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Entrainer Recycle for Batch Heteroazeotropic Distillation

Laszlo Hegely*, Peter Lang

Budapest University of Technology and Economics, Department of Building Services and Process Engineering, Hungary, H-1111, Budapest, Muegyetem rkp. 3.
hegely@mail.bme.hu

The influence of entrainer (and off-cut) recycle are studied by dynamic simulation for a batch heteroazeotropic distillation (BHAD) process. For the dehydration of isopropanol, toluene is applied as entrainer (E). The production cycle consists of processing three consecutive batches. Both BHAD operational modes (sequential (Mode I) and simultaneous (Mode II) distillation + decantation) are studied. The influence of the amount of E and of the reflux ratios are studied, as well as the effect of E recycle on the consecutive batches. The different operational modes and strategies are compared. For the calculations, a professional flow-sheet simulator is used.

1. Introduction

Distillation is the most frequently used method to separate liquid mixtures, based on the differences in the volatility of the components. Batch distillation (BD) is used to separate mixtures of varying quantity and composition in the fine chemical, spirit, pharmaceutical industry, and in solvent recovery. The main components to be recovered are produced in the main cuts (products). The polluting components and azeotropes are removed in off-cuts, which may contain the main components in considerable quantity and they can either be disposed of by incineration or can be recycled to the next batch to reduce the loss of the main components. However, the cuts recycled diminish the amount of the fresh feed in the next batch and vary the composition of the mixture (charge) to be separated.

For the separation of azeotropic mixtures a special distillation method must be applied. Non-pressure sensitive homoazeotropic mixtures can be separated by extractive and heteroazeotropic distillation both requiring the application of a separating agent (entrainer, E). By batch extractive distillation – BED (Yatim et al, 1993), E forming no new azeotrope is added continuously in considerable quantity to the binary mixture (A-B). Hegely et al. (2013) investigated the effects of off-cut recycle for six-batch BD and BED waste solvent regeneration processes. Hegely and Lang (2016a) performed the optimization of the above processes. The influence of the off-cut and entrainer recycling was studied without optimisation for two BED separations: that of the mixture acetone-methanol with water as entrainer by Hegely and Lang (2016b) and that of the mixture isopropanol-water with dimethyl sulfoxide as entrainer by Hegely and Lang (2017).

By batch heteroazeotropic distillation (BHAD) E is added in batch to the binary mixture before the start of the distillation and it forms at least one heteroazeotrope with the original components. The liquid-liquid split (decantation) makes the separation feasible. BHAD can be performed by two operational modes (Skouras et al, 2005).

In Mode I, the distillation and decantation are performed sequentially (the whole amount of the E-rich phase is withdrawn with the E-lean one) while in Mode II simultaneously. For Mode II, there are two strategies (Koehler et al., 1995). By Strategy A, the whole amount of the E-rich phase is refluxed, by Strategy B, one part of this phase is also withdrawn (Rodriguez-Donis et al., 2002). The whole amount of the E-lean phase is usually withdrawn for both Strategies - Version 1 (Lang and Modla, 2006). One part of the E-lean phase is refluxed only in the cases when the E-rich does not ensure sufficient reflux ratio - Version 2.

The majority of E applied will be present in the E-rich phase and a much smaller part of it in the E-lean phase. By Strategy A, the excess of E can be obtained in the form of binary azeotrope with the component to be recovered in high purity. For both economic and environmental reasons, E must be recycled and reused in the

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next batch. Luyben and Chien (2010) studied the dehydration of acetic acid by BHAD (Mode II, Strategy A) where the isobutyl acetate entrainer was recycled.

The goals of this paper: (1) to study the influence of the entrainer recycling for the batch heteroazeotropic distillation by simulation, (2) to compare the different operating modes (and strategies), (3) to investigate the influence of the amount of E and of the reflux ratios.

