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# DYNAMIC SIMULATION OF REACTIVE DISTILLATION PROCESSES TO PREDICT START-UP BEHAVIOR

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Abstract: In the last years, the integration of reaction and distillation in one process, has gained more interest. The mixing of these two operations is especially convenient and shows many advantages. The startup procedure of a conventional distillation column spends a lot of time and energy besides producing off-spec products. In reactive distillation, this problem becomes worse once the product cannot be easily recycled, making the start-up procedure very cost-intensive. In this work, the dynamic simulation of reactive distillation columns is studied in order to analyze different startup procedures. Different strategies were implemented and simulated. Furthermore, an evaluation of uncertainties in model parameters on the startup time was carried out.

Keywords: Reactive Distillation, Dynamic Simulation, Start-up

## 1. INTRODUCTION

Reactive distillation (RD) can be defined as the integration of chemical reaction and thermal separation in one process step. Examples of industrial applications are esterifications (e.g. production of ethyl acetate) or etherifications (e.g. production of MTBE) (Reepmeyer et al., 2004). This process can offer several advantages such as:

- it can reduce capital and production costs by combining two units into one;
- conversion in reversible reactions can be increased by overcoming chemical equilibrium limitations through the removal of reaction products;
- heat duty can be reduced by using the heat of reaction for thermal separation;
- limitations of separating azeotropic mixture can be overcome by reaction;
- recycle costs for excess reactant, which is necessary for a conventional reactor to prevent side reactions and chemical equilibrium limitation, can be reduced (Lee and Dudukovic, 1998).

Due the above and other reasons, the number of publications about simulation of reactive distillation has grown rapidly in the last years.

The start-up of a distillation column is a very hard to control procedure. All the process variables change very fast, making it even more difficult. Specially in a reactive distillation process, the off-spec product generated during the start-up cannot be easily refluxed because it displaces the kinetic equilibrium towards to reactants formation.

The studies of Reepmeyer et al. (2003) and Reepmeyer et al. (2004) assume phase equilibrium only if the bubble conditions of the liquid on the tray are reached. Before that, the authors do not consider the vapor phase in the simulation.

In this work, the thermodynamic equilibrium is considered since the beginning of the start-up. A dynamic model was built and three of the main strategies of start-up were simulated and compared. Moreover, a study about the effect of uncertainties in model parameters was carried out.

## 2. MODELING

In order to predict the dynamic behavior, needed to represent the start-up of a cold and empty column, a rigorous model for multicomponent reactive distillation was implemented in the equation-oriented dynamic simulator EMSO (Soares and Secchi, 2003). The physical and thermodynamic properties were obtained from the thermodynamic package VRTherm (VRTech, 2005).

The main assumptions to build the model were: the reaction takes place only in the liquid phase and phase equilibrium is assumed.

The model for each tray is described by the following equations:

Molar balance:

$$\frac{dM}{dt} = F_{in} \cdot z + F^l_{in} \cdot x_{in} + F^v_{in} \cdot y_{in} - F^l_{out} \cdot x_{out} - F^v_{out} \cdot y_{out} + r \quad (1)$$

where $r$ is the reaction rate, the subscript $in$ is used for inlet streams, the subscript $out$ the outlet streams, the superscripts $l$ and $v$ correspond to liquid and vapor phase. The feed, liquid, and vapor molar fraction are $z$, $x$ and $y$ respectively.

Energy balance:

$$\frac{dE}{dt} = F_{in} \cdot h_{in} + F^l_{in} \cdot h^l_{in} + F^v_{in} \cdot h^v_{in} - F^l_{out} \cdot h^l_{out} - F^v_{out} \cdot h^v_{out} + Q + H_r \cdot r \quad (2)$$

where $h$ is the molar enthalpy and $H_r$ is the reaction heat.

Holdup:

$$M = M^l \cdot x + M^v \cdot y \quad (3)$$

$$E = M^l \cdot h^l + M^v \cdot h^v - P \cdot V_{tray} \quad (4)$$

Equilibrium condition:

$$\phi_{liq} \cdot x_n = \phi_{vap} \cdot y^*_n \quad (5)$$

where $\phi_{liq}$ and $\phi_{vap}$ are the liquid and vapor fugacity coefficient.

