# ON THE REACTIVE DISTILLATION MODELING
# AND DYNAMIC SIMULATION

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Abstract: A reactive distillation plant is one of the most important and "delicate" functional components of a complex chemical plant. While its steady state modeling and simulation tend to become a standard today by using some well known dedicated software tools, only little is known about the dynamic simulation in the open literature. This paper presents the principles for a modern modeling approach with respect to reactive distillation processes, including the potential phase splitting detection. 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. A simple case-study (by applying this approach to a reactive distillation column for waste water treatment) is briefly 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.

Keywords: reactive distillation, mathematical model, dynamic simulation.

## 1. INTRODUCTION

As previously known, the reactive distillation (RD) process integrates the 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 a complicate 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; Rădulescu *et al.,* 2006; Rădulescu *et al.,* 2007; Sundmacher and Kienle, 2002).

As remark, this paper assumes the reader is used to deal with (reactive) distillation models, so it is intended to be more an outline on this modern modeling approach, which describes in an improved manner the real system behavior.

## 2. THE REACTIVE DISTILLATION PROCESSES MODELING PRINCIPLES AND GOALS

Generally, a model is a schematic representation of a (real) system, which describes in a given manner the system behavior. Usually the model consists in a set of mathematical equations, so it being called a "mathematical model"; this work also focuses only on this type of models.

There are several situations requiring the use of a mathematical model. Related to the announced reactive distillation processes topic, first, a model could be used to simulate a particular distillation column or even an entire plant. Simulators are the most used tools in research activities with a wide coverage area of interest: process intimacy investigation, plant structure and control systems design and test, state estimation (inferential measurements), plant operators training and so on. These models, well known as "simulation models", describe the process behavior (internal state and outputs evolution) for a specific set of input variables, taking into account the time (dynamic models) or not (steady state models) (Grüner et al., 2003; King, 1980; Rădulescu, 2000, 2002).

The mathematical models may be categorized according with many criteria, but only a few are significant when applied to the reactive distillation process models. Thus, the authors want to emphasize three of the most used types.

### A. EQ vs. NEQ models
For equilibrium (EQ) models, the vapor and liquid streams leaving the stage are assumed to be in equilibrium with each other, while the non-equilibrium (NEQ) models follow the philosophy of rate-based models for conventional distillation. In addition, in the NEQ model, hardware design information must be specified so that mass transfer coefficients, interfacial areas and so on can be calculated. In addition, physical properties such as surface tension, diffusion coefficients and so on for calculation of mass (and heat) transfer coefficients and interfacial areas are required.

### B. Steady state vs. dynamic models
These two types differ in the manner the time is taken into account or not. Of course, a dynamic model is supposed to better describe the process behavior than a steady state one. But there are many situations that do not require such a complexity; a well-known example is the distillation column design, which use only steady state models to determine the column geometry and operating parameters, as the design specifications would be accomplished.

On the other hand, a dynamic model is strongly required for post-design studies, when testing the plant behavior (before building it up). Even if the authors met a few different opinions, they do believe that only a dynamic simulation can offer a complete overview on the distillation plant.

### C. Rigorous vs. empirical models
A mathematical model may be formulated mainly through two techniques. First, using some basic principles leading the real system behavior (i.e. mass and energy conservation, liquid-vapor equilibrium), with usual simplifying assumptions, adequate relations between inputs, outputs and state variables are established. The used principles are chosen in a manner that can globally characterize the system (the reactive distillation process in our case), so the obtained equations system being that way a mathematical model for it. This is a so-called "rigorous model".

On the other hand, for many applications such a "complete" and complex model is not useful. The training software simulators and advanced control systems, for example, are based on reduced-scale models, still giving an acceptable overview on the reactive distillation plant behavior (input-output correlations) but without any details about "what is inside".

