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Comparison of the Startup of Reactive Distillation in Packed and Tray Towers

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Abstract

The startup of distillation towers and in particular reactive distillation (RD) towers is a very complex, time and energy consuming process. To analyze and optimize this process, a dynamic simulation model is developed which takes into account the changes of thermodynamic and hydraulic variables during the startup starting from a cold and empty state. Different aspects in modeling as well as in managing of the startup process for packed and tray towers are discussed and special startup strategies are analyzed considering as an example the methyl acetate synthesis in towers with different internals. Experimental validation results are presented showing good agreement between the measured and simulated temperature profiles during the whole startup.

Keywords: startup, reactive distillation, dynamic simulation, esterification

1. Introduction

The combination of reaction and distillation in one reactive distillation (RD) unit can lead to significant reductions of investment and operational costs. Conversion can be increased for equilibrium limited reactions. Heterogeneous reactive distillation in packed towers is of special interest because the catalyst does not have to be removed from the product and different reactive and non-reactive sections can be realized. At the same time the interactions of reaction and separation increase the complexity of the process and thus require a better understanding of the process dynamics.

In this contribution the whole startup of RD towers from the first feed entering the cold and empty tower to the final operating point is analyzed. For the case of tray towers Reepmeyer et al. (2004) have developed a dynamic startup model. Based on this model further developments for the simulation of heterogeneous RD in packed towers have been carried out. In this contribution the differences of the startup of tray and packed towers concerning both modeling aspects and startup strategies are discussed.

2. Modeling

For the simulation of RD, both equilibrium (eq) and nonequilibrium (neq) stage models have been considered and implemented in gPROMS®. Since the focus of this study is on general startup dynamics, sufficient accuracy for the description of these phenomena is required. For the considered case study (methyl acetate synthesis) it could be initially shown that the eq model predicts very well the experimental dynamic data published by

Noeres et al (2004). Thus in the following the eq model is used which consists of the MESH equations, reaction kinetics and hydraulic correlations. Both liquid and vapor phase are modeled. Non-idealities of the liquid phase are considered using activity coefficients γ_i calculated from the UNIQUAC model, vapor phase association is taken into account by considering fugacity coefficients φ_i from the chemical theory according to Marek (1955).

The modeling of packed and tray towers differs in the hydraulic correlations for pressure drop and liquid holdup. The pressure drop in tray towers is modeled as the sum of dry and hydrostatic pressure drop. The liquid holdup on a tray is calculated with the Francis weir formula. For pressure drop and liquid holdup in packed towers the empirical correlations presented by Engel et al. (2001) are implemented. In addition different forms of catalysis (heterogeneous or homogeneous) require different models for reaction kinetics. Heterogeneous catalysis is described using both pseudo-homogeneous and adsorption-based approaches (Pöpken (2001)). All further model equations are unaffected by the choice of the internals.

2.1. Modeling of the startup

During the startup of a distillation tower the hydraulic variables (flow rates, holdups) and thermodynamic variables (temperatures) undergo large changes (Ruiz et al. 1988). Due to these transitions it is not possible to describe the whole startup from a cold and empty state to the operating point with the eq stage model. Different sets of equations are needed for the different distinguishable phases of the startup requiring a switching between these model equations at certain points:

The above-mentioned holdup correlations are applied only if on the considered section j a certain level (on the tray) or static holdup (in the packing) is reached. Otherwise the liquid flow rate is set to zero. At low temperatures T_j the phase equilibrium equation can not be used because conditions are far from boiling and the pressure p_j can therefore not be calculated as the sum of the partial pressures of the components in the mixture. In the startup model the pressure is therefore first set to a constant value $p_{initial}$ until the temperature calculated from the balance equations is equal to the additionally calculated bubble point temperature $T_j^{LV}(p_j,x_{ij})$ at this initial pressure and current composition, Eq. (1).

IF $T_j \geq T_j^{LV}\left(p_j, x_{ij}\right)$ THEN

$$p_j = \sum_i \left(x_{ij}\gamma_{ij} p_{0ij}^{LV} \, \varphi_{0ij}^{LV} \big/ \varphi_{ij} \right)_{T_j} \tag{1}$$

ELSE

$$p_j = p_{initial}$$

In the following the equilibrium equation is used for the correlation of temperature and pressure. When consequently the pressure on this section is getting higher than the pressure on the section above then vapour starts to ascent and the vapour flow rate is correlated to the pressure drop. Otherwise the vapour flow rate is set to zero.

This modeling procedure has been explained in detail by Reepmeyer et al. (2004). In the special case of startup simulations, eq and neq modeling approaches only differ in the last phase of the startup simulation, when all stages have reached boiling temperature.