The separation process studied is the dehydration of isopropanol(A)-water(B) of azeotropic composition with toluene as entrainer. Three consecutive batches are studied for Mode I and II. For Mode II, both strategies are compared. The simulation is performed by using the dynamic modules of ChemCAD (Chemstations, 2016).

2. Separation process

The components form a ternary and three binary minimum boiling azeotropes. Vapour-liquid equilibrium is described by the NRTL model. The binary interaction parameters are taken from Luyben and Chien (2010) for the A-B pair, from Gmehling and Onken (1986) for A-E and the built-in parameters of ChemCAD are used for B-E. The liquid-liquid equilibrium is described by the UNIQUAC model with parameters taken from Sørensen and Arlt (1980) for 25 °C. Table 1 presents the composition and boiling points (T_{bp}) calculated of the azeotropes and boiling points of the pure components. The composition of the two liquid phases at 25 °C is also included. The calculated composition of the ternary azeotrope is much closer to the liquid-liquid phase envelope than the experimental one (33.6 mol% A, 38.5 % B and 27.9 % E (Horsley and Tamplin, 1962)). This means that the relative amount of the E-lean phase is lower, which results in a longer process if Mode II is applied.

The production cycle consists of three consecutive batches. The aim is to produce A as the still residue in 98 mol% purity. For Mode I, processing of the Batch I has the following steps:

Step 0: Warming up of the charge (fresh feed+E) onto its boiling point and heating-up of the column under total reflux ($R = \infty$). This step is finished when the composition of the distillate (condensate) is constant (close to that of the ternary heteroazeotrope).

Step 1: Production of distillate with composition close to that of the ternary azeotrope. The distillate has two liquid phases, and decantation is performed later in the distillate accumulator, that is, the presence of two liquid phases is not exploited during distillation. A finite reflux ratio ($R_1 < \infty$) is applied. This step is finished when the second liquid phase disappears. The E-rich phase of the accumulated distillate can be recycled to the next batch to reduce both the loss of A and E.

Step 2: Off-cut collection under $R_2 < \infty$. The off-cut is necessary to remove more B from the still. This step is finished when the concentration of A in the still (product) reaches its specified value. The off-cut cannot be recycled because of its high B content.

For Mode II, the steps of Batch I are the following ones:

Step 0: Warming up of the charge onto its boiling point and heating-up of the column under total reflux ($R = \infty$). E can be added to the fresh feed or filled into the decanter. This step includes the filling up of the decanter, and is finished when the prescribed levels of both liquid phases are reached. Because the volumetric phase ratio (E-rich/E-lean) of the ternary azeotrope is high (102), the accumulation of the E-lean phase determines the length of the step.

Step 1: Removal of B in the form of E-lean phase. Both liquid phases have a constant level in the decanter. The excess of E-lean phase is withdrawn as distillate, while that of the E-rich phase is refluxed to the column, either entirely (Strategy A) or partially (Strategy B). The reflux ratio is determined by the phase ratio of the condensate. This step is finished when the second liquid phase disappears or when the flow rate of the E-lean phase becomes zero. The step can be terminated earlier, as well, if the concentration of A in the still already reaches the prescribed purity. The E-rich phase remaining in the decanter at the end of the production can be recycled to the next batch.

Step 2: Off-cut collection under $R_2 < \infty$. If the specified purity is not reached in Step 1, an off-cut is necessary to remove excess of E from the still. The off-cut can be recycled, as its B content is low.

For Batches II and III, Step 0 is slightly different from those of Batch I. The E-rich phase and the off-cut of the previous batch are mixed to the fresh feed before distillation. When processing these batches, it is expedient at least to replace the amount of E lost with the E-lean phase, the product and the final hold-up with fresh E in the previous batch, which is also added to the charge before distillation.

