phase 1)
$\gamma_2$	activity coefficient (phase 2)
$\eta$	tray efficiency
$\theta$	solution vector
$\lambda$	continuation parameter
v	stoichiometric coefficient

## Superscripts

CRIT	critical point of the miscibility gap
PSA	value given by the Phase Splitting Algorithm
START	reference state (starting point for continuation)

## Subscripts

A, B, C	example states in the phase diagram
k	tray number
i	component indices
m	variable indices (in the solution vector)
s	current step

## REFERENCES

- Bausa, J. and W. Marquardt (2000). Quick and reliable phase stability test in VLE flash calculations by homotopy continuation. *Computers and Chemical Engineering*, **24**, pp. 2447-2456.
- Brüggemann, S., J. Oldenburg, P. Zhang and W. Marquardt (2004). Robust Dynamic Simulation of Three-Phase Reactive Batch Distillation Columns. *Industrial and Engineering Chemistry Research*, **43**, pp. 3672-3684.
- Gangadwala, J., A. Kienle, E. Stein and S. Mahajani (2004). Production of Butyl Acetate by Catalytic Distillation: Process Design Studies. *Industrial and Engineering Chemistry Research*, **43**, pp. 136-143.
- Gangadwala, J., S. Mankar, S. Mahajani, A. Kienle and E. Stein (2003). Esterification of Acetic Acid in the Presence of Ion-Exchange Resins as Catalysts. *Industrial and Engineering Chemistry Research*, **42**, pp. 2146-2155.
- Grüner, S., K.-D. Mohl, A. Kienle, E. D. Gilles, G. Fernholz and M. Friedrich (2003). Nonlinear control of a reactive distillation column. *Control Engineering Practice*, **11**, pp. 915-925.
- Grüner, S. and A. Kienle (2004). Equilibrium theory and nonlinear waves for reactive distillation columns and chromatographic reactors. *Chemical Engineering Science*, **59**, pp. 901-918.
- Luyben, W. L., K. M. Pszalgowski, M. R. Schaefer and C. Siddons (2004). Design and Control of Conventional Reactive Distillation Processes for the Production of Butyl Acetate. *Industrial and Engineering Chemistry Research*, **43**, pp. 8014-8025.
- Mangold, M., A. Kienle, K. D. Mohl and E. D. Gilles (2000). Nonlinear computation using DIVA – Methods and applications. *Chemical Engineering Science*, **55**, pp. 441-454.
- Saha, B., S. P. Chopade and S. M. Mahajani (2000). Recovery of dilute acetic acid through esterification in a reactive distillation column. *Catalysis Today*, **60**, pp. 147-157.
- Singh, A., R. Hiwale, S. M. Mahajani, R. D. Gudi, J. Gangadwala and A. Kienle (2005). Production of Butyl Acetate by Catalytic Distillation. Theoretical and Experimental Studies. *Industrial and Engineering Chemistry Research*, **44**, pp. 3042-3052.
- Steyer, F., D. Flockerzi and K. Sundmacher (2005). Equilibrium and rate-based approaches to liquid-liquid phase splitting calculations. *Computers and Chemical Engineering*, **30**, pp. 277-284.
- Sundmacher, K. and A. Kienle (2002). *Reactive Distillation – Status and Future Directions*. Wiley-VCH, Weinheim.
- Taylor, R. and R. Krishna (2000). Modeling reactive distillation. *Chemical Engineering Science*, **55**, pp. 5183-5229.
- Venimadhavan, G., M. F. Malone and M. F. Doherty (1999). A Novel Distillate Policy for Batch Reactive Distillation with Application to the Production of Butyl Acetate. *Industrial and Engineering Chemistry Research*, **38**, pp. 714-722.