STARTUP ANALYSIS OF MASS- AND HEAT-INTEGRATED TWO-COLUMN-SYSTEMS

Varbanov, P.*, Klein, A., Repke, J.-U., Wozny, G.
Technical University Berlin, Department of Process and Plant-Dynamics, Straße des 17, Juni 135, 10623 Berlin, Germany
E-mail: petar.s.varbanov@TU-Berlin.de; Phone: +49 30 2837 6921;
Mobile: +49 176 22612933, Fax: +49 30 314 26915

The start-up of a chemical plant is a complex and highly dynamic process. The complexity results from the variation of all process variables over a wide range until the required operating point is reached. In previous studies, the start-up of single columns for conventional and reactive distillation was considered. A two-column-system was also analysed, but without mass integration between the columns, which means with no positive feedbacks. In this work, a heat- and mass-integrated two-column system for continuous azeotropic Pressure Swing Distillation (PSD) is analysed. Improved models for the individual equipment units such as trays, condensers and heat exchangers have been formulated and simulation studies have been carried out to validate the models against a set of experimental data.

KEYWORDS: pressure-swing distillation, azeotropic separation, energy-and-mass integration, start-up

INTRODUCTION

The separation of homogeneous azeotropic mixtures is a very important process in chemical industry frequently employed for solvent recovery. To solve the separation problem, pressure-swing distillation (Knapp and Doherty, 1992), is often considered an efficient alternative to the broadly applied azeotropic and extractive distillation processes. Currently, only few theoretical results on this process have been published and experimental data are also scarce (Phimister and Seider, 2000), which seems to be the reason for its rare industrial application. An exception to this is the separation of Tetrahydrofuran (THF)-Water mixtures, for which Pressure-Swing Distillation is the method often used by industry (Knapp and Doherty, 1992). The main advantages of the Pressure-Swing Distillation are the improved energy efficiency and the elimination of entrainers. On the other hand, the material and energy integration of the columns results in a highly complex plant which is more difficult to control (Löwe and Wozny, 2001).

Forner (2003) and Repke et al. (2005) developed a simulation model of a two-column PSD system of established operation in continuous mode. This model was used to analyse the robustness of the system operation towards disturbances. Wang et al. (2003) presents a model for start-up simulation of a batch distillation column on the example of the methanol-water mixture. The main contribution of this work is the definition of two groups of

*Corresponding author.

equations, being switched when the tray reaches bubble point. Wendt et al. (2003) present an optimisation study for the start-up of a heat integrated two-column system for water-methanol separation. In this case, the two-column arrangement is used merely to achieve energy savings by means of heat integration and no mass integration is applied.

In the current paper, an analysis of the start-up of a two-column system for continuous Pressure-Swing Distillation of Acetonitrile-Water mixtures is presented, using an improved dynamic model. Acetonitrile-water is a binary mixture, featuring a pressure-sensitive azeotrope. The flowsheet of the considered system is given in Figure 1. The feed containing 27 mol% acetonitrile is introduced into the low-pressure (LP) column. Acetonitrile is obtained as the bottom product of the HP column and water as the bottom product of the LP column. The distillate of each column is recycled to the other one. The recycle from the HP column is introduced into the LP column several trays above the feed (see Figure 1). The mole fractions of the distillates are close to the azeotropic compositions at the respective pressures. The considered column system is also heat integrated by condensing the HP column distillate against the evaporation of the mixture in the LP column reboiler (WD201_HP in Figure 1).

