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EXPERIMENTAL VALIDATION OF A NEW DOUBLE-COLUMN SYSTEM FOR HETEROAZEOTROPIC BATCH DISTILLATION

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Abstract
A new double-column batch heteroazeotropic distillation system (DCS) operating in closed mode is studied by laboratory experiments. Our primary aim is the experimental validation of the DCS for the separation of the heteroazeotropic mixture 1-butanol – water in a simple laboratory equipment (glass columns packed by Raschig rings).

We compare its performance with that of the conventional batch rectifier (BR). Rigorous simulations are done by using a professional dynamic flowsheet simulator. In the case studied the separation by the DCS proved to be feasible and competitive with that of the BR: By using the DCS higher recovery for 1-butanol was reached during practically the same time.

Keywords: batch distillation, heteroazeotrope, laboratory experiment, closed operation, rigorous simulation

1. Introduction

The batch heteroazeotropic distillation (BHD) is frequently applied in pharmaceutical and fine chemical industries for the recovery of organic solvents. If the components of a mixture form a heteroazeotrope or by the addition of an entrainer a heteroazeotrope can be formed, the azeotropic composition (boundary) can be crossed by decantation. To our best knowledge the BHD is applied in the industry only in batch rectifiers (BR) in open operation mode (with continuous distillate withdrawal). The BR was investigated with variable decanter holdup by Rodriguez-Donis et al.[1] and with continuous entrainer feeding by Modla et al.[2,3] and Rodriguez-Donis et al.[4], respectively. The heterogeneous batch distillation in BRs and also in multivessel columns was extensively studied by Skouras et al.[5,6]. Pommier et al.[7] developed a specific software architecture based on the BatchColumn simulator and on both Sequential Quadratic Programming and Genetic Algorithm for the optimization of sequential batch columns and heterogeneous batch distillation. Lang et al.[8] suggested a new double-column system (DCS) for BHD. The DCS is operated in closed circuit without any continuous product withdrawal (*Figure 1*). They made feasibility studies based on a very simplified model (e.g. assumption of maximal separation, neglecting of plate and decanter hold-ups etc.).

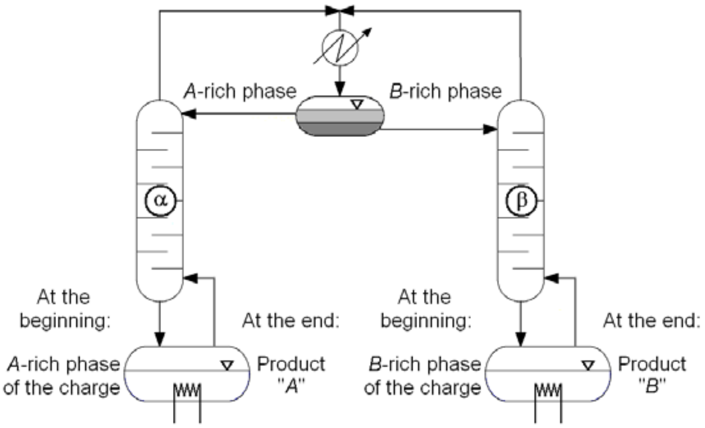

Figure 1. Scheme of the DCS (during the processing of a binary heteroazeotropic mixture)

The above authors (Denes et al.[9]) made also rigorous simulation calculations using the dynamic simulator CC-DCOLUMN of the professional flowsheet simulator ChemCad 6.0 for three test mixtures: for a binary heteroazeotropic mixture (1-butanol – water) and for the separation of the minimum azeotrope isopropanol – water by applying the classical entrainer benzene and the less environmental polluting cyclohexane.

Two different operation policies of the BR equipped with a decanter were compared with two variations of the DCS (Denes et al.[10]). The new configuration was found competitive with the BR and worthy of further investigations. For the latter, ternary mixture it gave even better results than the BR.
In this paper we study experimentally the separation of the heteroazeotropic mixture 1-butanol (*A*) – water (*B*) in the new (DCS) and the traditional configurations (BR) and the performance of the two configurations are compared by posterior simulation with the dynamic simulator CC-DCOLUMN.