Hydrodynamic equations:

$$F^l_{out} = 1.84 \cdot lw \cdot \frac{\left(\frac{Level-(\beta \cdot hw)}{\beta}\right)^2}{v_{liq}} \quad (6)$$

$$F^v_{in} = \frac{Ah}{v_{vap}} \sqrt{\frac{(P_{n+1} - P_n) - \rho_{liq} \cdot g \cdot Level}{\alpha \cdot \rho_{vap}}} \quad (7)$$

where, in Equation 6, $F^l_{out}$ is the liquid flow rate leaving the tray, $lw$ is the weir length, $hw$ the weir height, $\beta$ the aeration fraction, $Level$ is the liquid level in the plate and $v_{liq}$ the liquid molar volume. In Equation 7, the vapor flow rate entering the tray $F^v_{in}$ is calculated by the contribution of static pressure ($\rho_{liq} \cdot g \cdot Level$) and the tray pressure drop. $Ah$ corresponds to the plate total holes area, $v_{vap}$ the vapor molar volume, $\alpha$ the dry pressure drop coefficient, $g$ the gravitational constant and $P_{n+1} - P_n$ is the pressure difference between the plate below and the current plate.

The Murphree efficiencies, $E_{MV}$, are considered known model parameters:

$$E_{MV} = \frac{y_n - y_{n-1}}{y^*_n - y_{n-1}} \quad (8)$$

where $y_n$ is the molar fraction of vapor and $y^*_n$ is the vapor molar fraction in thermodynamic equilibrium with the liquid phase.

The main uncertainties considered in this model are associated with the model parameters $\alpha$, $\beta$ and $E_{MV}$.

## 3. START-UP STRATEGIES

Regarding ordinary distillation columns, there are a lot of studies about operational procedures to take the plant towards the steady state operation. Among the main strategies, three of them were considered. They are:

- Conventional Strategy: the empty and cold column is filled up with feed. Then, all the controllers are turn on and the unit goes to the steady-state operation.
- Total Reflux: the empty and cold column is filled up with feed. When the reboiler level is reached, the heating is turned on. Then, the column runs in loop operation. No distillate is taken from the top, the condensate is totally refluxed. At a given time, the control variables set points are set to their steady-state values.
- Total Distillate Removal: during the start-up, the distillate is completely taken away at the top, there is no reflux stream back into the column. At a given time, the control variables set points are

set to their steady-state values (Reepmeyer et al., 2003).

According to Reepmeyer et al. (2003), the time where the controllers are turned on is defined when the $MT$ function, stated by Yasuoka and Nakanishi (1982), become lower than a given tolerance:

$$MT = \sum_{trays} (T_{current} - T_{steady}) \leq \epsilon \qquad (9)$$

The $MT$ function can be understood as the distance from the steady-state of the current simulation state.

Besides these three start-up strategies, many other can be found in the literature. For more information, please refer to Reepmeyer et al. (2004).

## 4. SIMULATION

To test the developed model and to study the dynamic behavior of a reactive distillation column in start-up procedures, the esterification of ethanol and acetic acid yielding ethyl acetate was considered. The steady-state point resulting from the dynamic simulation was compared with literature data. This reaction was chosen because it is widely known and it represents a major group in reactive distillation applications, the esterification process. Unfortunately, it is a purely theoretical example and no experimental data is available in the open literature. However, this limitation does not compromise the comparative results of the start-up procedures.

Ethyl acetate esterification:

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O \qquad (10)$$

The process conditions and reaction kinetics were taken from Lee and Dudukovic (1998):

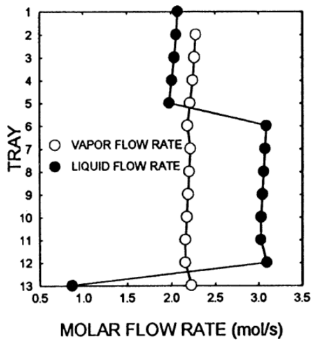
$$r = exp^{\frac{-7150}{T}} \left[4,85 \cdot 10^4 C_a C_b - 1,23 \cdot 10^4 C_c C_d\right] (11)$$

where $C_a$, $C_b$, $C_c$ and $C_d$ corresponds to the molar concentration of ethanol, acetic acid, ethyl acetate and water, respectively.

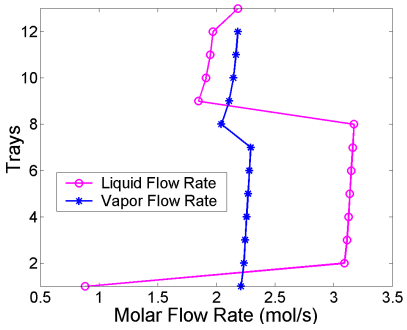
The thermodynamic model used to calculate the liquid behavior was UNIFAC and the vapor phase was considered as ideal gas.

The steady-state results from the dynamic simulation of the developed model were compared with those presented by Lee and Dudukovic (1998). The verification of the results can be seen in Fig. 1 – 4.