Table 1: Calculated boiling points (T_{bp}) and compositions of the azeotropes

	T_{bp} (°C)	A (mol%)	B (mol%)	E (mol%)
ABE	75.22	39.2	35.7	25.0
ABE – E-rich phase		39.7	34.6	25.6
ABE – E-lean phase		15.1	83.6	1.3
AB	80.44	66.3	33.7	-
AE	81.56	84.3	-	15.7
A	82.26	100	-	-
BE	84.36	-	55.7	44.3
B	100.00	-	100	-
E	110.63	-	-	100

3. Simulation results

The amount of the fresh feed (close to azeotropic A-B mixture containing 67.4 mol% A) is 20 kmol in Batch I. The column has 28 theoretical stages (excluding the reboiler and the condenser), with a liquid hold-up of 2 dm^3/stage. The heat duty of the reboiler is 400 MJ/h. The hold-up of the total condenser is 40 dm^3. The hold-up of the decanter (83.1 dm^3) is chosen to ensure a residence time of 5 min. The hold-up of the heavy (E-lean) phase is 6.4 dm^3 (higher than the value calculated from phase ratio). The temperature of the decanter is 25 °C. For Mode I, Step 0 lasts 1 h, for Mode II it is finished when the specified liquid levels in the decanter are reached. Figure 1 shows the ChemCAD model for Mode II. The following modules are used: SCDS (Simultaneous Correction Distillation) column (11), Dynamic vessels for the still (1), the decanter (3), and distillate tanks (4, 6), Heat Exchanger for the condenser (7), Time Switches (8, 10) to change the direction of liquid flow at the end of the steps, a Divider (9) to adjust R_2, and a Mixer (5) so that only one feed is present.