The current study presents a number of model improvements, together with the corresponding simulation and validation results.
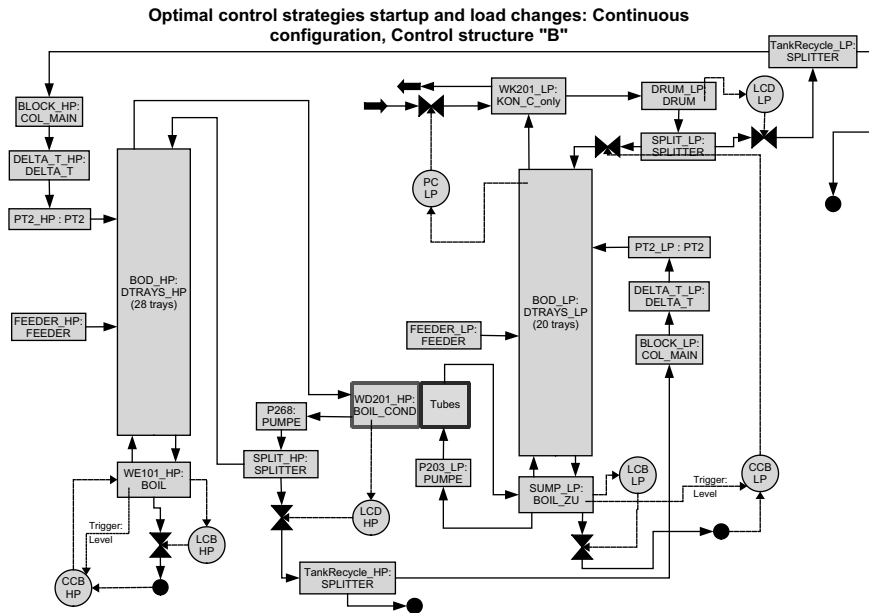

Figure 1. Flowsheet and control structure of the analysed system

IMPROVEMENTS IN THE UNIT MODELS

MODELLING THE TRAYS AND THE HP REBOILER

Both columns in the considered system contain bubble-cap trays with central down-comers. The HP column has 28 trays and the LP column – 20 trays. The geometric properties of the trays are described in detail in (Löwe and Wozny, 2001) and (Wang et al. 2003). In Forner (2003) and Repke et al. (2005), a dynamic model only for the case of established operation is given, which is an adaptation from Rix (1998) and Löwe (2001). This includes standard mass and energy balance differential equations, equilibrium and tray hydraulics equations. Perfect mixing and vapour-liquid equilibrium (VLE) are assumed on each tray and in the column bottoms. The VLE estimation is based on Wilson and Antoine equations and the tray equilibrium compositions are corrected using Murphree tray efficiencies. The described model was further improved by Wang et al. (2003) by accounting for the different thermodynamic and hydrodynamic modes on the tray, which are being switched as the simulation proceeds from cold and empty state through to established operation. The hydrodynamic mode has two states – vapour flowing into the tray (working) and no vapour inlet (during start-up). The "vapour flowing" state is switched to when the pressure of the vapour inlet from the tray below becomes sufficiently large to overcome the resistance of the current tray. The thermodynamic mode has also two states – below bubble point (during start-up) and VLE (working). The bubble point pressure is evaluated separately, serving as a criterion for switching the simulation to VLE state.

In the current work, this tray model from Wang et al. (2003) is used with minor changes. Firstly, the thermodynamic mode and the VLE are tracked by comparing the current tray temperature with the bubble point temperature for the current pressure. This is more convenient since the equations which are used for estimating the tray VLE properties during established operation, can be re-used for the start-up mode to estimate the bubble point temperature. The second change is the introduction of a heat loss term to the energy balance. The model of the utility reboiler, used in the HP column, has essentially the same features as the tray model. The main exceptions are that the reboiler does not have any vapour inlet, so there is no need to define a hydrodynamic mode. However, a thermodynamic mode is introduced in the same manner as for the tray model.

WATER CONDENSER

In this device, the vapour from the top tray of the LP column enters the shell side of a shell-and-tube heat exchanger and condenses on the outer surface of the tubes. Counter-currently inside the tubes flows cooling water, absorbing the heat released by the vapour condensation. In the work by Wang et al. (2003), the water condenser is modelled as a tray, with a complete set of equilibrium relationships and tray switching conditions as described above. However, for the purposes of more realistic modelling of the condenser dynamics and representation of the process of total condensation, it is necessary to drop the assumption for VLE, as well as to describe better the heat transfer to the water. The models used by Forner (2003) and Repke et al. (2005) introduced dynamic descriptions

of the heat transfer from the condensing vapour to the tube wall and from the wall to the cooling water.