As can be seen, the steady-state results are compatible with the literature but the dynamics still needs to be checked. To generate this results Lee and Dudukovic (1998) used the Modified Margules equation to predict the liquid behavior. In this work, was used UNIFAC model. This difference

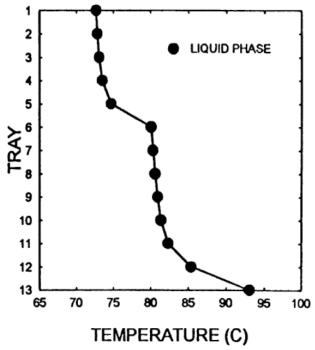



(a) Lee e Dudukovic (1998)

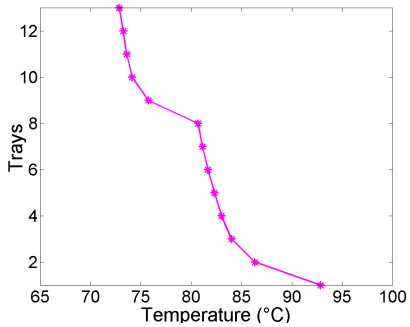



(b) Simulation

Fig. 1. Liquid and vapor flow rate profile.

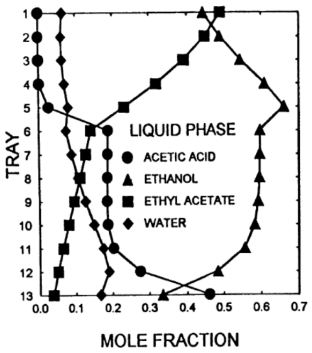



(a) Lee e Dudukovic (1998)

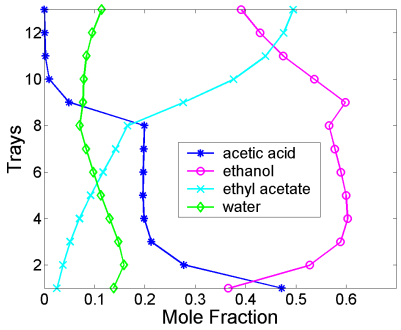



(b) Simulation

Fig. 2. Temperature profile.

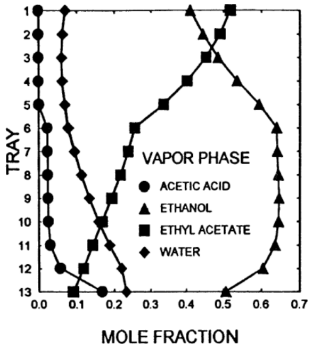



(a) Lee e Dudukovic (1998)

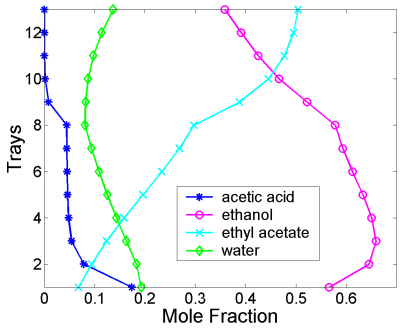



(b) Simulation

Fig. 3. Liquid molar fraction profile.




(a) Lee e Dudukovic (1998)




(b) Simulation

Fig. 4. Vapor molar fraction profile.

can be the reason of some little discrepancies in the steady state profiles.

## 5. START-UP TIMES

To measure the time needed to reach the steady-state, the $MX$ function developed by Yasuoka and Nakanishi (1982) was used:

$$MX_{top} = \sum_i \mid (x_{i,current} - x_{i,steady}) \mid \qquad (12)$$

This function is the sum of the absolute differences between the current composition in the top product and the steady-state composition. If $MX$ is below 0.001, the desired steady state is considered to be reached (Reepmeyer et al., 2004).

The three start-up strategies presented before, were simulated using the developed model. The results for the $MX$ function can be seen in Figure 5:

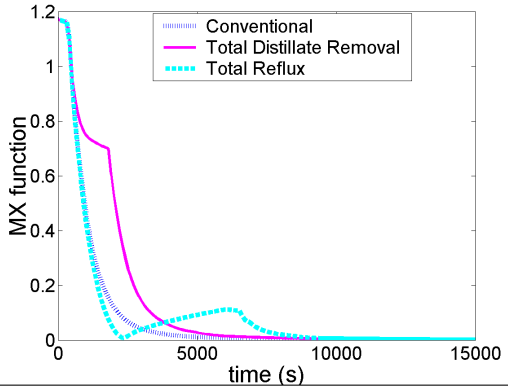



Fig. 5. MX function values during the start-up.

As can be seen in Figure 5, the total reflux strategy demanded more time to reach the steady-state. The other procedures took similar times with a little advantage to the conventional strategy. The start-up times are shown in Table 1:

Table 1. Time for different start-up procedures

| **Strategy** | **Start-up time (min)** |
|---|---|
| Conventional | 212 |
| Total Distillate Removal | 240 |
| Total Reflux | 273 |

The major time spend with the total reflux strategy can be easily explained. When the top stream is reintroduced into the column, the concentration of the reaction product increases. Because of this, the kinetic equilibrium is displaced towards the reactants formation. Then, the stabilization of the column top concentration is delayed.

