A Systematic Approach on the Dynamic Modeling of Reactive Distillation Processes

The standard mathematical model (NPHSP)

GABRIEL RADULESCU*, NICOLAE PARASCHIV, SANDA FLORENTINA MIHALACHE
Petroleum – Gas University of Ploiesti, Control Engineering, Computers and Electronics Department, 39 Bucuresti Blvd., 100680, Ploiesti, Romania

This work addresses the major problem of reactive distillation (RD) processes mathematical modeling, revealing also why detecting the presence of a three-phase regime (vapour-liquid-liquid) on the column stages is of utmost importance. In this paper, the authors present in detail their starting modeling approach, which describes the behaviour of a “classic” RD process (where the potential liquid phase splitting is not taken into account). This “no-phase-splitting” (NPHSP) model is suitable to be used, in connection with a robust phase splitting (PHSP) algorithm, in order to accurately simulate a real RD process – where the three phase regime may appear in some conditions.

Keywords: reactive distillation; phase splitting; nonlinear model

A reactive distillation column integrates chemical reaction and separation by distillation in a single processing unit [1]. This combined approach was proved to be more efficient with respect to conventional process design, where reaction and separation are carried out in different processing units [2,-5]. With RD, the plant costs (from design to normal operation) significantly decrease. But RD has also a big drawback, namely it is difficult-to-understand nonlinear dynamic behaviour, which includes nonlinear (self-sustained) oscillations and multiple steady states. As written in the open literature, including our previous works, a profound understanding of these phenomena as well as their reliable prediction is both of scientific interest and a necessary prerequisite for improved process design and plants control [6-8].

This objective can be fulfilled by dynamic simulation studies, but (only) when an adequate mathematical representation is available. In [6-8], the authors have presented how an original modeling approach, which takes into account the potential splitting of the liquid phase, encourages complex studies on different (proposed or existing) RD column structures.

After years of experiments in this field, the present work intends to reveal how such a realistic approach in RD modeling and dynamic simulation can be built-up, based on the ”classical” model (NPHSP). A special focus is put on the model principles, details, implementation and validation. Unlike the previous mentioned works [6-8], this paper is somehow a guideline on how a classical model (with no phase splitting) has to be set-up in order to be the base for a more realistic model (including phase splitting detection).

The mathematical NPHSP model for reactive distillation processes

This section deals with the basic principles, assumptions and algorithms which contribute in building-up the RD models. The widely used equilibrium stage is here presented in its “classical” form (assuming no liquid phase splitting occurs), but ready for extension to systems with potential liquid phases separation.

The development and use of the equilibrium (EQ) stage model for conventional distillation is widely described in the literature. This paper contributions are focused on adapting this model for RD systems, by including the reactive terms in a form suitable for high-speed numerical integration, offering also a unitary approach – with respect to chemical reaction presence – for all column stages and all catalyst types (liquid or solid). More, the developed model adopts an original unitary model structure for all column sections (top, middle, bottom). Another important contribution is that a real validation procedure (based on experimental data) was performed, being known that in literature there are only a few valuable examples in this field.

Because usually the distillation takes place in columns with trays, as shown in figure 1, the model description will involve the well-known three “sections”: the column top (represented by the condenser and reflux tank), a regular tray and the column bottom (usually the reboiler).

Figure 1 offers an overview on the distillation column characteristics: continuous process, multiple vapour/liquid feeds and sidedraws on trays (not considering here the condenser and reboiler), with variable-located reactive zone (supposing the catalyst can be placed/fixed on

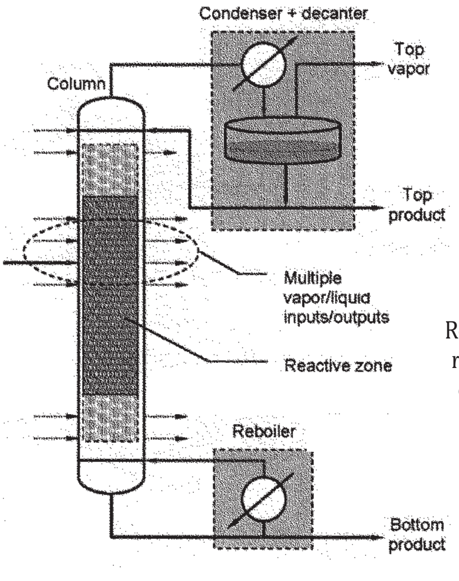

Fig. 1. Representation for a reactive distillation column with trays

---

* email: gabriel.radulescu@upg-ploiesti.ro

specific trays) [1]. As a consequence, the model has to include these aspects which will be emphasized while the equations are revealed, one by one.