2. Description of the laboratory equipment

The BR and the DCS (*Figure 2*) consist of the same laboratory means. Most of them are made of glass: boiling vessels (spherical flasks of volume 1000 and 2000 ml with three necks), columns, decanter and condenser. For both flasks there are electric heating mantles in convenient size. The nominal electric performances of the heating mantles are 300 W and 450 W. The two columns have the same parameters: both of them are double-walled, the height of the packing is 1 m, the internal diameter is 30 mm. The packing consists of Raschig rings made of glass whose average external diameters and heights are approximately 7 mm. Both columns are thermally isolated by foamed plastic mantle.

The volumetric liquid holdup of the decanter is 55 ml and it is also thermally isolated. The condenser is a spiral cooler cooled by running water. The liquid temperatures in the flasks are measured by mercury thermometers calibrated with water. The composition of the mixtures is determined on the basis of their refractive indices. The refractometer is thermostated by a liquid circulating thermostat.

3. Experimental results

3.1 Properties of the charges

The composition of the mixture is azeotropic (mole fraction of 1-BuOH is 0.256). The volume of the components (before mixing): 1270 ml of 1-BuOH (component *A*) and 730 ml of water (component *B*).

3.1.1 Double-column system

After mixing of the components the heterogeneous mixture is decanted (*Table 1*). The temperature of the charge is T_{ch} = 23 °*C*.

3.1.2 Batch rectifier

The volumes of the phases (*Table 1*) after the decantation slightly differ from those of the previous case. (A possible reason of this difference is that T_{ch} = 27 °*C*.)
The compositions of the phases are the same as in the case of the DCS.

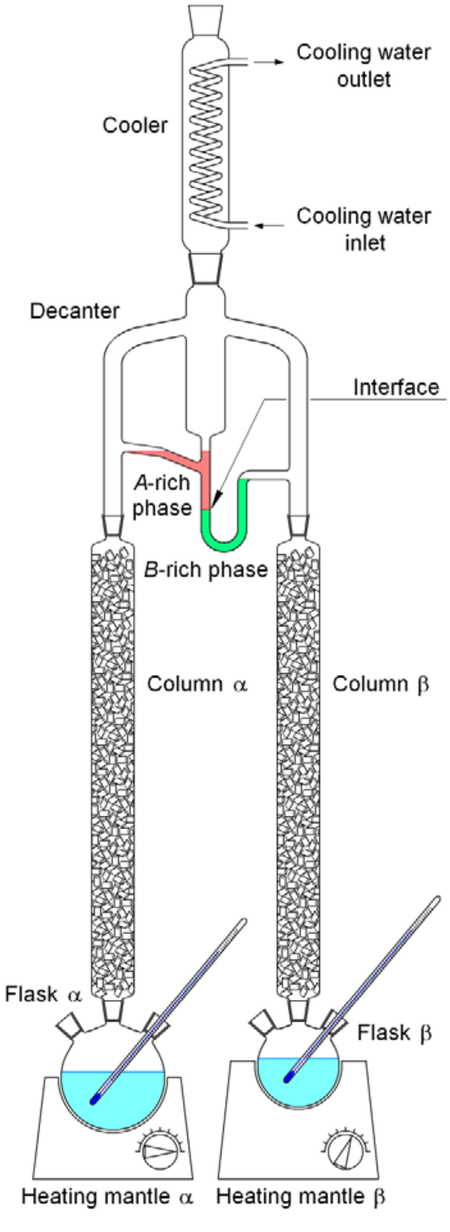

Figure 2. Laboratory double-column system

Table 1. Volumes and compositions of the liquid phases to be processed in the DCS

Configuration		DCS		BR	
Liquid phase	-	*A*-rich phase	*B*-rich phase	*A*-rich phase	*B*-rich phase
Volume	ml	1450	525	1445	550
Mole fraction of *A*	-	0.491	0.018	0.491	0.018

3.2 Operation of the distillation systems

3.2.1 Double-column system

After the decantation the organic (*A*-rich) phase is fed into the flask α and the aqueous (*B*-rich) one into the flask β. Initially the decanter is empty and the columns are dry. Both heating mantles are switched on at the same time. Their electric performances are controlled manually so that the two liquids start boiling nearly at the same time. After that the heatings are not modified and the system can be operated without any intervention. When the liquid temperatures in both flasks practically reach the boiling points of the pure components and become constant the heating is switched off. (The ambient pressure is 100.3 kPa and the ambient temperature is 23 °C.)

