Optimisation of the Dehydration of Isopropanol by Batch Heteroazeotropic Distillation with Off-cut Recycling

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Abstract. The dehydration of isopropanol (B) from a mixture containing methyl ethyl ketone (A) and toluene (E) as pollutants (E can be applied as entrainer as well) is studied by performing dynamic simulations for Mode II Strategy A of batch heteroazeotropic distillation. The goal is to minimise the batch time using the Box-complex method with a specified B recovery and purity (99.7 mol% in the residue). The optimisation variables are the reflux ratios of all distillation steps and the amount of entrainer added to the charge. The possibilities of recycling are studied. The production campaign consists of three batches. First, processing of all batches is performed with the operating parameters obtained from the optimisation of the first batch (Policy I). Second, processing of the three batches is optimised individually (Policy II); finally, the whole campaign is optimised simultaneously (Policy III). The different optimisation policies are compared on the basis of the minimal distillation time and computational intensity.

Keywords Heteroazeotropic batch distillation, Optimisation, Complex method, Off-cut recycle

Introduction

Batch distillation (BD) is frequently applied for the separation of mixtures with varying amount and composition, e.g. in the fine chemical and pharmaceutical industry. For the separation of azeotropic mixtures, a special distillation method, such as heteroazeotropic distillation, must be applied (Luyben and Chien, 2010), which requires the addition of a separating agent (entrainer), which forms at least one new heteroazeotrope. The condensate of the heteroazeotrope splits into two liquid phases. The liquid-liquid split (decantation) makes the separation feasible.

By batch heteroazeotropic distillation (BHAD), an entrainer is added to the feed mixture before the start of the distillation. BHAD can be performed by two operational modes (Skouras et al., 2005). By Mode I, the distillation and decantation are performed sequentially. The condensate is divided into distillate and reflux, and the decantation of the distillate, where the E-rich and E-lean phases are separated, is only performed after the end of distillation. By Mode II, distillation and decantation are performed simultaneously. The condensate enters the decanter from where the reflux and distillate are usually withdrawn from different liquid phases. For Mode II, two strategies are distinguished (Skouras et al., 2005). By Strategy A, the whole amount of the E-rich phase is refluxed, while by Strategy B, one part of this phase is also withdrawn as distillate (Rodriguez-Donis et al., 2002).

When off-cuts are produced, recycling them can increase the recovery of the target component and/or decrease the batch time (Mujtaba, 2004). It can also decrease the loss of entrainer, for example, in the case of extractive distillation (Hegely and Lang, 2017) or heteroazeotropic distillation (Hegely and Lang, 2018). There are several strategies for recycling off-cuts summarised by Mujtaba (2004):

- collecting and mixing all off-cuts produced in a cycle and reprocessing them in the next batch cycle (Luyben, 1988).
- collecting all off-cuts produced in a cycle separately and recycling them in the next batch in sequential order (Mujtaba, 1989)
- splitting all off-cuts collected from a cycle into fractions, which are fed to the next batches in sequential order (Bonny et al., 1996).

Optimising a batch distillation production campaign containing recycling can be done in several ways:

- Policy I: the first batch of the campaign is optimised, and the obtained optimal parameters are used for all other batches of the production campaign.
- Policy II: the production campaign is decomposed into individual batches, which are optimised separately (Hegely and Lang, 2016).

- Policy III: the whole production campaign is handled together and optimised simultaneously (Bonny et al., 1996). This policy enables the optimisation of the recycling, not only that of the operation of the column.

In this work, the recovery of isopropanol from a four-component waste solvent mixture, containing methyl ethyl ketone (A), isopropanol (B), water (C) and toluene (E), is studied by rigorous dynamic simulations performed in ChemCAD. The goal is to recover B in high purity (99.7 mol%) using batch heteroazeotropic distillation with toluene (E) as entrainer, which forms a ternary heteroazeotrope with B and C. Its main benefit is that it is already present in the feed mixture. Recycling off-cuts is also studied in a three-batch production campaign, where the recycling strategy presented by Luyben (1988) is used. The campaign is optimised using the Box-complex method (Box, 1965): the batch time is minimised with a specified recovery (η). The complex method is a direct search method, which means that no derivatives are used. It is based on the Nelder-Mead simplex method with the ability of handling inequality constraints. The Box-complex method was chosen for optimisation over a genetic algorithm (which is used widely), as it is expected to be much faster (requires less computational time). Finally, the results obtained from the different optimisation policies are compared also by considering the computational intensity.

