

PRESSURE SWING BATCH DISTILLATION FOR HOMOGENOUS AZEOTROPIC SEPARATION

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The separation of the homogeneous azeotropic mixture acetonitrile/water by pressure swing distillation (PSD) is considered. The PSD is operated as a discontinuous (batch) process and two batch modes, regular and inverted, are considered. The processes are analysed, aspects as to which batch mode should be preferred are discussed, and a dynamic model for both batch PSD processes is formulated. The model takes a cold and empty column as an initial condition. Because of the lack of experimental data, in particular for the inverted batch distillation, our own experiments were carried out. The regular and the inverted batch PSD consist of two steps, a low pressure and a high pressure run, and experiments are shown for every step. The simulations fit the experimental results with good accuracy.

KEYWORDS: pressure swing distillation, inverted batch distillation, simulation, experiments, start-up

INTRODUCTION AND PRINCIPLES OF THE PROCESSES

The separation of a homogeneous azeotropic mixture is a common task in the chemical industry. Often pressure swing distillation (PSD) is mentioned as an alternative process to the widely applied azeotropic or extractive distillation. In PSD the dependency of the azeotropic concentration on the system pressure is used to break the azeotrope, and this can be utilised in a continuous process but also semi-continuous and discontinuous (batch) operations are possible [1]. There are only a few results for the continuous process in the literature [2], while batch PSD has not been considered seriously until now. Furthermore no experimental data for these batch processes has been published.

The objective of our research activities is on the theoretical and experimental analysis of continuous and batch PSD, but in this paper we focus on the batch process for the separation of homogeneous azeotropic mixture with a temperature minimum azeotrope. The investigations were carried out for the example of the separation of an acetonitrile/water mixture. The mixture has a temperature minimum azeotrope at 1.013 bar around $x_{Ac}^{LP} = 0.68$ mol/mol, which is indicated as x_D^{LP} in the equilibrium diagram (Figure 1). Because of this the maximal achievable distillate concentration is on the low pressure (LP) step. On the other hand, the concentration of acetonitrile decreases with increasing column pressure, so the temperature minimum azeotrope has a concentration of about

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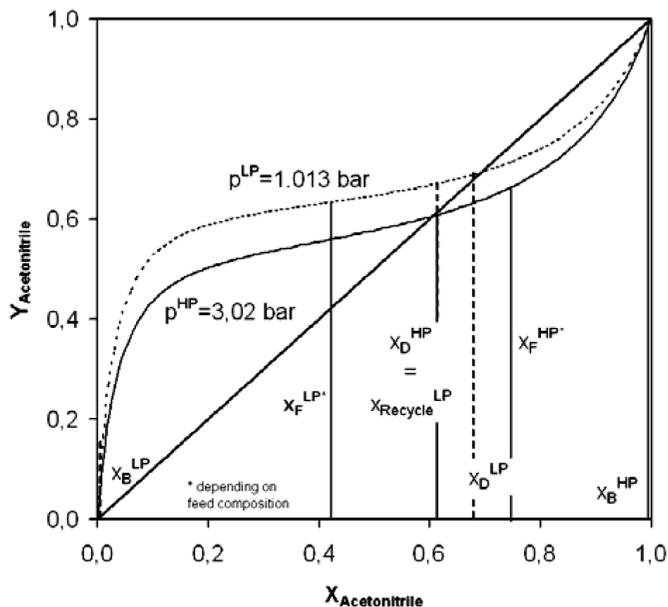


Figure 1. Equilibrium diagram acetonitrile/water for two different pressures

$x_{Ac}^{HP} = 0.6$ mol/mol around 3 bar. Again this represents the achievable distillate concentration but now in the high pressure (HP) step and is indicated as x_D^{HP} in Figure 1.