The current work goes further by dropping the VLE assumption. Moreover, it has been found that the vapour holdup can be neglected and all incoming vapour can be assumed to condense immediately. The reason for this is that the amount of the maximum possible vapour holdup ($\approx 3 \cdot 10^{-3}$ kmol) is insignificant in comparison with the usual flow-rates of vapour inlet and condensation (up to 5 kmol/s). The experimental data on the dynamics confirm this assumption. Other assumptions applied to the condenser model are:

- The material holdup of the condenser shell side is modelled as consisting of a perfectly mixed liquid phase, into which the incoming vapour flows immediately after condensation.
- The tubes are always full with water and the water specific heat capacity is constant with temperature.
- The amount of heat transferred from the condensate to the cooling water is neglected.

COUPLING (RECOVERY) HEAT EXCHANGER

In (Rix, 1998), the recovery heat exchanger, integrating the HP vapour condenser and the LP reboiler, is modelled for the case of natural circulation on the tube (LP) side. This model was re-used in the work by Forner (2003) to model the forced circulation case. Both models assumed VLE on the shell side, where the vapour from the HP column top tray condenses. Also, the tube side is modelled with the steady-state material and energy balances in order to avoid the occurrence of differential index higher than one. The tube-side mixture is modelled as a two-phase flow in suppressed nucleate boiling regime (Rix, 1998, Forner, 2003).

In the current paper, the shell side of the recovery heat exchanger is modelled in the same way as the water condenser shell side, thus eliminating the VLE assumption and bringing the model closer to the total condensation in the actual device. Regarding the tube-side model, where the heating of the LP column base takes place, several improvements have been made. Firstly, the material and energy balances on the tube side have been formulated with the corresponding derivative terms for the holdups in the form:

$$\frac{dM_{REB}(i)}{dt} = L_{IN,REB} \cdot X_{IN,REB}(i) - L_{OUT,REB} \cdot X_{OUT,REB}(i) \tag{1}$$

$$\frac{dH_{REB}}{dt} = L_{IN,REB} \cdot h_{IN,REB} - L_{OUT,REB} \cdot h_{OUT,REB} + Q_{REB} - Q_{VER} \tag{2}$$

The high differential index is avoided by implementing a mechanism to calculate the tube outlet flow rate without using the material balances from equation 1. To implement this, a fictional amount of liquid volume violation has been defined, using the condition that the volume occupied by the fluid inside the tubes must be constant, when the tubes are full. The rigorous condition is that the time derivative of the fluid

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volume inside tubes is zero. However, using it directly would involve serious compu-
tational problems with determining derivatives of holdups and densities as well as
linking them to the fluid flow rates throughout all operating modes of the device.
Therefore, a simplified scheme is applied, using the condition:

$$V_{REB} = V_{TUBES} \tag{3}$$

First, an error term is defined, expressing the violation of the condition in equation 3:

$$DV_{EXTRA} = V_{REB} - V_{TUBES} \tag{4}$$

Using this volume violation term, a compensation liquid outlet flow-rate, account-
ing for the effects of volume change due to the heating, is calculated in equation 5. It is
then used to estimate the outlet flow rate (equation 6):

[NOT Tubes full] $LV_{EXTRA} = 0$

$$[\text{Tubes full}] \ LV_{EXTRA} = K_{EXTRA} \cdot \frac{1 + \tanh(\beta_{EXTRA} \cdot (DV_{EXTRA} - Tolerance))}{2} \tag{5}$$

[NOT Tubes full] $L_{OVR} = 0$

[Tubes full] $L_{OVR} = L_{IVR} + LV_{EXTRA}$

The computational scheme formulated in equations 4–6 tends to keep the values of
DV_{EXTRA} negligibly small.

Equation 5 uses a special function to calculate the extra liquid outflow, resulting in a
sharp decrease of the LV_{EXTRA} value when the value of DV_{EXTRA} approaches zero.

Another important improvement, compared to the previous models, consists of
treating the tube-side mixture as liquid-only instead of a two-phase mixture. Although
in the real flow there may be some small amount of bubbles forming, experiment
results indicate values of the overall heat transfer coefficient in the coupling heat exchan-
ger in the interval 1000–1500 W/(m²·K), which is far away from the range of 5000–
10000 W/(m²·K) for boiling. As a result, it is assumed that inside the exchanger tubes,
the liquid superheats without evaporation due to the short residence time and the lack
of free volume. Then, when delivered back to the LP column base, it expands, mixes
with the column base contents and there reaches equilibrium.