Vapour-liquid equilibrium

The components form seven minimal boiling point azeotropes: five binary and two ternary ones, from which two and one are heteroazeotropes, respectively (Nemeth et al., 2019). The ternary BCE heteroazeotrope makes the regeneration of B by heteroazeotropic distillation feasible. The UNIQUAC model was used for describing the vapour-liquid and liquid-liquid equilibria of the mixture. The binary interaction parameters for each pair were chosen to obtain the best agreement of the measured and calculated data (Nemeth et al., 2019).

Process description and calculation methods

The separation of the feed mixture (containing 1.61 mol% A; 89.30 mol% B, 7.08 mol% C and 2.01 mol% E) is performed by using BHAD Strategy A, which has the following steps:

1. Addition of E (whose amount is an optimisation variable), warming up of the charge and heating up of the column under R=∞. The end of this step is when both liquid phases reach their specified levels in the decanter.
2. Heterogeneous distillation: Withdrawal (decantation) of the whole amount of E-lean (aqueous) phase until the flow rate of the aqueous phase withdrawn diminishes to a low value. The actual stopping criterion in the simulation is a water concentration in the still (1.83 mol%). This value was determined based on the evolution of mass flow of the withdrawn aqueous phase in time in the case of the first batch. The calculation is more stable if a concentration is chosen as stopping criterion instead of a very low mass flow. The E-rich phase hold-up of the decanter can be recycled to the next batch.
3. Homogeneous distillation: Distilling out the remaining A, C and E by BD to fulfil the purity criteria of the residue. In this step, the optimisation variable is the reflux ratio (R). This off-cut can be recycled to the next batch.

Fig. 1 shows the ChemCAD flowsheet of BHAD, which is used for the dynamic simulation for the dehydration of B.

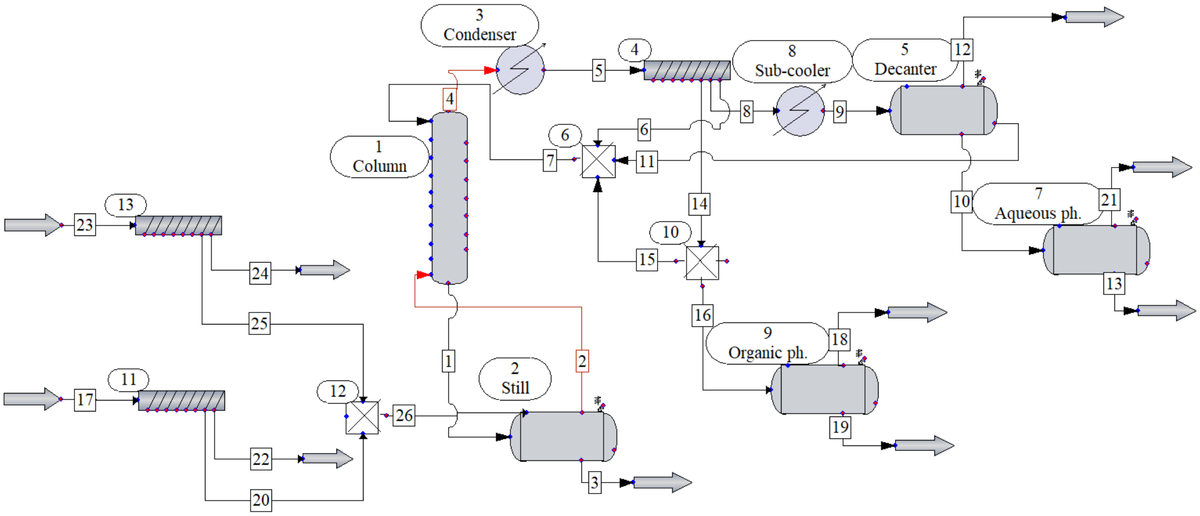

Fig. 1 ChemCAD flowsheet of the BHAD process prepared for dynamic optimisation.