An advantage of PSD when compared to other alternative processes is the removal of the need for feeding and recycling additional substances (entrainer). In PSD a certain amount of the azeotropic mixture is still in the process and is recycled into the other column in the continuous process or is accumulated at the top in the batch process. In batch PSD the feed is charged into a bottom tank (for regular batch) or into a top tank (for inverted batch) shown in Figure 2. Depending on the initial feed concentration the first batch step is either a HP or a LP distillation run. If the feed concentration of the acetonitrile composition is lower than the azeotropic point, then the first step is a LP step and pure water can be withdrawn from the bottom (inverted batch) or water is accumulated in the bottom (regular batch). At the top a mixture near or equal to the azeotropic composition is accumulated in the inverted case or is withdrawn as a distillate product in the regular case. This step runs until a certain water concentration is achieved in the bottom tank (regular batch) or the water concentration of the bottom product flow can no longer be guaranteed (inverted batch). Once the first step has been finished the process is switched over to the second step. For inverted batch distillation the feed for the next step is still in the top tank of the column and the mode can be started immediately. In the case of a regular batch the feed, which is the distillate of the LP run, is not in the

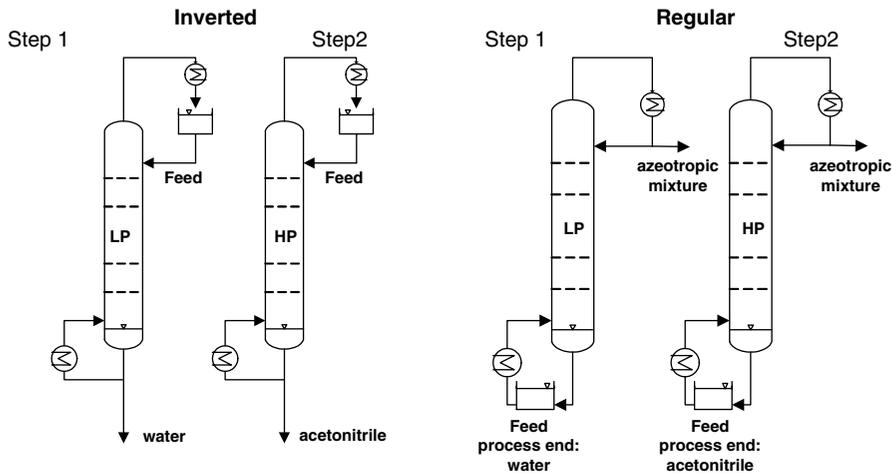


Figure 2. Process modes for the inverted and regular batch PSD (step 1 at low pressure (LP), step 2 at high pressure (HP))

system and has to be charged into the bottom tank first, before the next step can be started. The second step is a HP distillation run and acetonitrile is produced in the inverted and regular batch as described before for water production.

If the initial feed concentration is higher than the azeotropic point, then the first step is a HP step and acetonitrile is produced at the bottom. The subsequent procedure is analogous to that described above.

In all cases the maximum possible attainable amount of product is given by the overall component balance. For batch PSD an analogous determination was done as in [3], and can be formulated as in [4] for continuous PSD. Assuming pure water as bottom product and an initial acetonitrile feed concentration lower than the azeotropic point, the ratio between distillate and bottom for the LP step is given by the following equation:

$$\frac{D^{LP}}{B^{LP}} = \frac{z_{Ac}^{LP}}{(x_{D,Ac}^{LP} - z_{Ac}^{LP})}$$

For the subsequent HP period, assuming pure acetonitrile in the bottom, the ratio is given by:

$$\frac{D^{HP}}{B^{HP}} = \frac{1 - x_{D,Ac}^{LP}}{(x_{D,Ac}^{LP} - x_{D,Ac}^{HP})}$$

Obviously, the feed condition and the relationship of the azeotropic concentration to the respective pressures determine the achievable product amount in every period. Production in the HP step is fixed by the difference between the azeotropic concentrations. The above equations are validated for the regular batch PSD as well as for the inverted batch PSD and therefore the product amount should theoretically be the same for a given feed in both cases.

The initial feed composition and the desired product purity dictate whether the regular or the inverted process should be preferred. An additional influence is the pressure difference between the steps – when the pressure difference increases the amount of bottom product rises and that can change the preferred batch mode. The given ratio in the above equations is a function of all these mentioned factors and can therefore represent criteria for the choice of the batch mode. It is important to note that the volumetric ratio is decisive for practical reasons and not the molar ratio.

A comparison between regular and inverted batch distillation for the separation of a theoretical binary mixture with constant volatility is given by [5]. For further discussion of the regular and inverted PSD a detailed model and experimental experience are needed which will be introduced in the next paragraphs.

