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Off-cut Recycle for Batch and Batch Extractive Distillation Separation of a Multicomponent Azeotropic Mixture

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The influence of recycling off-cuts for the batch and batch extractive distillation separation of a four component (methanol- THF- water- toluene) waste solvent mixture of a pharmaceutical plant is studied by rigorous dynamic simulation. The evolution of the charge composition, of the amount of fresh feed and that of methanol product are determined for six consecutive productions of batch rectification. As an alternative of the traditional batch distillation, batch extractive distillation by using water as entrainer is also studied. Water feeding is applied during the heating-up phase, in order to decrease the methanol concentration in the column top, in this way reducing methanol loss with the fore-cuts. The profit of the productions is calculated on the basis of the operational and incineration costs and the price of the methanol. The influence of the volume of the first fore-cut, which is later incinerated, on the profit of the whole production process is also investigated and its optimal amount is determined for both separation methods. For the extractive process the profit of the regeneration is higher, the optimal volume of the first fore-cut is lower, which means a reduction in the air pollution caused by the incineration.

1. Introduction

The recovery of organic solvents from waste solvent mixtures produced in large quantities in the chemical and pharmaceutical industries is very important because of economic and environmental reasons. It is usually performed with batch distillation (BD). The advantages of the batch distillation are well known (e.g. flexibility of operation). One of its main benefits is that with a single batch column arbitrary number of products (and cuts) can be obtained.
A synonym of batch distillation is fractional distillation which refers to the possibility of taking arbitrary number of fractions (cuts). The main component to be recovered with the highest recovery possible is produced in specified purity in the main cut(s). The polluting components and azeotropes having

- Lower boiling point than that of the main component are removed in the fore-cuts (light off-cuts) before the main cut.
- Higher boiling point than that of the main component are withdrawn in the after-cuts (heavy off-cuts) after the main cut.

Both off-cuts may contain the main component in considerable quantity because of the occurrence of azeotropes containing the main component and/or the limited sharpness of the separation. The off-cuts can either be disposed of safely (meeting environmental constraints) by incineration or can be recycled to the next batch in order to reduce the loss of the main component. Recycle of the final hold-up serves for the same goal. However the cuts recycled

- Diminish the amount of the fresh feed in the next batch since the (mixed) charge will contain the cuts recycled, as well, and
- Vary the composition of the mixture (charge) to be separated.

In the book of Mujtaba (2004), an entire chapter deals with the question of off-cut recycles, both in the case of binary and multicomponent mixtures, with a particular emphasis on the optimisation of the recycle

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policy. Mayur et al. (1970) was the first to perform the dynamic optimisation of the periodic operation (with the off-cuts recycled to consecutive batches) of a binary separation. Mujtaba (1989), later Mujtaba and Macchietto (1992) and finally Bonny et al. (1996) investigated the dynamic optimisation of multicomponent separation with off-cut recycle. Miladi and Mujtaba (2005) also considered a fixed product demand for their optimisation of binary batch distillation with recycles, and stated that the storage cost can be a deciding factor for the production and recycling of off-cuts. The majority of the above works are not dealing with the separation of multicomponent azeotropic mixtures.

If the presence of azeotropes makes the separation infeasible or reduces the recovery of the main component to an unacceptable degree, special distillation methods must be applied. These methods include batch extractive distillation (BED), which combines the advantages of batch and extractive distillation. A separating agent (entrainer), which is not necessarily a new component, is fed continuously into the column, and it changes the relative volatilities of the original mixture favourably.

The batch extractive distillation with the application of a heavy entrainer in a batch rectifier was studied among others by Lang et al. (1994) and later by Lelkes et al. (1998). On the basis of industrial experiences obtained for the batch rectifier, Lang et al. (2006) suggested a new operational policy, with entrainer feeding already during the heating-up of the column.

In this paper we study the influence of recycling off-cuts for the regeneration of a waste solvent mixture (methanol(A) - THF(B) - water(C) - toluene (D)) of a pharmaceutical plant from which methanol must be recovered. Hegely et al. (2013) describes the new BED policy applied here in more detail, and presents the comparison of the traditional BD and two policies of BED separation of the same waste solvent mixture, by laboratory- and industrial scale experiments and rigorous simulation.

The program for the mass balance calculations is written in Visual Basic for Applications under EXCEL. It calls the built-in dynamic simulator (CC-DCOLUMN) of CHEMCAD 6.3 flow-sheet simulator (Chemstations, 2011) for the rigorous calculations and the module MIXER of CHEMCAD for calculating the volume after mixing recycled and fresh material.