2.2. Model validation

Before using the newly developed process model for simulation studies, validation with dynamic experimental data from RD columns with different internals is required. Since, especially for the startup from a cold and empty state, such data can hardly be found in the literature, experiments have been carried out with different laboratory scale columns. For the validation of the model for heterogeneously catalyzed reactive distillation in packed towers a glass column with an inner diameter of 50 mm and a packed height of 6m has been used. Further details on this RD column can be found in Steinigeweg and Gmehling (2004). The esterification of acetic acid with isopropanol forming isopropyl acetate and water has been studied as an example system. Data for the adsorption-based kinetics has been published by Pöpken (2001). The experimental setup is shown in Fig. 1 together with a comparison of the simulated and experimentally measured temperatures during startup at the reboiler and three points in the column.

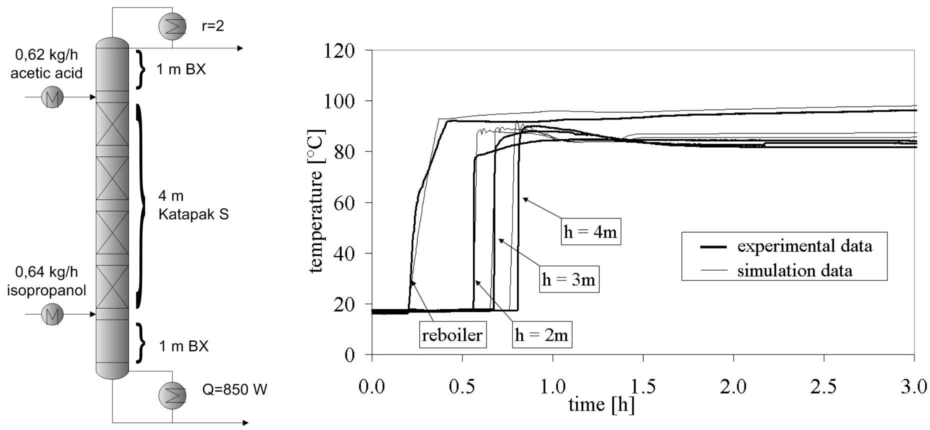


Figure 1. Packed column setup for the esterification of acetic acid with isopropanol and comparison of simulated and experimentally measured temperatures during startup.

The operating point has been reached without manipulation of reflux ratio or reboiler duty. The simulation reproduces very well the heating of the liquid in the reboiler and the ascent of the vapor in the column. Due to a first condensing of the vapor when heating up the liquid film and the column material (both column wall and internals are included), the rising of the temperatures at higher points in the column is delayed.

The simulation model has also been validated with experimental data from a homogeneously catalyzed transesterification process in a 100 mm tray column. Both temperature data (for the startup) and concentration data (steady state and dynamic) have been used. The validation results have been published in Reepmeyer et al. (2004).

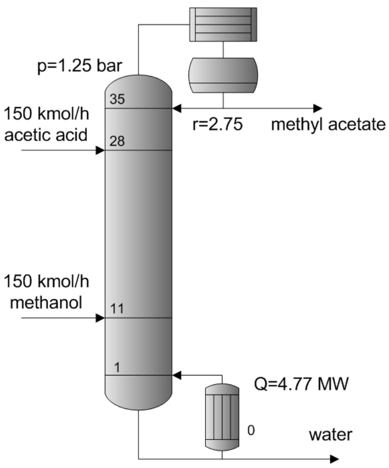
3. Startup strategies

The startup can be carried out following different strategies in order to reach the desired steady state as fast as possible in compliance with given constraints. Different startup strategies for conventional distillation have been proposed in the literature. Besides conventional startup (with manipulated variables fixed to their final values), alternatives such as startup with total reflux (Kister (1990)), total distillate removal (Flender (1999)) or with different manipulated variables (Löwe et al. (2000)) have been discussed. Optimal strategies have been presented for different processes by Wozny and Li (2004).

Reepmeyer et al. (2004) have proposed new strategies for reactive distillation in tray towers. In simulation studies average savings in startup time of about 45% compared to conventional startup were possible by initially charging product with different compositions (depending on the process). By recycling the off-spec top or bottom product with the feed during the startup, a reduction of disposal or processing costs could be achieved for some processes without significantly prolonging the startup time.
Due to the different hydrodynamics, the time-optimal strategy for tray towers (initial charging) can not be applied directly to packed towers. These differences in startup strategies have been studied for the methyl acetate synthesis.

4. Case study and results

The application of the above-mentioned strategies to packed and tray towers has been analyzed for the well known methyl acetate synthesis as introduced by Agreda and Partin (1984), following the design proposed by Al-Arfaj and Luyben (2002). The process design and the specifications of the studied tray and packed towers are presented in Fig 2. Holdups in sump and distillate drum are similar for both designs, so that the influence of the different column holdups on the dynamics can be compared. For the homogeneous process reaction takes place on every tray below the sulfuric acid supply on stage 28, including the reboiler. In the case of the packed tower, reaction is limited to the column sections between the two feeds which is equipped with Sulzer Katapak SP. Kinetic parameters for the homogeneous reaction have been taken from Rouzineau et al. (2003) and for the heterogeneous reaction (pseudo-homogeneous and adsorption-based approach) from Pöpken (2001). UNIQUAC parameters have been published by Pöpken (2001).