3.2.2 Batch rectifier

The binary mixture is processed in the DCS operated as a BR. It means that one of the flasks is empty at the beginning and it is not heated. (Since its holdup is very low, the cold column causes a negligible material loss.) The two phases of the charge are processed sequentially in two operation steps.

Step 1. Production of the n-BuOH

The *A*-rich phase is fed into the flask α and the flask β is left empty. Initially the decanter is empty and the columns are dry. Only the heating mantle α is switched on. Its electric performance is kept permanently at the maximum during the whole step. The system can be operated without any intervention. When the liquid temperature in flask α reaches the boiling point of the n-BuOH and becomes constant the heating is switched off. In flask β the distillate is collected which is the *B*-rich phase of the condensate. The decanter is not emptied because there is need for its liquid holdup in Step 2. (The ambient pressure is 100.1 kPa and the ambient temperature is 27 °C.)

Step 2. Purification of the water

The *B*-rich phase of the charge and the distillate of Step 1 are mixed and they are fed into the flask β. Flask α is emptied. In this step only the heating mantle β is switched on. Its electric performance is kept permanently at the maximum during the whole step. The system can be operated without any intervention. When the liquid temperature in flask β reaches the boiling point of the water and becomes constant the heating is switched off. In flask α the distillate is collected which is the organic phase of the condensate. (The ambient pressure is 100.1 kPa and the ambient temperature is 27 °C.)

3.3 Results of the experiments

3.3.1 Double-column system

The liquid temperatures in both flasks are registered during the whole process (*Figure 4*). The boiling temperatures of the products are higher than that of the pure components at the ambient pressure. The difference for *A* is 1.2 °C and for *B* is 1.5 - 2 °C. The boiling points elevated can be caused by the pressure drop of the columns and/or by some contaminations in the liquids. (It is possible that the pumice can contain some soluble components which can increase the boiling temperature.)

Table 2. Properties of the products and the byproducts of the experiment with the DCS

		Product *A*	Product *B*	Liquid holdup of the decanter	
				A-rich phase	*B*-rich phase
Volume	ml	1230	710	24.5	30.5
Mole fraction of *A*	-	1.000	0.000	0.485	0.018
Recovery	%	96.9	97.3	-	-

The liquid temperature β reaches much earlier its target value. (Since the setting of the ratio of the heat duties is not optimal.) Until $\tau = 200\,\text{min}$ both temperatures reach a constant value. Each component can be produced in high purity with good recovery (*Table 2*). The overall volume of the byproducts (60 ml) is nearly the same as the volume of the final liquid holdup of the decanter (55 ml). (It means that the holdups of the columns are negligible.)

3.3.2 Batch rectifier

The liquid temperature in the flasks is registered continuously (*Figure 5*). The boiling temperatures of the products are higher than expected also in this case. The total duration ($\tau = \tau_1 + \tau_2 = 144 + 53 = 197\,\text{min}$) is nearly equal to that of the DCS. Both products are very pure but their recoveries are much lower than in the case of the DCS (*Table 3*). By this configuration not only the final holdup of the decanter is the byproduct but also the distillate of Step 2. Because of the construction of the system a part of the condensate flowing from the cooler gets directly to the cold column β (and then to the distillate flask) bypassing the decantation space. This phenomenon results in a heterogeneous distillate whose *B*-rich phase is added to the *B*-rich phase of the charge to be processed in Step 2 but the *A*-rich phase is considered as a byproduct. The overall volume of the products and the byproducts is 1922 ml. The reason of the higher loss is that in the case of the BR more fillings and emptying (draining) operations are needed.

Table 3. Properties of the products and the byproducts of the experiment with the BR

		Product *A*	Product *B*	Byproducts from the distillates of Step 1 & 2		Liquid holdup of the decanter	
				A-rich phase	*B*-rich phase	*A*-rich phase	*B*-rich phase
Volume	ml	1110	620	118	20	24	30
Mole fraction of *A*	-	1.000	1.000	0.488	0.019	0.495	0.018
Recovery	%	87.4	84.9	-	-	-	-

4. Simulation method

When making rigorous simulation calculations the following simplifying assumptions are applied:

- theoretical trays,
- constant volumetric liquid holdup on the trays and in the decanter,
- negligible vapour holdup,
- negligible duration of pumping between the two steps (BR).