Before going into details, here are the basic assumptions which are used in order to have a robust and pertinent-dimensional model, as explained in the previous works [6-8].

The column has NSTAGE theoretical stages, including the assembly condenser + reflux tank ("decanter") and the reboiler.

The liquid (molar) holdup on all trays, decanter and column bottom is constant, the vapour holdup on trays being neglected.

The energy balance is not considered – in this respect 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 phase (assuming a perfect mixture of reactants and catalyst) and a kinetic 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 of the column top (condenser + decanter) is detailed. For the nomenclature, the reader has to consult the list at the end of this paper.

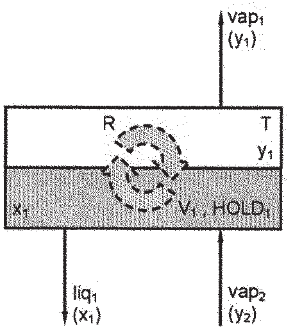

Fig. 2. Schematic representation for the column top - classical approach

As mentioned above, at the column top there are not any external material exchanges, such as liquid or vapour feeds/sidedraws. Also, in figure 2 the "reactive stage" symbol (as the dashed arrow) appears. Usually the condenser and decanter are not reactive, but for maximum model flexibility the authors prefer to take into account this case too: as the reaction rate R depends on catalyst concentration, by simple nullifying it on desired trays, including this first stage, these trays become non-reactive, without any need to modify the model. One final remark: the homogenous filled zone is the liquid phase where no phase splitting is taken into consideration. Accordingly, the mathematical model for the column top consists in the following equations.

Component material balance

$$HOLD_1 \frac{dx_{i,1}}{dt} = vap_2 \cdot y_{i,2} - liq_1 \cdot x_{i,1} - vap_1 \cdot y_{i,1} + \\ + \nu_i \cdot R(x_{1,1},\ldots,x_{NC,1}) \cdot V_1 \\ i = 1,\ldots,NC-1 \qquad (1)$$

For better readability, the reactive term in the balance, $\nu_1 \cdot R(x_{1,1},\ldots,x_{NC,1}) \cdot V_1$, is written separately, emphasizing the only difference between the non-reactive and reactive distillation models (this convention will be followed as much as possible in this paper).

Summation condition for liquid and vapour phase compositions:

$$\sum_{j=1}^{NC} x_{j,1} = 1 \qquad (2)$$

$$\sum_{j=1}^{NC} y_{j,1} = 1 \qquad (3)$$

Phase equilibrium

$$y_{i,1} \cdot p = \eta \cdot psp_{i,1} \cdot \gamma_{i,1} \cdot x_{i,1} \quad i = 1,\ldots,NC \qquad (4)$$

Total material balance (with the reactive term written separately):

$$0 = -liq_1 + vap_2 - vap_1 + \sum_{j=1}^{NC} \left[\nu_j \cdot R(x_{1,1},\ldots,x_{NC,1}) \cdot V_1\right] \qquad (5)$$

Free variables

ν_{ap1} = ...user given... (liq_1 =- ...user given...) (6)

These two variables may be freely specified by the user, but not simultaneously (because vap_1 and liq_1 are both part of the total material balance equation, they are not independent).

The regular stage (tray k)

Figure 3 illustrates how a normal tray, situated somewhere in the column, is approached. Multiple feeds and sidedraws are considered for flexibility (although not all of them are present). Also, a homogeneous liquid phase is taken into account, as well as the tray reactive feature.

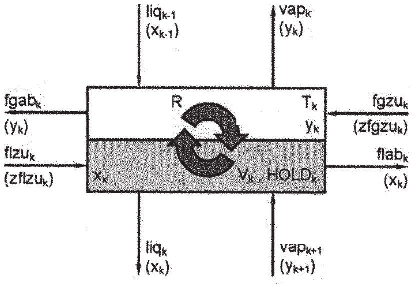

Fig. 3. Schematic representation for a regular tray - classical approach

Considering the representation for a regular tray in the figure above, the model is:

Component material balance:

$$HOLD_k \frac{dx_{i,k}}{dt} = liq_{k-1} \cdot x_{i,k-1} + vap_{k+1} \cdot \\ \cdot y_{i,k+1} - liq_k \cdot x_{i,k} - vap_k \cdot y_{i,k} + \\ + flzu_k \cdot zflzu_{i,k} + fgzu_k \cdot \\ \cdot zfgzu_{i,k} - flab_k \cdot x_k - fgab_k \cdot y_k + \\ + \nu_i \cdot R(x_{1,k},\ldots,x_{NC,k}) \cdot V_k \\ i = 1,\ldots NC-1 \qquad (7)$$

Summation condition for the liquid and vapor phase compositions:

$$\sum_{j=1}^{NC} x_{j,k} = 1 \qquad (8)$$

$$\sum_{j=1}^{NC} y_{j,k} = 1 \qquad (9)$$

Phase equilibrium:

$$y_{i,k} \cdot p = \eta \cdot psp_{i,k} \cdot \gamma_{i,k} \cdot x_{i,k} \quad i = 1,\ldots,NC \qquad (10)$$

Total material balance for the liquid phase:

$$0 = liq_{k-1} - liq_k + flzu_k - flab_k + \sum_{j=1}^{NC} \left[\nu_j \cdot R\left(x_{1,k},\dots,x_{NC,k}\right) \cdot V_k \right] \tag{11}$$

Total material balance for the vapour phase:

$$vap_k = vap_{k+1} \tag{12}$$

It must be noticed that, for a regular distillation stage, there are no free variables (as “degrees of freedom”).

The column bottom (“tray” NSTAGE)

Figure 4 shows a simplified representation for the column bottom (the reboiler).

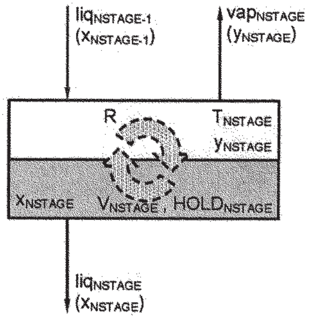

Fig. 4. Schematic representation for the column botton - classical approach

No external feeds or sidedraws are considered, no liquid phase splitting is taken into account and the reboiler is also regarded as possible, but less likely to be a reactive stage. Correspondingly, the mathematical model for the column bottom is:

Component material balance:

$$\begin{aligned} HOLD_{NSTAGE} \frac{dx_{i,NSTAGE}}{dt} &= liq_{NSTAGE-1} \cdot x_{i,NSTAGE-1} - \\ &- liq_{NSTAGE} \cdot x_{i,NSTAGE} - vap_{NSTAGE} \cdot y_{i,NSTAGE} + \\ &+ \nu_i \cdot R\left(x_{1,NSTAGE},\dots,x_{NC,NSTAGE}\right) \cdot V_{NSTAGE} \qquad i = 1,\dots,NC-1 \end{aligned} \tag{13}$$

Summation condition for liquid and vapour phase compositions:

$$\sum_{j=1}^{NC} x_{j,NSTAGE} = 1 \tag{14}$$

$$\sum_{j=1}^{NC} y_{j,NSTAGE} = 1 \tag{15}$$

Phase equilibrium:

$$y_{i,NSTAGE} \cdot p = \eta \cdot psp_{i,NSTAGE} \cdot \gamma_{i,NSTAGE} \cdot x_{i,NSTAGE} \qquad i = 1,\dots,NC \tag{16}$$

Summation condition for vapour phase compositions:

Total material balance:

$$\begin{aligned} 0 &= liq_{NSTAGE-1} - liq_{NSTAGE} - vap_{NSTAGE} + \\ &+ \sum_{j=1}^{NC} \left[\nu_j \cdot R\left(x_{1,NSTAGE},\dots,x_{NC,NSTAGE}\right) \cdot V_{NSTAGE} \right] \end{aligned} \tag{17}$$

Free variables:

$$vap_{NSTAGE} = \dots user\ defined \dots \quad \left(liq_{NSTAGE} = \dots user\ defined \dots\right) \tag{18}$$

As for the case of column top, here there are again two possibilities to choose a free variable, because vap_{NSTAGE} and liq_{NSTAGE} are linked by the total material balance equation and are not independent.