2. Vapour-Liquid Equilibrium Conditions

For the calculation of vapour-liquid equilibria, the UNIQUAC model is used. The boiling points and compositions of the components and of the 5 minimum boiling azeotropes (including the heteroazeotrope C-D) are presented by Hegely et al. (2013).

Homoazeotropes A-B, A-D and B-C have lower boiling point than component A. The recovery of A is limited by the occurrence of azeotropes A-B and A-D. The azeotrope B-C does not render the production of A more difficult if B is distilled off with the azeotrope A-B. This is the case with the usual composition of the waste solvent mixture. Pure A can be produced only after the removal of components B and D in the azeotropes A-B and A-D.

The addition of moderate amount of water, however, changes the relative volatilities of the azeotropic mixtures A-B and A-D favourably. By adding 25 kg water to 100 kg of A-B and A-D mixtures of azeotropic composition, the relative volatilities decrease from 1 to 0.535 and 0.430. For the mixture A-B, this also means that the volatility order of components is reversed, as B became more volatile than A, the desired product.

Batch extractive distillation with water, which is already present in the mixture in high concentration, seems to be a promising separation method. Unlike the traditional applications of BED, where pollutants are removed from beside the main component, the aim here is to wash out A, the main component from the column top, and to increase the concentration of organic pollutants, B and D, in the distillate. Therefore, a new BED policy is applied (Hegely at al., 2013), where water feeding starts as vapour reaches the feed location and it is only applied during the total reflux start-up of the column. The increased B and decreased A concentration in the top of the column at the end of the start-up period reduces the loss of A in the fore-cuts.

3. Rigorous simulation

The calculations are performed by using the following algorithm (Figure 1). First, the rigorous dynamic simulation is carried out with CC-DCOLUMN for the fresh charge composition. On the basis of the simulation results, the mass and composition of the recycled material is calculated by the code in EXCEL. These data are then used to compute the mass of the fresh charge needed for the prescribed charge volume, in the following way. CHEMCAD calculates the volume of the mixture of the recycled material and an estimated amount of fresh feed. The mass of the fresh feed is varied with the bisection algorithm, until the calculated volume equals to the prescribed one. The new charge composition is calculated from the

compositions and amounts of the recycled material and the fresh charge, and the rigorous dynamic simulation is repeated. The calculation cycle is performed for the given number of batches.

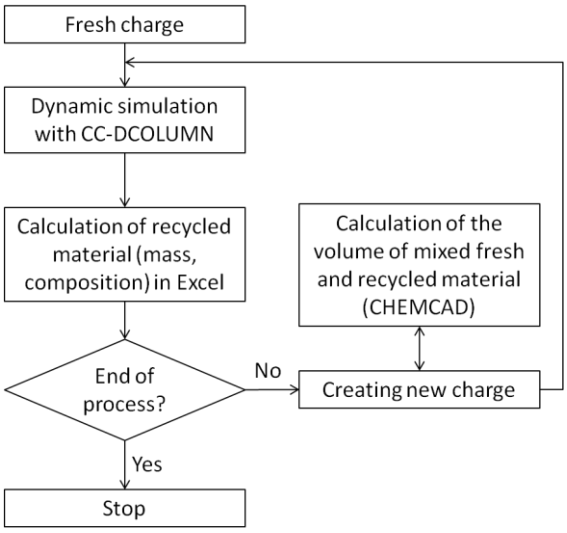

Figure 1: The algorithm of calculation

3.1 Input data

The state-task-network of the methanol regeneration process in the pharmaceutical plant is shown in Figure 2. Six consecutive batches are processed in two cycles (1 - 3 and 4 - 6). The bottoms (B) of each batch and the final hold-up of a cycle are withdrawn and sent to biological treatment (done in the plant itself). The second fore-cut and the after-cut are always recycled to the next charge. The hold-up (U) within a cycle remains in the column, that is, it is recycled to the next charge, as well. The regeneration process is the same for BED production, as well, the only difference is the water feeding (E) during the heating-up period.