The model equations to be solved are:

- non-linear ODEs (material and heat balances),
- non-linear algebraic equations (VLLE, hold-up and physical property models etc.).

The phase equilibrium is described by the NRTL model. For the solution of the above equations the dynamic simulator of ChemCAD 6.0 (CC-DCOLUMN) is applied (*Figure 3*).

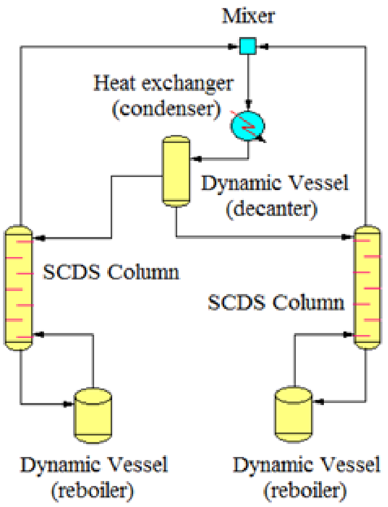

Figure 3. ChemCAD model of the DCS

5. Simulation results

5.1 Input data

The number of theoretical plates of the columns (of holdup 5 ml) without condenser, decanter and reboiler is estimated 5. Both reflux and distillate (BR) are homogeneous. The holdup of the decanter is 55 ml and the levels of liquid phases are prescribed constant (after the start-up). The liquid temperature in the decanter is specified as 60 °C. The heat duties of the spherical reboilers are so chosen to give boiling-up periods as long for the DCS as in the experiment (Q^{α} = 195 W, Q^{β} = 145 W). The prescribed purity of both products is 99.5 mol%. The calculations are started with dry plates and decanter excepted Step 2 of the BR at the start of which the decanter is filled with the liquid remained from Step 1.

5.2 Results

5.2.1 Simulation of the DCS experiment

Similarly to the experiment the purification of *A* demands much more time (147 min) than that of *B* (26 min, *Figure 4*). Because of the different experimental and calculated durations the reboiler liquid temperature profiles do not coincide but their characters are similar. The product quantities are in good agreement with those of the experiment (*Tables 2* and *4*). (Simulations were also repeated by different numbers of plates (N=3, N=10). These simulations gave almost identical results.)

Table 4. Properties of the products and the byproducts of the simulation of the DCS

		Product *A*	Product *B*	Liquid holdup of the decanter	
				A -rich phase	*B* -rich phase
Volume	ml	1218	683	16	37
Mole fraction of *A*	-	0.995	0.000	0.489	0.019
Recovery	%	97.5	93.8	-	-

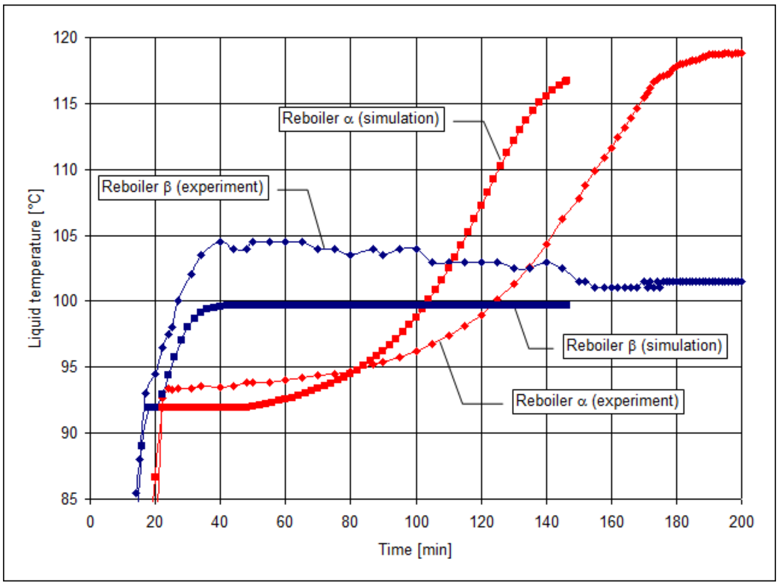

Figure 4. Evolution of liquid temperatures in the reboilers of the DCS (after the start of boiling)