The following ChemCAD modules are used for modelling the separation: SCDS (Simultaneous Correction Distillation) column (1), DYNAMIC VESSELs for the still (2), for the decanter (5), for the accumulator of the aqueous phase (7) and that of the organic phase (9), HEAT EXCHANGERs for the condenser (3) and for the sub-cooler (8), DIVIDER for the reflux splitter (10), TIME SWITCHes for manipulating the direction of the liquid flow at the end of each step (4), for adding E (11) and charge (13) to the still, MIXERs for the reflux (6) and for the feed of the still pot (12). These mixers ensure that only one stream enters to the top of the column (as reflux) and to the reboiler. The charge is filled to the still in 2 min via Stream 25; after that E is also added in 6 min via Stream 20. By Strategy A, the condensate goes to Stream 8 in Steps 1 and 2. The heat exchanger subcools the condensate to 25 °C.

In Step 2, the total amount of the organic phase is refluxed from the decanter via Stream 11, while the aqueous phase is withdrawn to Vessel 7.

In Step 3, R is adjusted in Divider 10 by setting the split ratio (the fraction of the condensate refluxed to the column) of Stream 15, which is calculated from the optimisation variable (R) by $\frac{R}{R+1}$.

The column was simulated with 10 theoretical plates (excluding the condenser, decanter and reboiler), the hold-up of the condenser was 25 dm^3, while it was 4 dm^3/plate for the column, the heat duty of the reboiler was 750 MJ/h, which was set in Dynamic Vessel 2. The volume of the charge was 8.5 m^3 (without the additional amount of E, which is an optimisation variable). The dimensions of the decanter (d=0.5 m, h=1 m) were calculated to obtain at least 5 min residence time. The decanter was operated at 25 °C.

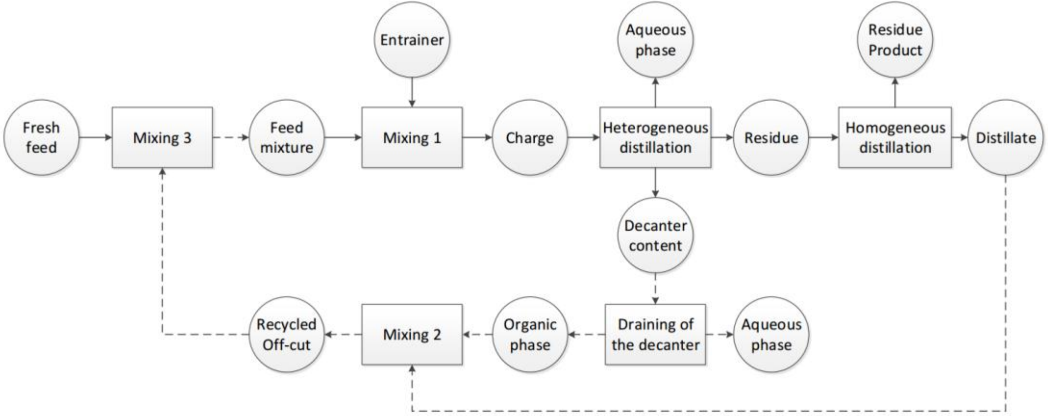

Fig. 2 State-Task-Network of the BHAD production campaign.