	Tray Tower	Packed Tower
specifications		
diameter	2 m	
reactive sections	0-28	11-28
catalyst	H_2SO_4 (5ml/l)	Amberlyst 15
simulation results		
conversion	96.6 %	98.1 %
$X_{D,MeAc}$	0.956 mol/mol	0.962 mol/mol
$X_{B,H2O}$	0.958 mol/mol	0.977 mol/mol

Figure 2. Setup for methyl acetate synthesis in tray and packed tower and simulation results.

The simulation results in Fig. 2 show that for the two chosen configurations the product purities and the conversion are relatively close. To evaluate the startup time, the MX function has been calculated which gives the summation of the deviations between the current concentrations and their steady state values at the top of the column, where methyl acetate is produced. A first comparison between the simulation results for the packed tower using both pseudo-homogeneous and adsorption-based kinetics showed only very little differences that were due to the slightly different steady state results

(Fig. 3 *left*, curves 2 and 3). Therefore the simpler pseudo-homogeneous kinetic model can be used for further studies of the startup of the packed tower. To analyze the process dynamics for the two different designs, first the startup according to the conventional strategy has been simulated. Due to the different holdups in the towers, the startup times are very different (Fig. 3 *left*). The startup of the tray tower with fixed reboiler duty requires a large reboiler holdup because it takes longer to fill up the upper part of the column with the reflux so that a lot of product from the bottom with a high water fraction is evaporated before reflux reaches the bottom. This leads to high water concentrations in the lower part of the column during startup before real separation by counter current distillation can take place, so that the settling of the concentrations to their steady state values takes very long (Fig. 3 *right*). This phenomena cannot be observed for packed towers, since in this case reflux reaches the bottom faster and the counter current flow is established earlier. In addition, the steady state concentration profiles are quite different for the two designs (although close at the bottom and top), for the packed tower the water fraction in the lower part of the column is considerably higher.

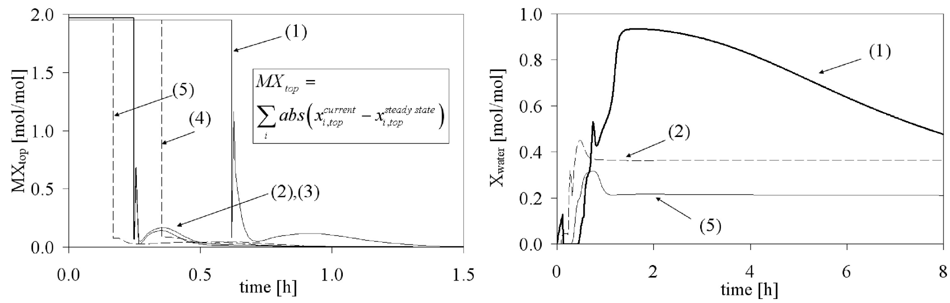


Figure 3. *left:* Comparison of startup times for packed and tray towers following different strategies. (1): tray tower, conventional; (2): packed tower with pseudo-hom. model, conventional; (3): packed tower with ads.-based model, conventional; (4): packed tower with pseudo-hom. model, methyl acetate feed; (5): tray tower, initial methyl acetate charging; *right:* Comparison of the water fraction on section 7

The described behavior of the tray tower can be changed by initially charging top product (methyl acetate) on the trays (curve 5). Even without changing the feed specifications, this leads to a significant reduction of startup time, since in this case very little water is produced during the startup due to the relatively high methyl acetate fractions throughout the column. Comparable effects can be achieved by supplying the catalyst later to the system.

Initial charging of product is not possible for packed towers. Alternatively feeding with a different composition is simulated until the reflux is turned on (curve 4). It is found that because of the smaller holdup the influence of the feed concentrations during the first part of the startup is not so important. At the top the product specifications can be reached faster but it takes longer for the whole tower to reach steady state. For all the studied cases the bottom product meets the specifications later than the top product as can be seen from the different time scales of the two graphs in Fig. 3. This behavior is due to the large reboiler volume.

5. Conclusions and future work

A dynamic startup model for homogeneously and heterogeneously catalyzed reactive distillation in packed and tray towers has been developed and validated. The dynamic behavior of packed and tray towers during startup has been analyzed and differences have been pointed out. Especially the different size of the liquid holdup on the different internals has a large influence on the startup time so that for tray towers startup time can be minimized by initially charging product to the column. For packed towers different feed concentrations during startup affect the startup time only slightly.

In a next step experimental investigations of the methyl acetate system in a laboratory scale column equipped with Katapak SP will be carried out to further validate the simulation results for the startup. To draw more general conclusions concerning the different dynamics of RD in packed and tray towers, additional systems will be studied for both configurations.

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