

Homogeneous azeotropic pressure swing distillation: continuous and batch process

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Abstract

The separation of a binary homogeneous azeotropic mixture using pressure swing distillation will be analysed on the example of acetonitrile/water. Two different processes are considered: the continuous heat- and mass-integrated process and the inverted batch process. For both processes a model is developed and experimental data are given. In the paper the potential of the pressure swing distillation for the separation of binary homogenous azeotropic mixtures will be demonstrated, in particular the process performance is investigated and application aspects for the continuous as well as the inverted batch process are discussed.

Keywords: homogenous azeotropic distillation, inverted batch, pressure swing process

1. Introduction

For the separation of a binary homogeneous azeotropic mixture using a two column system operated by different pressures is one of the simplest solutions for this task. But other alternative processes such as azeotropic distillation or extractive distillation have a great industrial relevance whereas the pressure swing distillation is only seldom applied. There are only a few theoretical results of pressure swing distillation for the separation of binary homogeneous azeotropic mixtures in the literature and experimental data are needed Phimister and Seider (2000). The only significant application is the continuous pressure swing distillation of tetrahydrofuran and water Knapp and Doherty (1992). The main advantages of the pressure swing distillation are the saving of energy (heat-integrated distillation columns) and the abdication of recycling additional substances (entrainers) compared to the other alternatives. The mass- and heat-integration of the column systems yields to a high complexity of the plant which requires a higher effort for process control. On the example of the pressure swing distillation of the acetonitrile/water mixture Repke et al. (2004a) developed a control structure for the heat- and mass-integrated column system. The considered process was a continuous process. The dependency in the azeotropic concentration from the system pressure (Figure 1) can not only be utilised in a continuous process, also semicontinuous and discontinuous (batch) operation are possible Phimister and Seider (2000).

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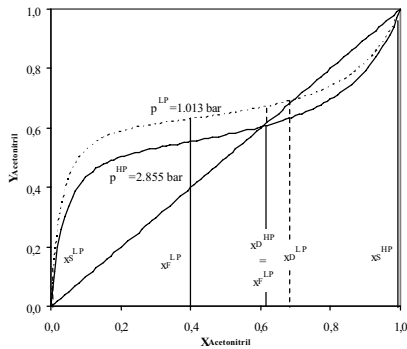


Figure 1. Equilibrium diagram acetone/nitrile/ water for two different pressures.

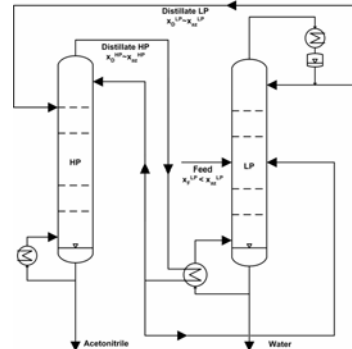


Figure 2. Flow sheet for the continuous process.

In the continuous process two integrated columns are needed. In opposite, for the semicontinuous and batch process only one column is required, what save investment cost and can be a more efficient process depending on the amount of the purified mixture. Further, if the azeotropic point is a temperature minimum azeotrope, the conventional batch, where the feed is charged into the reboiler and the products are withdrawn from the top, is not always the best configuration. In the recent time novel batch configuration, as inverted batch or middle- and multivessel batch are intensive discussed in the literature. Depending on the initial feed, for a temperature minimum azeotrope the inverted batch should be used in some cases.

In the following the continuous and the inverted batch pressure swing distillation process are analysed on the example of the acetone/nitrile/water mixture. For both processes, a rigorous model is developed, experimental investigations will be carried out and the potential of both processes will be discussed.

2. Principles of the processes

As mentioned before, the dependency of the azeotropic concentration from the system pressure is used for the separation of the mixture. Has the feed a lower acetone/nitrile concentration than the azeotropic point, the feed is fed into the low pressure (LP) column, otherwise the feed has to be fed into the high pressure (HP) column. A principle process flow sheet for the continuous process is sketched in Figure 2. Water is the bottom production of the LP column and acetone/nitrile is the bottom product of the HP column. The top concentrations are closed to the azeotropic concentrations at the respective pressure. The distillate of the HP column is recycled back into the LP column and the distillate of the LP column is fed into the HP column. Therefore, there are two recycle streams which circulate in the system and whose flow rates influence the effectiveness of the whole process. Assuming very pure products ($x_{B,Ac}^{HP} = 1$ & $x_{B,Ac}^{LP} = 0$), the flow rates are influenced by the feed and the difference in the azeotropic concentrations by the respective pressure (equations 1 and 2).

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

$$D^{HP} = F^{LP} z_{Ac}^{LP} \frac{(1 - x_{D,Ac}^{LP})}{(x_{D,Ac}^{LP} - x_{D,Ac}^{HP})} \quad (2)$$

Notice, if $x_{D,Ac}^{LP}$ achieves $x_{D,Ac}^{HP}$ the recycle flow rates increase rapidly and that corresponds to a higher energy consumptions of the process. On the other hand, the difference between the azeotropic points increases with higher pressure difference of both columns. In their paper Abu-Eishah and Luyben (1985) discussed an optimum in pressure for the HP column for a heat integrated system.