MODELLING ASPECTS

Within the scope of our investigations, a rigorous model of the two different process structures for regular and inverted operation as shown in Figure 2 has been developed and implemented in the simulation environment gPROMS[®]. The model consists of a reboiler, a column, a condenser, a pot and accumulator units. All balances in the units are dynamic equations.

In the dynamic balances the vapour and liquid phases in each unit are considered together. Both vapour and liquid hold-up are completely calculated (see the following equations for one tray):

Component balance:

$$\frac{d(HU_{n,i})}{dt} = L_{n-1} \cdot x_{n-1,i} - L_n \cdot x_{n,i} + V_{n+1} \cdot y_{n+1,i} - V_n \cdot y_{n,i} \quad i = 1, \dots, Nc$$

Energy balance:

$$\frac{d(HU_n)}{dt} = L_{n-1} \cdot h_{n-1}^L - L_n \cdot h_n^L + V_{n+1} \cdot h_{n+1}^V - V_n \cdot h_n^V$$

with

$$HU_{n,i} = HU_n^L \cdot x_{n,i} + HU_n^V \cdot y_{n,i}$$

and

$$HU_n = HU_n^L + HU_n^V$$

Summation:

$$\sum_{i=1}^{N_c} y_{n,i} = 1 \quad \sum_{i=1}^{N_c} x_{n,i} = 1$$

Within the phase equilibrium model the activity coefficients of the liquid phase are calculated using the Wilson model and the vapour phase is considered as an ideal gas. The Murphree efficiency is integrated in the model to consider real effects and the efficiency was adjusted by previous experiments [2]. The parameters for the Antoine equation to calculate vapour pressures and for the Wilson equation are taken from the DECHEMA data series [7].

The fluid dynamics on the trays is described with the Francis weir equation. Different empirical approaches were used to calculate the pressure drop over the trays. This rigorous modelling of pressure drop permits a detailed reproduction of the dynamic behaviour of the column. The core of the model is similar to the model developed for continuous PSD introduced in [2] and [4].

To solve the dynamic batch model, initial values are required. A common procedure for the generation of initial values is to give every tray the feed concentration and corresponding equilibrium condition and then simulate under total reflux condition until a stationary column profile is achieved. These results are often taken as initial conditions for the subsequent batch simulation. This procedure is not adequate for the discussion of the two different batch processes (regular and inverted). Consistent initial conditions are required and a cold and empty column state are used here.

A detailed description of a start up model is beyond the scope of this paper. The model follows the idea of the description of the start up process of a reactive distillation column, which we have presented in [6]. In order to describe the dynamic column performance from a cold and empty state, different equation sets with three conditions for switching between these equations are necessary:

1. liquid leaving a tray: *IF level* \geq *weir height* *THEN*
 $L_n = f(\text{Francis weir})$
ELSE
 $L_n = 0$
2. vapour leaving a tray: *IF* $p_n \geq p_{n-1}$ *THEN*
 $V_n = f(\Delta p, \dots)$
ELSE
 $V_n = 0$

3. phase equilibrium can be assumed: *IF* $T_n \geq T_{boil}$ *THEN*
- $$y_{i,n}P_n = x_{i,n}\gamma_{i,n}P_i^{vap}$$
- ⋮
- ELSE*
- $$y_{i,n} = x_{i,n}$$
- ⋮

A complete explanation of this modelling aspect is given in [6]. Before the model can be used for the analysis of the regular and inverted batch PSD an experimental validation has to be carried out.

EXPERIMENTAL RESULTS AND DISCUSSION

Because of the lack of experimental data in the literature and to achieve detailed knowledge of the inverted process, experimental investigations have been carried out and will be presented here to our knowledge for the first time. The experiments were made on a