Usually, these models are obtained through identification (observing the real plant or making use of a software simulator based on a rigorous model) or other reduction techniques and mainly do not take into account the physical principles leading the reactive distillation process, so being called "empirical models". This type is very useful when a fast simulation is required, as in real-time systems (Grüner et al., 2003).
Because the EQ are the most frequently used and studied models, the remarks on our paper refer only to that model.

## 3. CONSIDERATIONS ON THE REACTIVE DISTILLATION DYNAMIC SIMULATION

To simulate a given physical system means in fact to use a representation for this one, which can offer a qualitative and/or quantitative image over the real system behavior when a set of inputs changes. This representation must have at least two functional sections: a model for the physical system and a "simulation engine" (see figure 1). There also must be a correlation between the physical system inputs/outputs (real

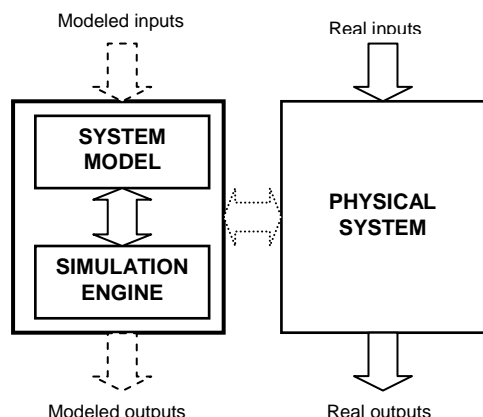inputs/outputs) and the simulator inputs/outputs (modeled inputs/outputs).



Fig. 1. The general simulator architecture.

As first problematic aspect in the dynamic simulation, it must be mentioned the mathematical model translation, from standard equations to a computer-coded representation. Then, the model equations being a differential algebraic system, the main problem is to determine consistent initial values for the integration. Another problem could be how to choose an appropriate integration method. Most of the software simulation environments provide different solutions, suitable for some type of applications.

But, nevertheless, the hardest to solve problem is to answer the question: are the simulation results systematically correlated with the real system response or these are only the simulator response? Many others also ask themselves about this (Mohl, 1999). The authors of this work do strongly believe that being able to give this answer, when simulating such a complex process like reactive distillation, means in fact to pass from the simulation usual techniques to the simulation art.

## 4. A CASE-STUDY: THE RD WITH POTENTIAL PHASE SPLITTING MODELING AND DYNAMIC SIMULATION

In this work, the case of a classic RD column, as depicted in fig. 2, 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).
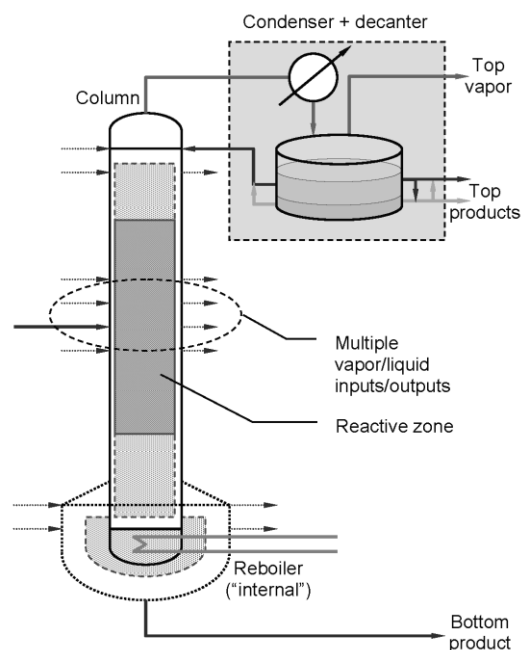


Fig. 2. Schematic representation for the RD column.

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.