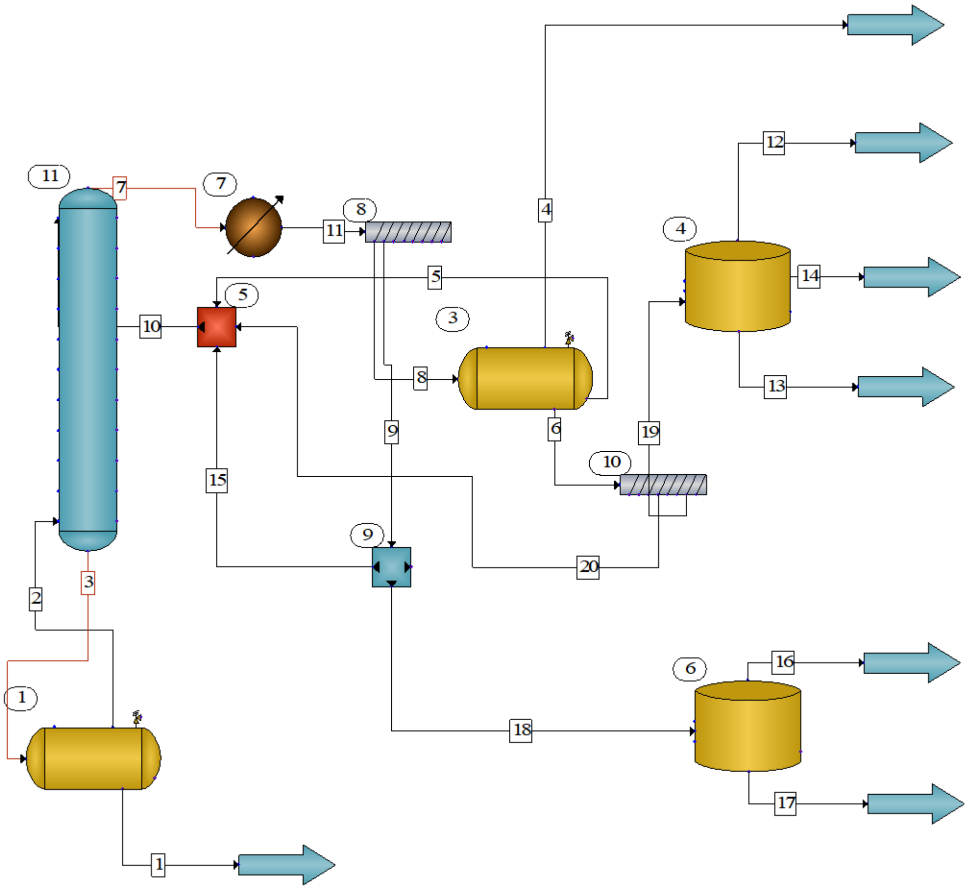

Figure 1: ChemCAD model for Mode II

For Mode I, the specific product flow rate (SPF), defined as the ratio of the amount of product and the duration of the process is maximised by varying the reflux ratio of Step 1 (R_1) and 2 (R_2) for three different values of the amount of the entrainer (F_E, Table 2). The maximum of SPF is determined by varying one reflux ratio while keeping the other one constant, then the previously constant reflux ratio is varied and the other one fixed. The procedure is repeated until no improvement in SPF can be attained. The optimal values and results are presented in Table 2. If the difference between R_1 and R_2 is high enough, as in the case of the optimal ones, liquid-liquid split may appear again in Step 2. To exploit this, the process is modified as follows. Step 1 is divided into two substeps whose reflux ratios are R_1 and R_2. The reflux ratio is changed at time t_{RCh}, immediately before the separate aqueous phase disappears. Step 2 then continues with R_2. This modification reduces the amount of off-cut.

The highest SPF and recovery (η_A) are reached at F_E=4 kmol. Although further increase of F_E makes the process faster, but the amount of product is decreased. The high amount of E-rich phase, containing 34.7 % B, explains the low recoveries of Mode I.

For Mode II, the influence of the amount of E added is investigated for Strategy A. The minimum E needed can be calculated by supposing that the total amount of B is withdrawn in E-lean phase of the ternary azeotrope. The minimum value (0.102 kmol) is, however, lower than the E-lean phase hold-up of the decanter (0.228 kmol). The amount of E also has a maximum value (2.47 kmol). When this value is exceeded, the charge composition belongs to the batch distillation region with the stable node E, and no A can be produced. The maximum value can be calculated by determining the intersection of the mixing line between pure E and the charge and the separatrix joining the ABE and AE azeotropes. Calculations are performed for F_E=0.5, 0.7, 0.843 and 1.4 kmol. By F_E=0.5 kmol, no liquid-liquid split is observed. By F_E=0.843 kmol, two versions are studied: mixing E with the charge (as for the other E amounts) and placing it into decanter. The value of 0.843 kmol corresponds to filling the decanter completely with E. We also studied the policy of mixing E to the charge and placing the ternary azeotrope in the decanter, but in this case, there was no liquid-liquid split. Strategy B is studied for F_E=0.7 kmol with two E-rich phase reflux ratios: R_{ER}=49 and 499. The results for Batch I are presented in Table 3.

The value of F_E determines whether an off-cut is necessary or not. B is always removed in the E-lean phase, but if F_E is high (1.4 kmol), Step 2 is necessary for the removal of excess E from the still. The optimal R of this step is found to be 11. Using too much E reduces the recovery and increases production time. From the F_E values studied, 0.843 kmol gives the best results. Placing E into the decanter instead of the still makes the production faster and slightly increases η_A, but the difference is not high. The ratio B/E in the product is also determined by the value of F_E: the product almost only contains B when F_E=0.7 kmol, E when F_E=1.4 kmol, and contains both in significant quantity when F_E=0.843 kmol. Strategy B is not recommended: although the production is faster, the amount of product is significantly decreased.

Based on the results for Batch I, the three-batch cycle is modelled for two cases of Strategy A of Mode II: 0.843 kmol E in the decanter (Case 1), 1.4 kmol E mixed to the charge (Case 2). The E-rich phase, the off-cut and the final column hold-up is recycled to the next batch. For Batches II and III, the amount of fresh feed is calculated so that the volume of the charge (including the fresh E added) is equal to that of Batch I. F_E equals the amount of E lost in the previous batch (that is, the amount of E present is always the same). For both Batch II and III, the amount liquid recycled is ca. 3 (Case 1) and 6.6 kmol (Case 2).