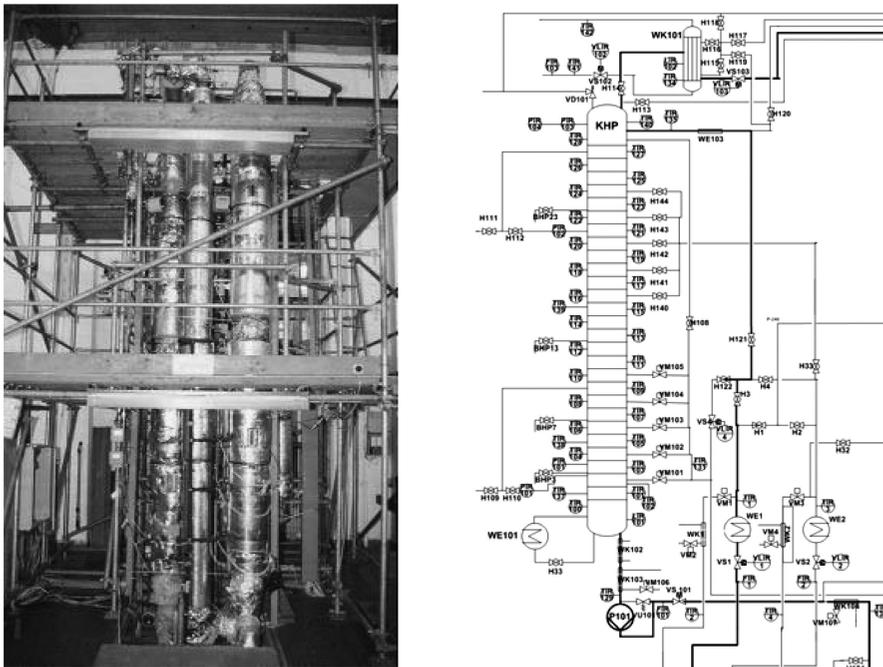


Figure 3. Two pressure column system (left – only one column is used for the batch distillation investigations; right – P&ID of the batch column (cut-out of the complete two column system))

Table 1. Pilot plant specifications

| | Batch column |
|--------------------|--------------------|
| Number of trays | 28 |
| Diameter | 100 mm |
| Reboiler duty | 30,7 kW |
| Operating pressure | max. 5 bar |
| PCS | ABB Freelance 2000 |

column system (see Figure 3) which consists of two coupled columns and can be used in the continuous PSD mode with two columns, or with only one column for the regular or inverted batch PSD. The experimental setup used for the batch distillation runs is listed in Table 1.

In the following we present the dynamic concentration trends for the inverted and regular PSD. The experiments for the both PSD started at low pressure because the acetonitrile feed concentration is lower than the azeotropic point and then the HP runs follow. In Table 2 the main experimental data are listed.

In the Figure 4 the temperature trends for the bottom and the top of the low pressure regular batch are displayed. The simulation and the experiments start from a cold and empty column and the curves are in good agreement.

In the following figures (Figure 5 and Figure 6) the simulated and measured concentration trends for the top and the bottom products for the two steps of the inverted and the regular PSD are shown from a cold and empty column. Again the simulations are in good correspondence with the experiments.

As one can see in the inverted PSD (Figure 6) the product purity is rapidly achieved and product can be withdrawn from the column bottom product until the desired composition cannot be guaranteed any longer. In the regular batch PSD (Figure 5) the

Table 2. Setup of experiment and simulation

| | Regular batch | | Inverse batch | |
|-------------------------------|---------------|---------------|---------------|---------------|
| | Low-pressure | High-pressure | Low-pressure | High-pressure |
| Hold-up feed tank [l] | 190 | 120 | 180 | 150 |
| Hold-up product tank [l] | 40 | 27 | 30 | 29 |
| Pressure [bar] | 1,013 | 4,4 | 0,998 | 3,7 |
| Feed-conc. (ACN) [mol/mol] | 0,37 | 0,65 | 0,38 | 0,67 |
| Feed stream [l/h] | 60 | 70 | 40 | 55 |
| Reflux [l/h] | 20 | controlled | – | – |