For the inverted batch process a lower acetonitrile feed concentration than the azeotropic point is assumed in the following, which is charged into the pot at the top of the single column. The column is operated by low pressure condition first. In the bottom water is accumulated (cyclic operation) or water is withdrawn from the bottom. If the desired water quality in the bottom is achieved (cyclic operation) or the purity can not keep longer, this operation period is finished. Preconditioned, a certain minimum amount of water is removed from the system in the next period the pressure is changed to the HP level, otherwise an intermediate charge is needed to guaranteed the change to the opposite distillation region due to the pressure increase. In the high pressure period acetonitrile is the product at the bottom. In the HP and LP pressure period a mixture which is close to the azeotropic concentrations is accumulated in the pot at the top. Using the overall material balances, a similar estimation as was done before for the continuous process can be carried out for the inverted batch process. The ratio between the amount of distillate and bottom for the first process period (LP run) is given in the equation (3) under the assumption of pure water as bottom product and for the subsequent HP period assuming pure acetonitrile in the bottom yields to equation (4).

$$\frac{D^{LP}}{B^{LP}} = \frac{z_{Ac}^{LP}}{(x_{D,Ac}^{LP} - z_{Ac}^{LP})} \quad (3)$$

$$\frac{D^{HP}}{B^{HP}} = \frac{1 - x_{D,Ac}^{LP}}{(x_{D,Ac}^{LP} - x_{D,Ac}^{HP})} \quad (4)$$

Obviously, the feed and the difference in the azeotropic concentration by the respective pressure determine the amount of product which can be achieved in every period. Especially in the high pressure run the possible amount of product is fixed by the difference in the azeotropic points. Equations (3) and (4) give a limitation of the volume ratio between the top pot and the reboiler which has to be considered in design and operation. These points and the effect on the operation will be explained in the lecture.

3. Process models

In the scope of the analysis of the continuous and the inverted batch pressure swing distillation a rigorous dynamic model is formulated in the simulation package gProms[®]. The model for the continuous mass- and heat-integrated process was introduced in Repke et al. (2004a and 2004b). The model considers the vapour and liquid phase together in detail (material, energy, component balances). Further, the pressure drop is modelled in detail. The shell and tube heat exchangers are exactly modelled too.

Based on this model a rigorous model for the inverted batch process is formulated. The model consists of a reboiler, a column, a condenser, a pot and an accumulator unit. Because the condenser hold-up can neglected concerning the large pot hold-up the condenser model is a steady state model. For the accumulator model the dynamic component balances and the summation equation are formulated. All other balances in the units are dynamic equations.

Because of the lack of experimental data in the open literature own experiments are required. Therefore for the continuous heat- and mass-integrated process as well as the inverted batch process pressure swing distillation runs were carried out on a pilot plant at the institute. Details for the applied pilot column system see Repke et al. 2004b.

4. Model validation

In Figure 3 the experimental and calculated bottom concentrations of an inverted batch process is displayed, that will be specified in the presentation.

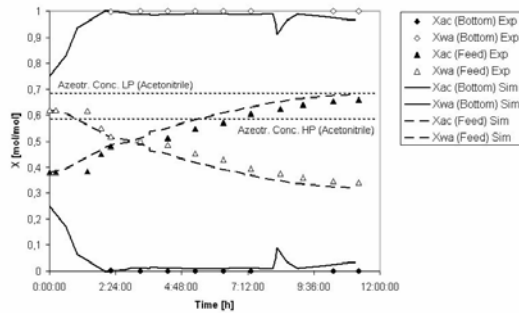


Figure 3. Bottom concentration trend for the inverted batch process; LP site.

For the continuous process a first model verification is given in the following, where the feed is fed into the LP column.

Table 1. Model verification (Feed into LP column, continuous, heat- and mass integrated).

	High-pressure column HP		Low-pressure column LP	
	Experiment	Simulation	Experiment	Simulation
Feed flow [l/h]	0	0	9,9	10
Bottom flow [l/h]	6,65	5,75	4,2	4,76
Reflux flow [l/h]	18,9	20,9	9,9	10
Pressure [bar]	2,78	2,78	1,013	1,013
Heat duty [kW]	8,43	8,43	0	0
Heat loss per tray [W]	-	14	-	14

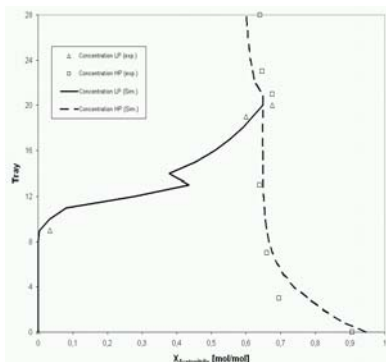


Figure 4. Temperature profile.