Table 2: Results of Batch I for Mode I

F_E kmol	R_1	R_2	t_{RCh} h	E-rich phase kmol	E-lean phase kmol	Off-cut kmol	Product kmol	Duration h	SPF kmol/h	η_A (%)
3	1	6	2.62	10.9	0.230	7.06	3.28	9.75	0.336	23.8
4	2	9	5.03	14.8	0.312	2.38	4.92	9.05	0.544	35.8
5	1	6	3.73	16.9	0.355	2.96	3.43	8.23	0.416	24.9

Table 3: Results of Batch I for different operational policies of Mode II

Policy	F_E kmol	E-rich phase kmol	E-lean phase kmol	Off-cut kmol	Product kmol	Duration h	SPF kmol/h	η_A (%)
Strategy A, E in still	0.7		6.551	-	11.11	66.4	0.167	80.8
	0.843	1.299	6.628	-	11.19	66.9	0.167	81.3
	1.4		6.964	3.637	7.867	74.2	0.106	57.2
Strategy A, E in decanter	0.843	1.299	6.566	-	11.22	65.3	0.172	81.5
Strategy B, R_{ER}=49	0.7	2.074	0.150	15.00	1.311	19.3	0.068	9.53
Strategy B, R_{ER}=499	0.7	1.975	3.080	9.435	4.583	42.8	0.107	33.3

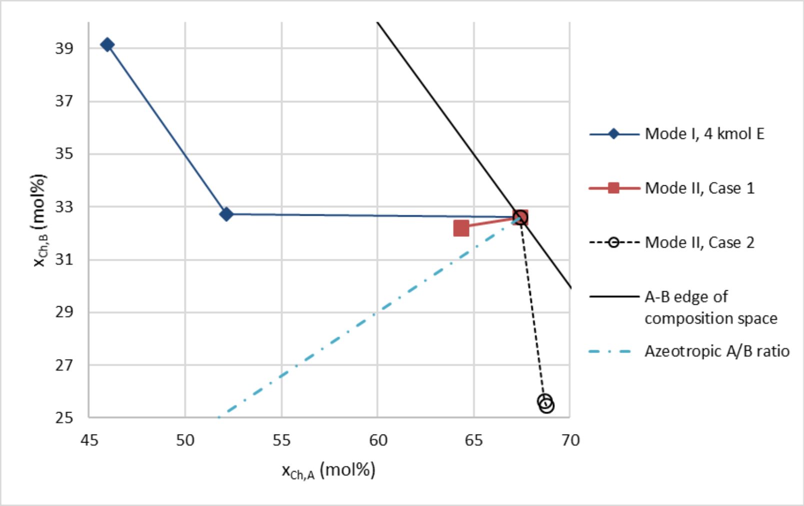

Figure 2: The effect of recycling on charge composition by the different operational policies

Table 4: Results of the three-batch process for the operational policies studied

Policy	F_E in Batch I kmol	Total F_E kmol	Fresh feed kmol	Product kmol	Total non-recycled off-cut (kmol)	Duration h	SPF kmol/h	η_A %
Mode I, no recycle	4	12.0	60.0	14.8	52.5	27.2	0.544	35.8
Mode II, Case 1, no recycle	0.843	2.53	60.0	33.7	23.6	195.8	0.172	81.5
Mode II, Case 1, with recycle	0.843	1.18	53.1	32.0	20.5	192.7	0.166	87.5
Mode II, Case 2, no recycle	1.4	4.20	60.0	23.6	31.8	209.9	0.113	57.2
Mode II, Case 2, with recycle	1.4	1.90	47.0	24.7	29.0	186.4	0.132	76.2