SIMULATION AND VALIDATION OF THE MODELS

An overall model for the two-column system, following the flowsheet in Figure 1 has
been constructed. The system startup is simulated for a typical feed containing
27% (mol) Acetonitrile and 73% (mol) water. An auxiliary feed for filling up the HP
column is assumed containing 81% Acetotintile. The latter is used only until distillate

flow becomes available from the LP column condenser. Both columns start from atmospheric pressure and the pressure in the HP column is gradually increased. The operating schedule, followed in the experiment and reproduced in the simulation, is presented in Figure 2.

The simulations have been able to match the temperature profiles from the experimental data quite precisely. Figure 3 shows the resulting temperature profiles for the system startup. The "integral error" indicated in each chart in Figure 3 refer to the differences between the time integrals of the temperature profiles from the simulations relative to those from the experimental data. The results from Figure 3 illustrate that the formulated model can adequately simulate the startup from a cold and empty state of a heat and mass integrated system of two distillation columns working at different pressures. The main computational difficulty of the simulation has been observed to take place in the period from the simulation start until vapour reaches the top of the LP column.

In Figure 3, charts (c) and (d), it can be noticed that the simulation indicates LP reboiler boiling start a little earlier than the experimental curve. This difference between the simulation results and the experimental records is attributed to the fact that the recovery heat exchanger WD201_HP physically is located closer to the LP column and the vapour from the HP top tray is delivered to the heat exchanger through a 6 meters long pipe. The timing for the latter transport during start-up (3–6 minutes) amounts approximately to the observed discrepancy.
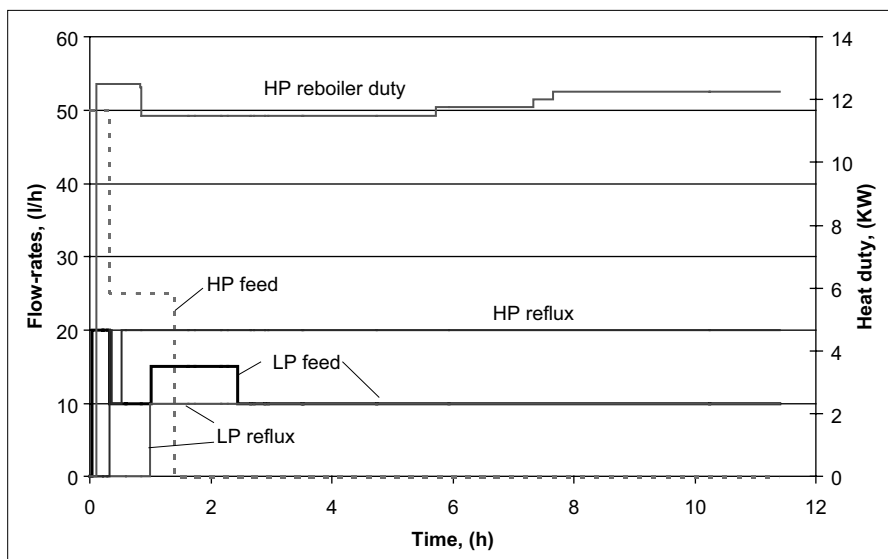