In Batch 1 8.5 m^3 fresh feed is processed and optimised by Box-complex method. The goal is to minimise the batch time with a minimal B recovery of η_1=75%. The optimisation variables are the molar amount of toluene (F_E) added to the feed mixture (Mixing 1) and R (in Step 3). Then the off-cuts are recycled for Batch 2 and 3, which is shown in the State-Task-Network (STN) of the production campaign with dashed lines (Fig. 2). The campaign consists of three batches (recycling two times). The organic phase from the decanter is united (Mixing 2) with the distillate of Step 3 (Batch distillation) and then mixed with fresh feed (Mixing 3), whose amount is determined to obtain 8.5 m^3 feed mixture for each batch. Mixing is performed by an algorithm, which uses the bisection method running under Excel coupled to ChemCAD. The algorithm varies the amount of fresh feed in ChemCAD until the volume of the feed mixture is equal to 8.5 m^3.

By Policy I in Case 1 the distillation is performed two times again with off-cut recycling with the optimal F_E and R obtained for Batch 1, and the B recovery is calculated for each batch. In Case 2 the calculations with off-cut recycling are repeated without the addition of further amount of E to the feed mixture, that is, for Batches 2 and 3 F_E=0.

By Policy II Batches 2 and 3 are optimised separately by the Box-complex method, but the recovery constraint of each batch is set to the recovery obtained for the corresponding batch using Policy I, Case 1, since the recovery decreases from batch to batch.

By Policy III the whole production campaign is optimised simultaneously. A constraint is now given for the total recovery (η_{total}) of the campaign (the total amount of B in three still residues divided by the total amount of B in the three fresh feeds. The value of the constraint is set to the η_{total} of Policy I, Case 1. The parameters of the complex method are: the initial value of the reflection coefficient (α) is 1.3 and the number of points in the complex was twice the number of variables. The allowed ranges of the optimisation variables are summarized in Table 1, along with the narrower starting ranges, within which the points of the starting complex are randomly generated. The worst point (with highest OF) of the complex is reflected to the centroid of the other points in a distance scaled by α, and a new complex is obtained. This procedure is repeated until the size of the complex becomes sufficiently small; in this work, when the highest of the distances between the points of the complex becomes lower than 1 %. The distances are calculated by scaling the value of each variable to its allowed ranges. (For example, 1 % corresponds to a ΔF_E=0.02 kmol or ΔR=0.15 in the case of Policy II.)

Table 1. Ranges of optimisation variables.

		Allowed ranges		Starting ranges	
		F_E, kmol	R, -	F_E, kmol	R, -
Policy II	All batches	0 – 2	5 – 20	0 – 1	10 – 18
Policy III	Batch 1	“	5 – 20 (2 – 20)	0 – 0.6	12 – 18
	Batch 2	“	5 – 20 (2 – 20)	0 – 0.1	“
	Batch 3	“	5 – 20 (5 – 30)	“	“

For Policy III, two optimisation variable ranges are given for R, because it was changed during the optimisation after 110 iterations as the R values were close to their lower bounds for Batch 1 and 2, and to its higher bound for Batch 3.

Results

Main results for the whole production campaign calculated by each optimisation policy are summarised in Table 2.

Table 2. Main results of all optimisation policies for the whole production campaign.

		F_E, kmol	R	t_{aq}, min	t_{BD}, min	t_{batch}, min	η_{batch}, %	t_{camp}, min	η_{total}, %	no. of simn.
Policy I, Case 1	Batch 1	0.346	16.13	1148	1456	2906	76	10012	83	132
	Batch 2	“	“	1162	1948	3364	70			1
	Batch 3	“	“	1070	2422	3742	62			1
Policy I, Case 2	Batch 2	0	“	1248	1872	3378	71	10018	84	1
	Batch 3	“	“	1220	2260	3734	64			1
Policy II	Batch 2	0.015	15.38	1242	1828	3328	70	9742	83	38
	Batch 3	0.013	13.67	1202	2050	3508	62			38
Policy III	Batch 1	0.004	4.07	1306	998	2624	43	8644	84	144·3
	Batch 2	0.008	6.66	918	1252	2492	54			
	Batch 3	0.199	19.85	1008	2238	3528	72			