The effect of recycle on the charge composition without the fresh E added (x_{Ch}) is presented in Figure 2, which shows one part of the ternary diagram. Batch I is the A-B azeotrope, it lies on the A-B edge of the composition space. The greatest changes are observed for Mode I, where the A/B ratio in the charge becomes significantly less than the azeotropic one (2.07) due to the accumulation of B to the point that the processing of Batch III becomes infeasible. For Mode II, Case 2, the change in x_{Ch} is advantageous as the A/B molar ratio increases. For Case 1, the A/B ratio decreases, but the change is so slight that it does not to disturb the separation process. For both cases of Mode II, the difference between Batches II and III is very low. This indicates that it is likely possible to extend E recycle for more than three batches. The results of the different operational policies for three consecutive batches are compared in Table 4. Mode I with recycle is not included, as recycling the high amount of E-rich phase makes the process infeasible. Batch II has a very low η_A (9.7 %), while no A can be produced in Batch III: the still residue is B. Mode I is the fastest process, but its recovery is very low. It also has the highest E consumption and non-recycled off-cut produced. Operation by Mode II always takes much (at least 7 times) longer time, but the recovery greatly increases. The highest recovery is reached for Case 1 with recycling. The E consumption and the amount of non-recycled off-cut are also the lowest here. However, the amount of product is higher without recycling. The effects of recycling are the following ones. The amount of fresh feed decreases; this effect is more important for Case 2, since the off-cut is also recycled beside the E-rich phase. The recovery increases, because less A is lost. Depending on the magnitude of the above effects, the amount of product may increase or decrease. The increase in η_A is more important for Case 2. The results show that although adding too much E to the charge can be disadvantageous (need for off-cut, decreased η_A), the recycling can greatly improve the recovery. This is important in practical operation, since it is not always possible to determine the amount of E needed precisely. The E consumption is decreased to less than half by recycling. Recycling also makes the production faster, since $x_{Ch,B}$ is lower.

4. Conclusions

The dehydration of mixture isopropanol(A)-water(B) of azeotropic composition with toluene as entrainer (E) by batch heteroazeotropic distillation was investigated. The production cycle consists of three consecutive batches. The E-rich phase and the off-cut is recycled to the next batch to reduce the loss of both A and E. First, only the first batches were compared. The optimal reflux ratios of Mode I were determined for three values of E quantity (F_E). For Mode II, the effect of F_E was studied for Strategy A. The application of Strategy B was also investigated. Mode I resulted in the fastest process with the highest specific product flow rate (SPF: amount of product/duration of process), but provided only low (35.8 %) recovery. By Mode II, both recovery and SPF had a maximum as a function of F_E, which was lower than for Mode I. Adding too much E to the fresh feed makes necessary to remove the excess E in an off-cut after the disappearance of the second liquid phase. Placing E in the decanter instead of mixing it to the fresh feed in the still made the production faster and slightly increased the recovery. By this policy, a recovery of 81.5 % was reached. However, by using Mode II, production was always much (at least 7 times) slower than by Mode I. Strategy B is not recommended for the separation process studied, as it had low recovery. The effect of recycling was studied for Mode I and two cases of Mode II: placing 0.843 kmol E in the decanter (Case 1) or 1.4 kmol E in the still (Case 2). For Mode I, recycling made the processing of Batch III infeasible. This is explained by the accumulation of B in the charge due to the high amount of E-rich phase recycled. By Mode II, recycling made the production faster by 2 % (Case 1) and by 11 % (Case 2), and increased the recovery of A by 7 and 33 %. The consumption of E decreased to less than half for both cases. Recycling decreased the amount fresh feed treated as well (by 12 % and 22 %), but for Case 2, the increase of recovery was high enough to increase the amount of product obtained. As explained by the higher amount of material recycled, the effect of recycling was more important for Case 1. This means that even if excess E is added, which is disadvantageous, recycling can greatly improve recovery.

Acknowledgments

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