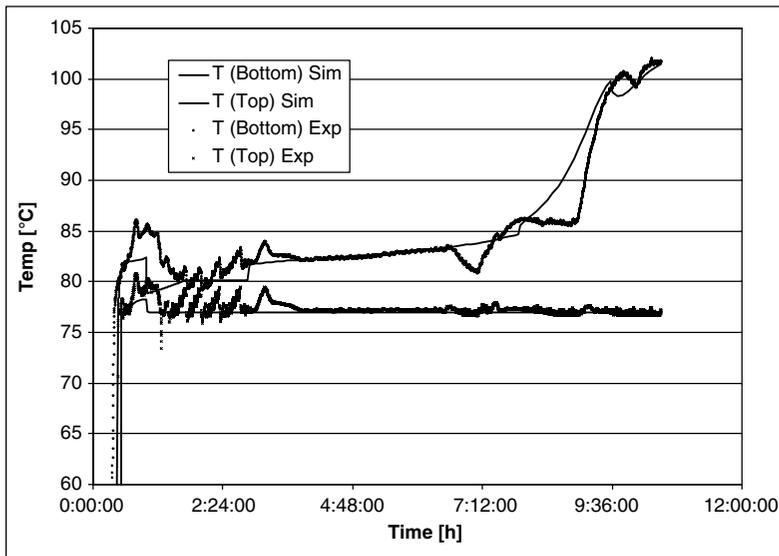


Figure 4. Regular batch PSD 1. step (LP), dynamic model validation temperature trends simulation vs. experiment

purity in the bottom increases over the time and the step ends when the desired bottom product purity is achieved.

In a simulation study with the validated model for regular and inverted batch PSD, different feed concentrations were investigated, and will be discussed in the presentation.

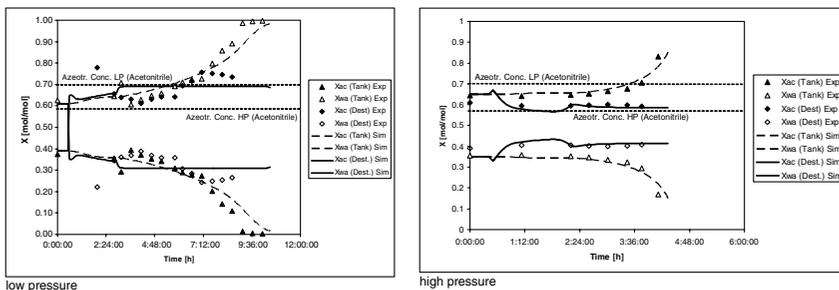


Figure 5. Regular batch PSD 1. step (LP) and 2. step (HP), dynamic model validation concentration trends simulation vs. experiment

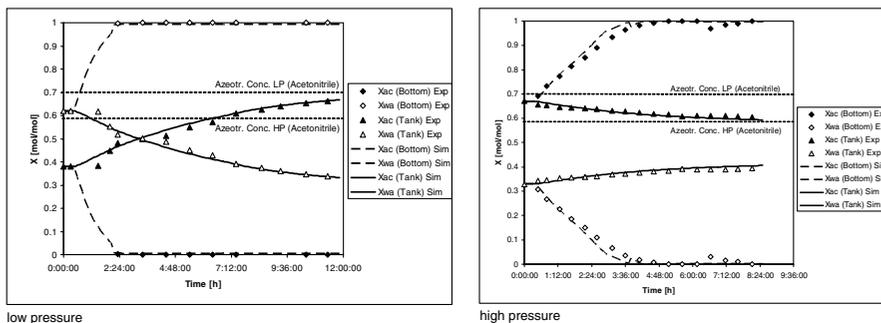


Figure 6. Inverted batch PSD 1. step (LP) and 2. step (HP), dynamic model validation concentration trends simulation vs. experiment

The analysis shows that for a low concentration of acetonitrile in the feed, the inverted process should be preferred for the first step (which is a LP step). When the acetonitrile feed concentration is lower than 0.25, the inverted process has advantages. For acetonitrile feed concentration of 0.25 the molar ratio between distillate and bottom amount is around 0.58 but the volumetric ratio is around 1.2 which shows the practical relevance of the volumetric ratio.

This confirms the statement of [5] "... , it is more time consuming to remove a small amount of light component overhead from a regular column ... than to remove a large amount of heavy component from the bottom of an inverted column ...". For the second step the ratio between top and bottom is fixed for all cases and therefore the preferred batch process is defined.

CONCLUSION

The separation of a binary homogeneous azeotropic mixture by pressure swing distillation (PSD) is discussed. The PSD is carried out as a discontinuous (batch) process with two process modes: regular and inverted batch PSD are considered. A rigorous dynamic model was developed for the regular and for the inverted batch PSD. The model considers the dynamic process performance from a cold and empty state and is validated on a series of experiments. A first discussion of the different batch strategies is made, considering particularly the ratio between the amount top and bottom product, and these analyses will be continued.

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