By Policy I in Case 1, the distillation time of each batch (t_{batch}) increases, while the recovery of the individual batches (calculated for the given charge) decreases quickly. However, the recovery of the production campaign increases due to the recycling of the off-cuts. t_{aq} (duration of withdrawing the aqueous phase from the decanter) does not change significantly from batch to batch. Adding the same amount of E to the feed mixture for each batch results in the accumulation of E in the charge (Table 3), which highly increases t_{BD} (duration of conventional batch distillation, Step 3) because E must be removed from the still with distilling the BE azeotrope containing a low amount of E (18.7 mol%). This highly increases the duration of Step 3 and decreases the B recovery. Besides the accumulation of E, A also accumulates in the charge from batch to batch for all optimisation policies, while the concentration of C does not show a monotonous change: for Policy I and II, it shows a maximum, while a minimum for Policy III for Batch 2. In the composition of the charge in Table 3, the additional amount of E is also included.

For Policy 1 in Case 2 processing of Batches 2 and 3 was recalculated without adding fresh E to the feed mixture. Similarly to Case 1, the distillation time of each batch increases, while the recovery decreases. By comparing the results of Case 2 to Case 1, slightly higher recoveries can be achieved, while the distillation times are almost the same: it is slightly higher for Batch 2 and lower for Batch 3. The time difference is less than 1% for both batches. However, the total distillation time of the campaign (t_{camp}) is almost the same (there is only 6 min difference). t_{aq} is higher for Case 2 than for Case 1 for all batches of the campaign. For Batch 2, t_{BD} is lower by 76 min and for Batch 3, it is lower by 162 min compared to Case 1. This is caused by the fact that E accumulates in the charge to a lower extent for Case 2.

By Policy II, the two batches with recycling are optimised individually: the optimal amount of E added to the charge is negligible for Batches 2 and 3 (Table 2), while R decreases from batch to batch. As the amount of E added is negligible, t_{aq} is almost the same as for Case 2 of Policy I. The optimal R decreased; hence t_{BD} also decreased. The batch times and also the total time of the production campaign are lower than for both cases of Policy I. The highest time difference is reached for Batch 3, where the batch time is by 7% lower for Policy II than for both cases of Policy I. Both for Policy I and II, the amount of fresh feed decreased as the recycled amount increased due to the accumulation of E (Table 3): a higher amount of distillate must be withdrawn in Step 3 to reach the specified purity of B in the still.

By Policy III, the whole production campaign is optimised simultaneously, the lowest t_{camp} can be achieved, while fulfilling the η_{total} constraint: t_{camp} is by 14% lower compared to Policy I, while it is 11% lower compared to Policy II. By Policy III, the amount of the fresh feed increased, while that of the recycled cuts decreased as R was lower at the beginning of the production campaign. This also meant that the recovery of the individual batches increased from batch to batch (Table 2). For Batches 1 and 2, the optimal amount of E added was negligible, while it was already significant for Batch 3. This resulted in lower t_{aq} for Batches 1 and 2, while higher for Batch 3. However, t_{aq} of Batch 2 was particularly low, which is caused by the high amount of recycled material (with relatively low water content) mixed with a lower amount of fresh feed: the charge of Batch 2 contained a low amount of water; hence the flow rate of the aqueous phase became low earlier. Similarly to Policies I and II, t_{BD} increased from batch to batch due to the accumulation of E. The calculations for Policy III were repeated with F_E=0 for Batches 1 and 2 while using the optimal amount of E for Batch 3 and the optimal R for all batches. The results were similar to the previous ones, but the total time of the campaign increased by 10 min.

Table 3. Composition and amount of each charge of the production campaign.