## 6. STUDY OF MODEL PARAMETERS UNCERTAINTIES

Another important part of this work is the evaluation of the uncertainties effects in the dynamic model response. The model presented here have basically four types of parameter, that are:

- geometrical parameters
- kinetic parameters
- thermodynamic parameters
- hydrodynamic parameters

The geometrical parameters are easily obtained and can be measured directly in the plant. The kinetic parameters are out of the scope of this work, it was considered that they were correctly determined and represent the real behavior of the system with accuracy. The thermodynamic and physical properties are calculated by the proprietary package VRTherm and likely the kinetic parameters are out of the scope of this work. The Murphree efficiency, $E_{MV}$ (Eq. 8), included to the model to take account the nonidealities of the phases, has a uncertainty associated on its value and it was included in this study. The hydrodynamic parameters, $\alpha$ in Eq. 7, related to the dry pressure drop coefficient and $\beta$ in Eq. 6, related to the aeration fraction, do not have an analytical approach or correlation to determine them, they are set only by empirical known.

In resume, the parameters chosen were: (1) the Murphree efficiency, $E_{MV}$; (2) the parameter $\alpha$, Equation 7, related to the dry pressure drop coefficient and (3) the parameter $\beta$, Equation 6, related to the aeration fraction.

The results shown in Section 4 were obtained with the values: $E_{MV} = 1$, $\alpha = 30$, and $\beta = 0.8$. In order to evaluate the effect of the parameters, several simulations were run with variations on the parameters values. The $MX_{top}$ function was used to determine the start-up time of each experiment.

The Murphree efficiency was changed around 50%. For each variation, a new simulation was made. For conventional and total distillate removal strategies, the start-up time has varied around 7% and for total reflux strategy no significant variation has been observed.

For the parameter $\alpha$, related to the dry pressure drop coefficient, simulations were run with values ranging from 15 to 45 (variation around 50% off default value). Different start-up times have been observed only for lower values (other than the default) and the variations have not been larger than 8.5%. No significant variation has been perceived for total reflux strategy

Finally, the parameter $\beta$, related to the aeration coefficient was checked. This parameter is used in Eq. 6 to calculate the tray liquid flow rate. Simulations were made with $\beta$ ranging from 0.60 to 1.00. This parameter presented the largest influence in start-up time because it affects straightly the liquid residence time in the tray and consequently the reaction environment. The results are shown in Table 2-4.

Table 2. $\beta$ influence in start-up time with the conventional strategy.

| $\beta$ | **Start-up time (min)** | **%** |
|---|---|---|
| 0,60 | 285 | 34.4 |
| 0,70 | 228 | 7.5 |
| 0,80 | 212 | 0 |
| 0,90 | 210 | −0.9 |
| 1,00 | 202 | −4.7 |

Table 3. $\beta$ influence in start-up time with total distillate removal strategy.

| $\beta$ | **Start-up time (min)** | **%** |
|---|---|---|
| 0,60 | 315 | 31.3 |
| 0,70 | 258 | 7.5 |
| 0,80 | 240 | 0 |
| 0,90 | 235 | −2.1 |
| 1,00 | 227 | −5.4 |

Table 4. $\beta$ influence in start-up time with total reflux strategy.

| $\beta$ | **Start-up time (min)** | **%** |
|---|---|---|
| 0,60 | 352 | 28.9 |
| 0,70 | 310 | 13.6 |
| 0,80 | 273 | 0 |
| 0,90 | 267 | −2.2 |
| 1,00 | 267 | −2.2 |

In relative terms, the total reflux strategy was the least affected by $\beta$ uncertainty, probably because of the greater internal liquid flow rates in the column.

## 7. CONCLUSIONS

In this work, the start-up simulation of a reactive distillation was accomplished. A dynamic model was built and implemented in EMSO simulator using its modelling environment.

Different from the literature models for this kind of system, the existance of both phases (liquid and vapor) were considered since the beginning of the simulation. The three main start-up procedures found in the literature, from cold and empty column, were simulated. As it is well known, the total reflux strategy has showed the largest instability time. Although this strategy is more time consuming, it cannot be considered the less indicated. While the others generate off-spec products, that need to be discarted, the total reflux procedure do not and this fact must be considered. Obviously a more rigorous evaluation needs to consider operation and raw-material costs.

Besides, the model has been shown well appropriate to start-up simulations. Mainly because

possible difficulties to determinate the main model parameters almost do not affect the start-up time. The exception is the parameter $\beta$ that presents a significant influence in the liquid hold-up and consequently in the residence time of the reaction mixture.

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