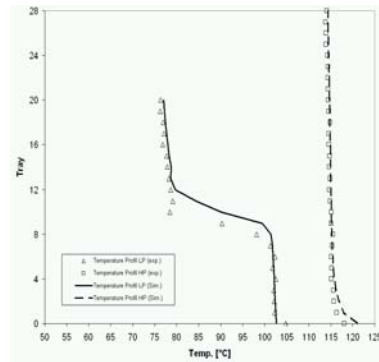


Figure 5. Concentration profile.

Table. 1 shows the comparison between the simulation and the experiment. In Figure 4 the temperature and in Figure 5 the concentration profiles are sketched. The model fit the experimental data.

5. Different control structures for the continuous process

In addition to the control structure B introduced in Repke et al. (2004a and 2004b, Figure 6), a new structure (Figure 7) is developed which might be more sensitive than the control structure B where the LP bottom purity is controlled by the LP reflux.

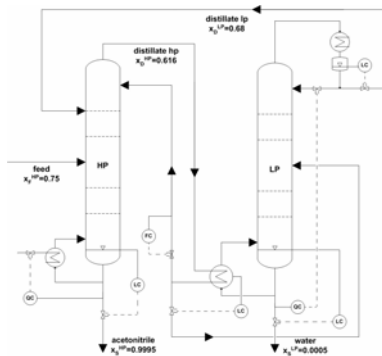


Figure 6. Control structure B: LP bottom purity control with LP reflux Repke et al. (2004a).

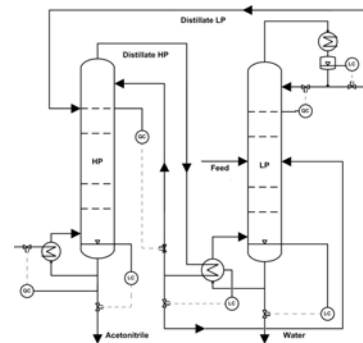


Figure 7. New Control structure: No LP bottom concentration control.

The quality control of the LP bottom is not so sensitive and not very practicable because of the long distance between the reflux LP stream and the bottom quality. The time constant is very large for practical application. To avoid this, a new control structure with more direct control and better sensitivity and response was examined. In this structure the distillate concentrations will be controlled with the corresponding reflux streams on the top of both columns. This might be contrary to the statement that the distillate streams are no product streams, so they haven't been controlled Repke et al. (2004a). But to make the system more effective and sensitive the streams have been controlled to decrease the flow rates and build up a different and more direct control structure. The desired concentration of the LP bottom stream will be a result of the optimal control of the others.

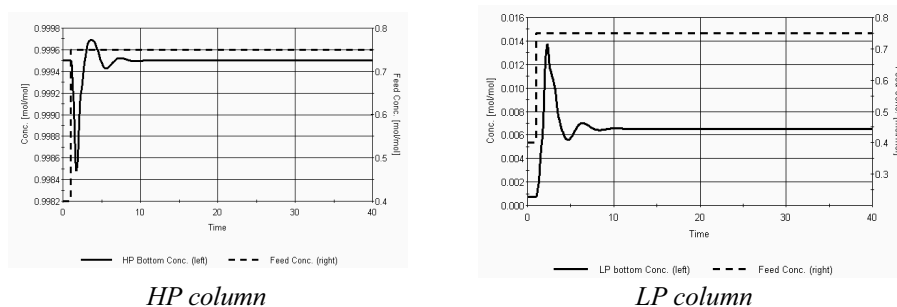


Figure 8. System response in the bottom concentration for a disturbance of the feed concentration (LP) from $x_F=0.4$ to $x_F=0.75$.

In Figure 8 the dynamic responds are shown for a feed disturbance into the other distillation region from $x_F = 0.4$ to $x_F = 0.75$. The LP bottom purity shows a small step to lower water purity, but if this matches the specification, the process can be run in a stable condition in spite of the great disturbance. Furthermore studies with variation of the set point of the distillate concentration in the HP column show that it is possible to influence the LP bottom purity in a positive way, because the distillate purities have direct influence on the distillate streams. If we decrease the distillate concentration set-point, the flow rates will also be decreased (equations 1 & 2) and this has also positive influence on the purity of the bottom product.

6. Conclusion

The separation of a binary homogeneous azeotropic mixture by pressure swing distillation is considered. Two different processes variants, the well-know mass- and heat-integrated continuous consists of two columns and the novel inverted batch consists of a single column, are discussed. For both a rigorous dynamic model is developed and verified by own experiments. Using the models the operation performances are investigated. For the inverted batch process a limitation of the product amount is described and a new control structure of the continuous process is developed. The control structures work stable in spite of a disturbance in the feed concentration that change from one distillation region into the opposite region.

7. Nomenclature

ac; wa	acetonitrile; water	HP	high pressure
az	azeotropic point	LP	low pressure
B, S	bottom	p	pressure
D	distillate	x	liquid mole fraction
F	feed	z	feed mole fraction

8. References

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Acknowledgements

The authors gratefully acknowledge the financial grants from the Max-Buchner Forschungsstiftung and the Fonds der Chemischen Industrie.