Results

The NPHSP model above, based on the simplifying assumptions already mentioned, has to be validated in order to use it. This is why the model was configured for a real RD column used for acetic acid (AcH) recovery from waste water through esterification with n-butanol (BuOH). The products are the butyl acetate BuAc and purified water (if the process is adequately operated) [1]. This 22-trays RD column (with the standard structure in fig. 1) gets a totally refluxed organic phase (separated in decanter after condensation). As a consequence, the top product is an aqueous phase, while the bottom product consists of the organic phase. Following the experimental frame from work [1], the column is fed on the 8th tray with a mixture of unpurified water (with 0.1136 AcH mole fraction) and butanol (in excess, the mole ratio AcH:BuOH being 1:2); the total feed flowrate is 0.00675 kmol/h. The column has a constant liquid holdup of 2×10^{-4} m^3 on each tray. The reactive zone (heterogeneous type) is located below the tray 8, with a catalyst load of 0.0024 kg per stage.

This particular example was chosen because the authors of this paper had access to a real column with this configuration (at the Max-Plank Institute, Magdeburg, Germany), making possible a relevant comparison between the experimental data and the simulation results. After extensive tests, especially for operating regimes where the liquid phase splitting does not occur (so the NPHSP model is appropriate), a strong concordance between the simulated and experimental results was observed. Just as example, figure 5 depicts the RD system dynamic behaviour when the AcH concentration in feed increases with 5%. The evolution of liquid composition profiles along the column for BuOH, AcH, BuAc and water are presented, from the light gray line (initial state) to the dark gray line (final state). The light/dark gray dots correspond to real plant data for the initial and final states, respectively.

One can observe there is a very good agreement between the experimental data and the simulation results, both qualitatively and quantitatively (with an average error of 1.195%, in terms of measured compositions on trays). The same accurate results were obtained when studying the system behaviour with respect to changes in the feed flowrate. As figure 6 depicts, the evolution of liquid composition profiles for a 5% decrease in column feed flowrate, obtained by simulation, follow in a good manner the experimental results (with an average error of 1.247%).

Concluding remarks: why and how the NPHSP model has to be used for realistic (PHSP) simulations

Although the above model describes in an appropriate manner the process behaviour, there are some cases when the classical approach in RD modeling may not be satisfactory. For instance, production of high purity substances can be facilitated by using a “smart” and adaptive reflux policy that exploits the appearance of a miscibility gap at the condenser and in the upper part of the column (a typical example being the production of butyl acetate [8]). Although extremely beneficial for the process itself, considering as possibility the appearance of a second liquid phase makes the dynamic simulation of the column a much more difficult task [3, 6, 9]. In [8] it is shown that the main problems are the rapid, robust and reliable determination of the phase state on each tray during the simulation horizon, the calculation of

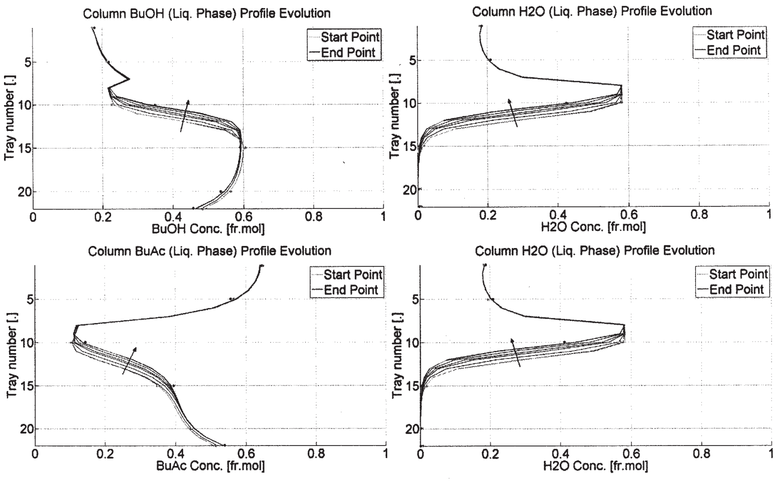

Fig.5. Simulation results vs. experimental data for the NPHSP model, for a 5% AcH concentration increase in feed

