BATCH EXTRACTIVE DISTILLATION AS A HYBRID PROCESS: SEPARATION OF MINIMUM BOILING AZEOTROPES



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Objectives: The comparison of the batch extractive distillation with the hybrid process (absorption + distillation) by feasibility studies and rigorous simulation calculations for the separation of the azeotropic mixtures of minimum boiling point with heavy solvents.

INTRODUCTION

Distillation: widespread method for the separation of liquid mixtures, based on the difference of the volatility of components.

Special distillation methods: methods for the separation of azeotropic and low relative volatility ($\alpha_{AB}\approx 1.0$) mixtures (e.g. extractive and heteroazeotropic distillation).

Batch distillation (BD): very frequent separation process in the pharmaceutical and other chemical industries, where the composition and quantity of the mixture to be separated (charge) varies widely from period to period.

Extractive distillation (ED): a third, component (solvent, E) is added to the mixture A-B, which makes the separation of A and B possible without forming a new azeotrope.

Batch extractive distillation (BED): simultaneously provides the advantages of BD and ED

Mixtures studied:

1. Acetone (A) – methanol (B) + water (E)2. Ethanol (A) – water (B) + ethylene glycol (E)

Batch extractive distillation

BED separation steps:

- 1. Start up under total reflux (R=∞, F=0)
- 2. Purification of the distillate under R=∞ and continuous feeding of E (F>0).
- Production of A under continuous feeding of E (0<R<∞, F>0).
- Separation *B*/*E* (0<*R*<∞, *F*=0).

Important features of BED:

- Continuous solvent feeding in Steps 2 and 3.

The column is operated under significant reflux ratio (R>0) in Step 3.
 The solvent can be fed into an inner plate of the column (Fig. 1.a), that is, the column contain rectifying plates.

Hybrid process

Düssel and Stichlmair [1] and Stichlmair and Fair [5] considered the BED as a hybrid process.

Hybrid separation steps:

Separation A/B by absorption (R=0, F>0).
 Separation B/E by distillation (0<R<∞, F=0).

By this method in the absorption step there is no reflux and the column (Fig. 1.b) contains only one section (extraction/absorption section).





FEASIBILITY STUDIES

a. BED

Simplifying assumptions: - negligible tray hold-up, - quasi-steady state, - constant molar overflow.

The feasibility method is based on the analysis of the still path on the map of

The feasibility method is based on the analysis of the still platf on the map of possible column section profiles. In order to study the hybrid process we extended the feasibility method of Lelkes et al. [3] by making possible the variation of the heat condition of the solvent feeding (q) and that of the reflux for the BED.

The results of the feasibility studies for the mixture ethanol - water + ethylene glycol show the decisive role of q (Fig. 2). In the case q=1 the profiles arrive at the *BE* edge from the whole triangle, the component *A* can not be produced in the prescribed purity. In the other case a considerable part of the profiles arrive at the *AE* edge and the separation can be feasible (with the aid of the feed plate since $\alpha_{AE} > 1$).

RIGOROUS SIMULATION RESULTS

For the more accurate modelling of the process rigorous simulation calculations were done.



Fig. 2 The map of the extractive profiles (x_D =0.99, 0.0005, 0.0095) Solvent feeding: a. boiling point liquid (*q*=1) b. strongly subcooled liquid (*q*=1.32)

- Simplifying assumptions:
- theoretical trays,
- negligible vapour hold-up,
- constant volume of liquid hold-up,
 negligible fluid dynamic lags.

Model equations:

 a. Non-linear differential equations (material balances, heat balances)
 b. Algebraic equations (VLE relationships (with NRTL and UNIQUAC models), summation equations, hold-up equivalence, physical property models).

Solution method

Use of a professional simulator (CCBATCH): quasi-steady state approximation, simultaneous correction method.

Calculations for the mixture acetone (A) – methanol (B) + water (E)

The BED separation had been formerly studied also by pilot plant experiments. Input data:

The column contains 18 theoretical plates, the solvent is fed to plate 6 (f=6). The quantity of (the binary, equimolar) charge: U_{ch} =156.9 mol (9 dm³). The heat duty of the reboiler: 1.5 kW, the liquid holdup: 70 cm³/plate, P=1.013 bar. The solvent is pure water. The prescribed purity of product: $x_{D,Aav}$ =0.94. The other input data are given Table 1.