				Charge				Recycled to the next batch/Waste*			
					Composition, mol%				Average comp., mol%		
	Batch	Fresh feed, kmol	F_E, kmol	Amount, kmol	A	C	E	Total amount, kmol	A	C	E
Policy I, Case 1	1	116.63	0.346	116.98	1.61	7.06	2.30	27.80	5.52	9.63	8.94
	2	87.52	“	115.67	2.54	7.67	3.97	37.17	8.68	7.25	11.71
	3	76.79	“	114.31	3.31	7.11	5.46	46.20	7.44	5.83	13.05
Policy I, Case 2	2	87.52	0	115.32	2.55	7.69	3.68	35.74	7.11	7.51	11.27
	3	78.41	0	114.15	3.33	7.21	4.91	43.14	7.92	6.23	12.43
Policy II	2	87.52	0.015	115.33	2.55	7.69	3.69	36.48	6.95	7.35	11.08
	3	77.63	0.013	114.12	3.32	7.17	4.92	45.60	7.48	5.91	11.87
Policy III	1	116.63	0.004	116.63	1.61	7.08	2.01	62.74	2.48	4.27	3.56
	2	51.09	0.008	113.84	2.09	5.53	2.87	52.53	4.06	5.13	6.02
	3	61.29	0.199	114.02	2.74	6.17	4.03	35.24	8.00	7.69	12.34

*Waste is the mixture of distillate withdrawn in Step 3 and the organic phase from the decanter of Batch 3.

As for the calculation time requirement, the Box-complex method proved to be effective for all optimisation policies. The total number of simulations was 208 for Policy II, while it was 432 (simulating the production campaign consisting of three batches 144 times) for Policy III. In the latter case, the number of simulations was higher because it was difficult (slow) to find the 12 points of the first (starting) complex that all fulfilled the recovery constraint. Although the time requirement of Policy III is twice as much as the individual optimisation, the total distillation time of the campaign is much lower. The processing capacity calculated as the total amount of fresh feed divided by the total production time of the campaign was the lowest for Policy III (38.2 kmol/day), while it was the highest for Policy II

(41.7 kmol/day). The reason for this difference is the relatively high amount of recycling (due to the low R for Batches 1 and 2) for Policy III.

Conclusions

The recovery of isopropanol (B) with batch heteroazeotropic distillation (BHAD) from a mixture containing methyl ethyl ketone (A), water (C) and toluene (E) as pollutants was studied by dynamic simulation. The entrainer was toluene, which was already present in the feed mixture. Off-cut recycling was studied for Mode II Strategy A in a three-batch production campaign. The off-cuts recycled were the organic phase from the decanter (in Step 2) and distillate of the conventional batch distillation step (Step 3, necessary for final purification of B residue after the amount of aqueous phase had become very low in Step 2). The production campaign was optimised by using the Box-complex method with a specified minimum recovery as constraint. The goal was to minimise the batch time of the process. For one batch, the optimisation variables are the amount of E added to the feed (F_E) and the reflux ratio of Step 3 (R).

The following optimisation policies were studied:

I. Only Batch 1 is optimised, while Batch 2 and 3 are calculated with the optimal R and F_E values obtained for Batch 1 (Case 1) or with F_E=0 (Case 2).

II. Each batch of the campaign is optimised individually.

III. The whole production campaign is optimised simultaneously.

The total amount of E added to the feed was the lowest by Policy III, while the highest by Policy I (Case 1). Considering the individual batches of each policy, F_E was the highest for Batch 3 by Policy III and for Batch 1 by Policy I and II. In all cases, E accumulated in the recycled cuts, but the extent of increase was the lowest for Policy III, while it was the highest for Policy I (Case 1). For Case 2 of Policy I, the E accumulation in the charge was lower than for Case 1, but the total distillation time of the campaign was almost the same. The lowest optimal reflux ratios were obtained for Batch 1 and 2 by Policy III, and the highest optimal reflux ratio for Batch 3 was also obtained by Policy III. As expected, the lowest process time was achieved by Policy III: it was by 11% lower than by Policy II and by 14% lower than by Policy I. However, Policy III gave the lowest processing capacity, while Policy II the highest (by 8%).

The Box-complex method proved to be efficient and fast; hence it is likely that it can be effectively applied for optimisation problems in the field of chemical engineering. The optimum was found with a relatively low number of simulations: it was 144·3=432 simulations (simulating the production campaign 144 times) for the simultaneous optimisation (Policy III) with altogether six optimisation variables.

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