5.2.2 Simulation of the BR experiment

The duration computed of Step 1 (141 min) is in good agreement with the measured one. For Step 2 the duration is prescribed (53 min as in the experiment) instead of the product purity. (It results for the product *B* in much higher purity than 99.5 mol% (*Table 5*) similarly to the experiment.) The evolution curves of the reboiler liquid temperatures are almost congruent with the experimental ones (especially for Step 1, *Figure 5*). The reason of the nearly constant difference between the curves is probably the error of the thermometers. The small difference between the measured and computed quantities of product *A* is caused by the limitedness of the laboratory equipment. The amount of the byproducts also differs for this reason. If the branches of the decanter would be closable the vapour could not get to the cold column and condensate there. In the case of product *B* a greater difference can be found.

Table 5. Properties of the products and the byproducts of the simulation of the BR

		Product *A*	Product *B*	Byproducts from the distillates of Step 1 & 2		Liquid holdup of the decanter	
				A -rich phase	*B* -rich phase	*A* -rich phase	*B* -rich phase
Volume	ml	1162	703	52	0	15	38
Mole fraction of *A*	-	0.995	0.000	0.567	-	0.488	0.020
Recovery	%	93.0	93.9	-	-	-	-

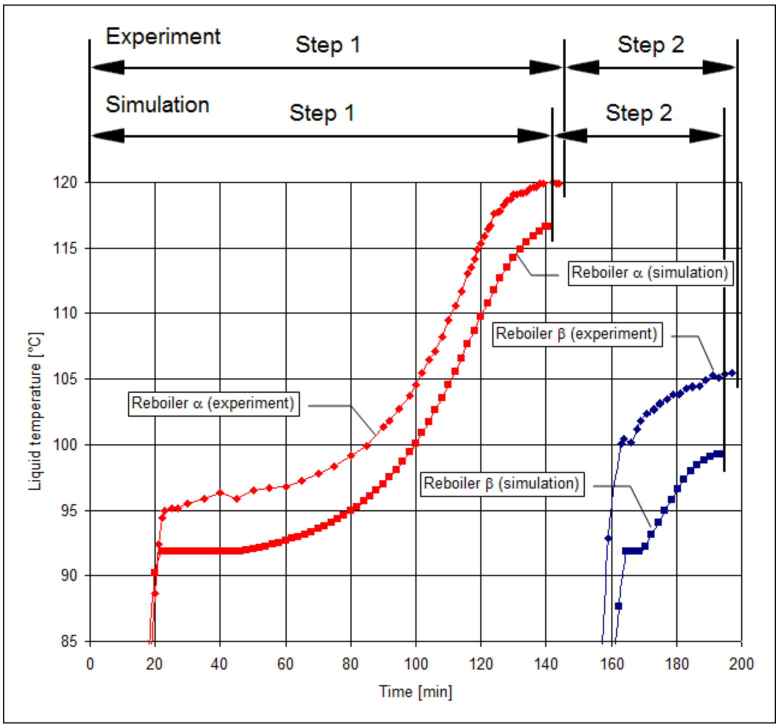

Figure 5. Evolution of liquid temperatures in the reboiler(s) of the BR (after the start of boiling)

6. Conclusions

A new double-column batch heteroazeotropic distillation system (DCS) operating in closed mode was studied by laboratory experiments. Our primary aim was to investigate the feasibility of the separation of the 1-butanol – water heteroazeotropic mixture by the DCS, therefore a very simple laboratory equipment was applied. We compared the performance of the DCS with that of the conventional batch rectifier (BR). We also performed rigorous simulations by using a professional dynamic flowsheet simulator (ChemCAD 6.0 CC-DCOLUMN). On the basis of the results the separation in the DCS proved to be feasible and competitive with that of the BR. By using the DCS higher recovery for 1-butanol was reached during practically the same time and the quantity of the byproducts was also less for the DCS. We intend to study the separation of a ternary heteroazeotropic mixture by laboratory experiments, as well.

Acknowledgements

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