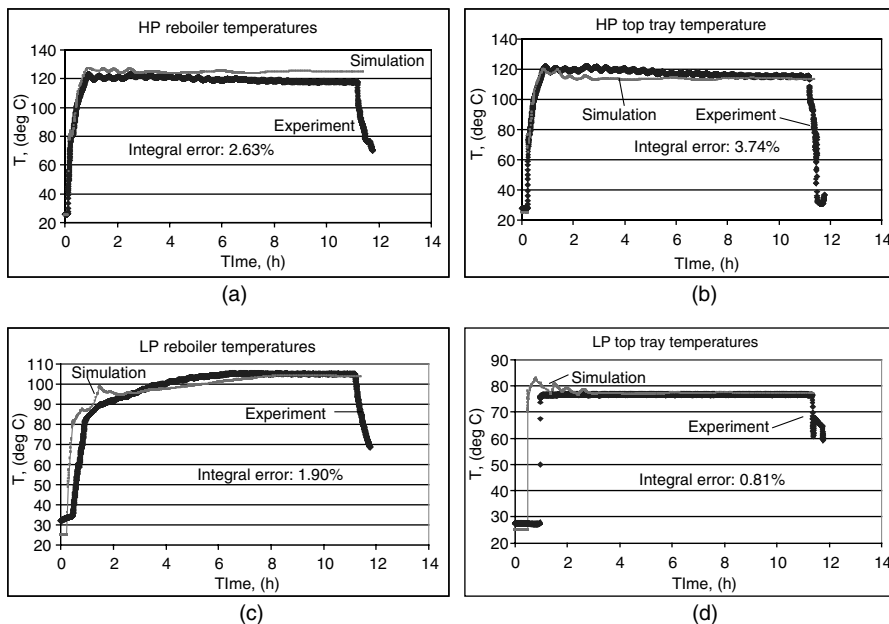**Figure 2.** Operating schedule for the start-up simulation

Figure 3. Model validation using the temperature profiles

CONCLUSIONS AND FUTURE WORK

The current paper presents a part of a larger study aiming at the optimal start-up of the described two-column distillation system. Several models of the unit devices in the system have been substantially improved together with the overall process model. These include the re-definitions of the water condenser model and the recovery heat exchanger (HP condenser – LP reboiler). The presented simulation results clearly show that the developed models are capable of adequately simulating the start-up and operation of a two-column system for the separation of the homogeneous azeotropic mixture Aceto-nitrile-Water by Pressure-Swing Distillation in continuous mode. The simulation shows realistic time durations for vapour propagation inside each of the distillation columns (7.7 minutes for the HP column and 6.3 minutes for the LP column), which are comparable with the previous similar works dealing with the same pilot plant.

Also, the simulation results have been validated against available records of in-house experiments with the pilot plant PSD system separating an Acetonitrile-Water mixture. The validation shows that the model produces good estimates of the process beha-viour featuring very small error levels of maximum 3.7%. The further steps of the study are to subject this model to optimisation runs in order to derive optimal start-up strategies for different process configurations and feed compositions.

ACKNOWLEDGEMENTS

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SYMBOLS

DV_{EXTRA}	Volume violation term, m^3
$h_{IN,REB}$, $h_{OUT,REB}$	Tube-side inlet and outlet specific enthalpies of the coupled heat exchanger, (MJ/kmol)
H_{REB}	Tube-side enthalpy holdup of the coupled heat exchanger, (MJ)
$i = \{1,2\}$	Number of the current mixture component
K_{EXTRA}	Amplification coefficient, $(-)$

$L_{IN,REB}$, $L_{OUT,REB}$	Tube-side inlet and outlet flow rates of the coupled heat exchanger, (kmol/h)
L_{IVR}	Inlet flow rate, l/h
L_{OVR}	Outlet flow rate, l/h
LV_{EXTRA}	Compensation liquid outlet flow-rate, l/h
$M_{REB}(i)$	Tube-side component material holdups of the coupled heat exchanger, (kmol)
Q_{REB}	Heat transfer flow from the tube walls to the inner liquid in the coupled heat exchanger, MJ/h
Q_{VER}	Heat losses from the tubes in the coupled heat exchanger, MJ/h
V_{REB}	Volume occupied by the fluid inside the coupled heat exchanger tubes, m^3
V_{TUBES}	Volume of the coupled heat exchanger tubes, m^3
$X_{IN,REB}(i)$, $X_{OUT,REB}(i)$	Tube-side inlet and outlet component mole fractions of the coupled heat exchanger, $(-)$
β_{EXTRA}	A switching coefficient in equation 5, $(-)$

ABBREVIATIONS

HP	High Pressure
LP	Low Pressure
PSD	Pressure-Swing Distillation
VLE	Vapour-Liquid Equilibrium