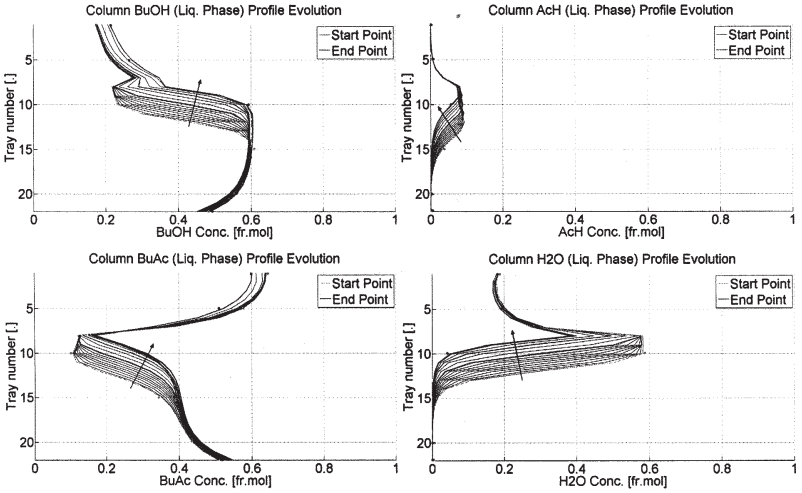

Fig.6. Simulation results vs. experimental data for the NPHSP model, for a 5% increase in feed flowrate

compositions in both phases (on trays in heterogeneous regime) and the phases ratio, as well as the determination of the switches in the process model (NPHSP vs. PHSP), associated with a change in the phase state on some trays. Obviously, although these problems arise when building the PHSP model, they can be addressed only after an appropriate NPHSP model setup is a-priori performed.

Practically, the above presented mathematical NPHSP model, validated through extensive studies, is ready to be used for phase-splitting computing steps. This classical approach cannot be avoided, as time as solving the NPHSP model is the only way to provide the required information for any PHSP algorithm – and this is why this modeling approach must get a special attention in terms of model relevance and accuracy.

Nomenclature

fgab – vapor sidedraw molar flowrate;
fgzu – external vapour feed molar flowrate;
flab – liquid sidedraw molar flowrate;
flzu – external liquid feed molar flowrate;
HOLD – molar liquid holdup on tray;
liq – internal liquid molar flowrate;
vap – internal vapour molar flowrate;
NC – number of components;
p – pressure;
psp – saturation pressure in the vapour phase;
R – reaction rate;
T – temperature;
V – volumetric liquid holdup on tray;
x – mole fraction, liquid phase;
y – mole fraction, vapour phase;
zflzu – mole fraction in external liquid feed;
zfgzu - mole fraction in external vapour feed;
γ – activity coefficient;
η – tray efficiency;
ν – stoichiometric coefficient;
i – component indices;
k – tray number.

Acknowledgements:The authors express their gratitude to Prof. Dr. Eng. Achim Kienle from The Max-Plank Institute, Magdeburg, Germany for his support and valuable input during the research period.

References

1.RADULESCU, G., GANGADWALA, J., PARASCHIV, N., KIENLE, A., STEYER, F., SUNDMACHER, K., Buletinul Universitatii Petrol-Gaze din Ploiesti, **LVIII**, Seria Tehnica Nr.1, 2006, p.1.
2.SUNDMACHER, K. KIENLE, A. Reactive distillation: status and future directions, Wiley –VCH, Weinheim, 2002.
3.GANGADWALA, J., MANKAR S., MAHAJANI, S., KIENLE, A. , STEIN, E. Ind. Eng. Chem. Res., **42**, no.10, 2003, p. 2146
4.SINGH, A. HIWALE, R. MAHAJANI, S.M., GUDI, R.D., GANGADWALA, J., KIENLE, A., Ind. Eng. Chem. Res., **44**, no.9, 2005, p. 3042.
5.AVAMI, A., MARQUARDT, W., SABOOHI, Y., KRAEMER, K. Chem. Eng. Sci., **71**, 2012, p.166.
6.GANGADWALA, J., RADULESCU, G., KIENLE, A., SUNDMACHER, K., Comput. Chem. Eng., **31**, No.11, 2007, p. 1535.
7.GANGADWALA, J., RADULESCU, G., PARASCHIV, N., KIENLE, A., SUNDMACHER, K., Comput.-Aided Chem. Eng., Elsevier, 2007, **24**, p. 213.
8.RADULESCU, G., GANGADWALA,J. PARASCHIV, N., KIENLE, A., SUNDMACHER, K., Comput. Chem. Eng., **33**, No. 3, 2009, p. 590.
9.STEYER, F., FLOCKERZI, D., SUNDMACHER, K., Comput. Chem. Eng., **30**, No. 2, 2005, p. 277

Manuscript received: 25.07.2013