At first the BED was simulated (Case 1) then the absorption step of the hybrid process was studied (Case 2). First the solvent feed flow rate of the BED was applied (Cases 2 and 2c) then five times greater F was applied (Cases 2) and 2d). The results (including the initial distillate composition of the *A*/*B* separation step $(x_0/t_3=0)$) are shown in Table 1. Results:

Case	1	2			
		а	b	с	d
f	6	1	1	1	1
$F^{\rm vol},{\rm dm^3/h}$	2.0	2.0	10.0	2.0	10.0
T_F , °C	80	80	80	20	20
R	4	0	0	0	0
Δt_2 , min	60	-	-	-	-
Δt_3 , min	138	10	60	10	60
SD, mol	80	-	-	-	-
x _{D,A,av}	0.940	0.614	0.389	0.642	0.641
X _{D,B,av}	0.029	0.135*	0.013*	0.128*	0.009*
$x_{D,E,av}$	0.031	0.251	0.598	0.229	0.350
$x_{D,A}(t_3=0)$	0.972	0.779	0.779	0.779	0.779
$x_{D,B}(t_3=0)$	0.006	0.221	0.221	0.221	0.221
$x_{DF}(t_3=0)$	0.022	0.000	0.000	0.000	0.000



Comparison of the hybrid process with the BED (acetone - methanol + water)

a a su u sa asa

We obtained the prescribed purity acetone with high recovery.

b. Hybrid process

a. BED

Without distillate purification preparatory step the original solvent flow rate (2 $dm^3/h)$ was not sufficient even in the case of strongly subcooled solvent (of 20 °C) for the absorption of the methanol (Case 2c, in the table the minimal methanol content of the top product and its time are given).

With the increased solvent flow rate (Case 2d) the absorption of the methanol was more successful but the water content of the distillate was enormously high (Fig. 3). By the hybrid process the prescribed purity could be reached only by distilling the top product again, that is, an additional A/E separation step is indispensable (in total not one but two distillation steps should be done.)



Then we tried to obtain the product *A* in the quality and quantity obtained by the BED. We inserted an additional *A/E* separation step. In this case the aim of the absorption step was only the *A/B* separation (the absorption of the methanol to a prescribed extent ($x_{D,B,w} < 0.006$)) independently of the *E*-content of the distillate. Afterwards we produced *A* in the prescribed quality by the distillation of the *A-E* product obtained in the absorption step. On the basis of our favourable experiences before the absorption step similarly to the Step 2 of the BED we performed a short purification step ($R=\infty$, F>0). Even by this improved hybrid process we were able to obtain the same quality and quantity of *A*-product under much higher solvent and energy consumptions than by the BED (increase of about 400% and 40%, respectively).

Calculations for the mixture ethanol (A) – water (B) + ethylene glycol (E) The difference between the boiling point of E (197 °C) and that of the original

components (78.3 and 100 °C, respectively) is enormous. Azeotropic charge ($x_{a,k}=0.9$, $x_{c,k}=0.1$) was separated. Under conditions similar to those of Case 2c of the previous example (U_{ch} , T_F and the molar flow rate of the solvent (F) were unchanged) we were able to absorb water from beside ethanol and the pollution of ethylene glycol was quite low (Fig. 4). During the absorption step the temperature of the reboiler varied a lot (from the initial azeotropic temperature of 78.2 °C to 190 °C).

However by BED even better results were achieved also for this mixture since we were able to considerably decrease the solvent consumption (59%) with only a slight increase of the energy consumption (30%) of the *A*-production step.



CONCLUSION

By the hybrid process we can produce pure enough A in one step only if the A/E separation is very easy $(\alpha_{AE}^{>>1})$ and the difference between the boiling and freezing point of the solvent is very great (it can be subcooled to a great extent). The BED process provides higher degree of freedom, greater flexibility and can produce better results than the hybrid process. In the case of BED the boiling point of the solven ta be much closer to those of the original components, since by applying a sufficient reflux ratio and number of rectifying plates the product A can be purified from E in the rectifying section simultaneously with the A/B separation taking place in the extraction section. In this case there is no need for the application of vacuum for the B/E separation.

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