### 4.1. The 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 ($x1$ and $x2$) and ratios ($\Phi$).
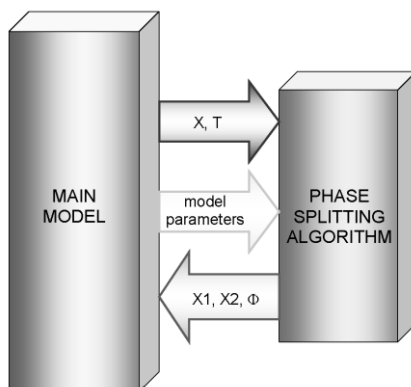


Fig. 3. The structural modeling approach for RD processes with potential liquid phase splitting.

This new model structure can be seen in fig. 3. 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 – <u>D</u>ynamische <u>S</u>imulation <u>V</u>erfahrenstechnischer <u>A</u>nlagen, working coupled with an external FORTRAN routine which run the phase splitting algorithm.

*4.2. 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.

For each equilibrium stage, the model mainly consists in total/component material balance (liquid and vapor phases), phase equilibrium, and reaction rate equations, as extensively presented in a previous paper (Rădulescu *et al.,* 2006).

**B. Phase splitting algorithm**
As mentioned before, the phase splitting algorithm is performed in a separate routine, as depicted in fig. 3. 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 paper a phase splitting algorithm originally presented by Bausa and Marquardt (2000), in the improved form proposed by Steyer, *et al.* (2005). As shown in our previous work, it is a hybrid method using a-priori knowledge of phase diagram properties in order to tune-up the computational algorithm. For further details, the reader is kindly asked to read the quoted references (Rădulescu *et al.,* 2006; Gangadwala *et al.,* 2006).

## 5. RESULTS

At present, many studies concern 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 leaded their own research, identifying some alternative process structures where a conversion of up to 99% could be achieved.

Because these design studies are the subject of a separate work (Gangadwala *et al.*, 2006), only some of our 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. 4 shows 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.
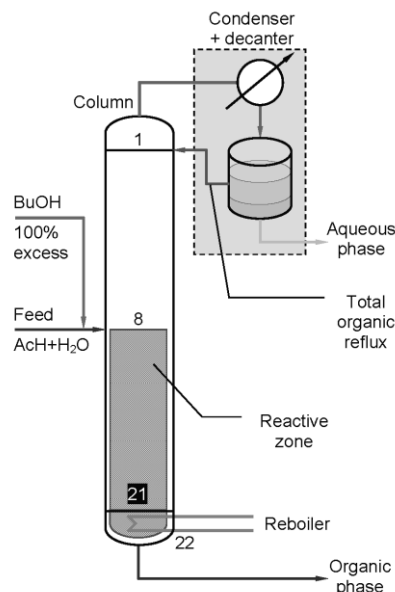


Fig. 4. RD process for acetic acid recovery from waste water.

The column is fed with unpurified water and excess of butanol (such as the mole ratio AcH:BuOH is 1:2) on the 8th tray, right above the reactive zone. The total feed flowrate is 0.00675 kmol/h, liquid holdup is $2 \times 10^{-4}$ 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. 5 and 6 shows the butyl acetate and water concentration along the column (in both cases).
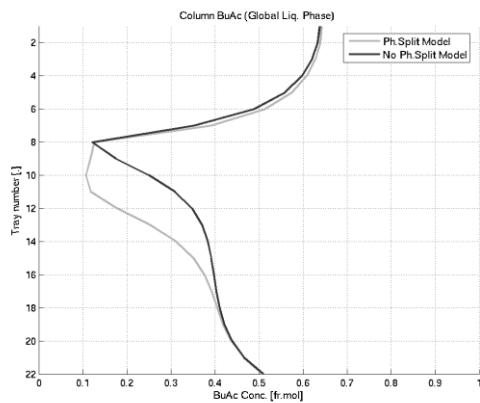
Fig. 5. Comparison between butyl acetate concentration profile when simulating the column with "phase split" model (light gray line) vs. "no phase split" model (dark gray line).
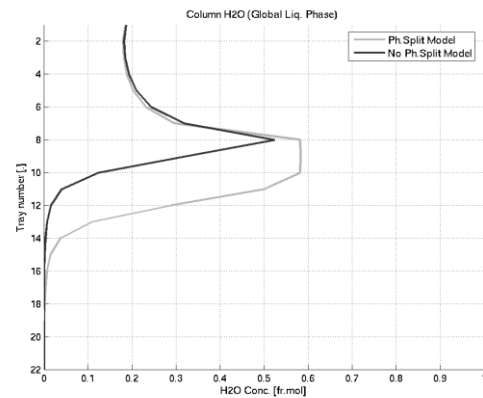
Fig. 6. Comparison between water concentration profile when simulating the column with "phase split" model (light gray line) vs. "no phase split" model (dark gray line).

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. 7), 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. 8 and 9, the non-reactive zone above the feed tray remains unaffected. Also, fig. 10 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.
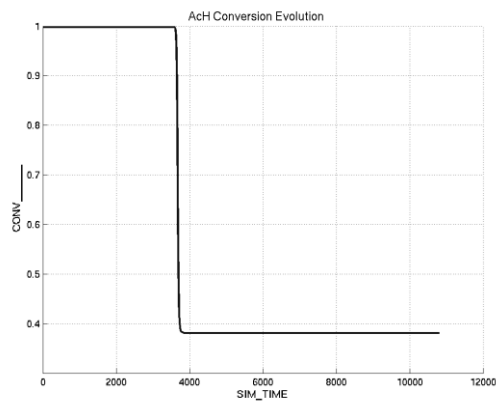


Fig. 7. The evolution of acetic acid conversion, subject to a 5% increase in feed flowrate, after 3600 sec. since the simulation start. SIM_TIME is expressed in [sec].
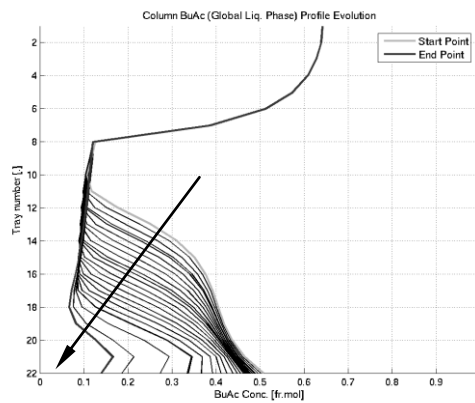
Fig. 8. The butyl acetate profile evolution, after a 5% increase in feed flowrate.
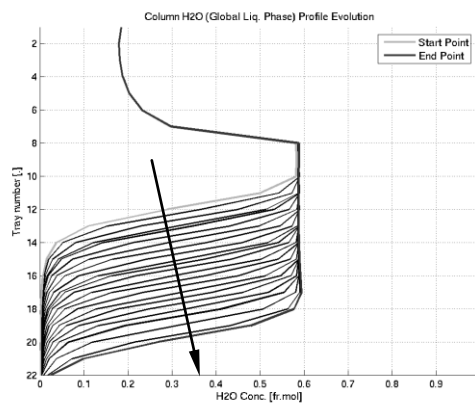


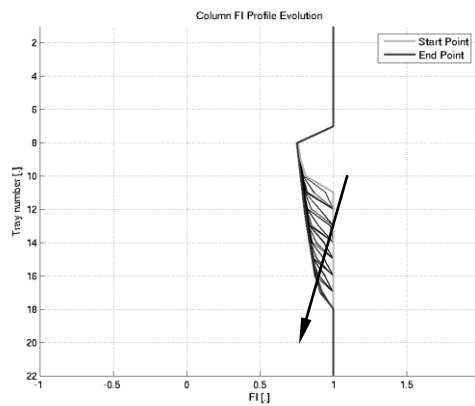Fig. 9. The water profile evolution after a 5% increase in feed flowrate.



Fig. 10. The $\Phi$ ("Fl") 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.

## 6 CONCLUSION

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.

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