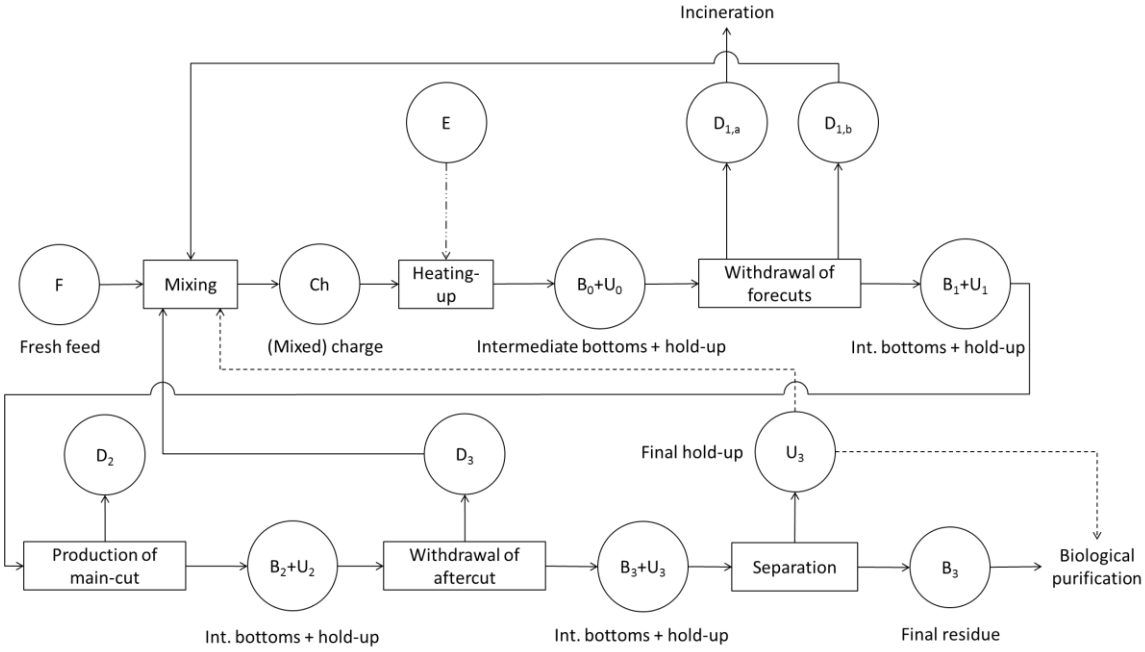

Figure 2: The state-task-network of methanol regeneration process (—··—: for BED only)

During the simulation we fixed:

- the composition of the fresh feed: 40 wt% methanol (A), 6.5 % THF (B), 52 % water(C), 1.5 % toluene (D),

- number of theoretical stages: 25 (excluding the reboiler and the total condenser),
- volume of the charge: 25 m^3 (T = 20 °C),
- purity of methanol product: 99.5 wt%,
- top pressure=1.013 bar (atmospheric pressure), pressure drop=0.25 bar
- volumetric hold-ups: condenser: 0.45 m^3, column: 1.25 m^3
- reflux ratios (R): start-up:∞, fore-cuts:6, main-cut:2, after-cut:6

The stopping criteria applied were the following ones:

- the end of start-up: 300 min of operation,
- the end of taking the first fore-cut: $x_{D,B}$<20 wt% (distillate composition of B) for the base case, or a specified fore-cut volume ($V_{D,1a}$),
- the end of taking fore-cuts: $x_{D,B}$<2 wt%,
- the end of taking after-cut: $x_{B,A}$<0.25 wt% (bottoms composition of A).

The ratio of the first fore-cut ($V_{D,1a}/V_{D,1}$) to be incinerated is varied between 0 (no incineration) and 100 vol% (no fore-cut recycled: $V_{D,1b}$=0).

The operational costs and the profit of methanol regeneration were calculated for every batch. The data used for the operational cost calculations (capital cost, costs of cooling water and electricity can be neglected):

- steam: 57.6 US$/t (with a pressure of P = 3 bar),
- price of methanol: 0.46 $/kg, fee of incineration (for water contents below 20 wt%): 0.21 $/kg.

The cost of the biological purification of the final residue and hold-up can also be neglected.

In the BED process, the water is fed in the top of the column with a flow rate of 1,100 kg/h and a temperature of 20 °C. Water feeding is started after 100 min of operation.

3.2 Results

First the variation of the charge composition (Figure 3), the volume of fresh feed and the mass of methanol product (Figure 4) and the profit (Table 1) during six consecutive batches was studied for the basic case of traditional batch distillation. In the base case the charge composition varies only slightly (Figure 3). The concentration of methanol at the beginning rises, it shows greater increase at Batch 4, then it slightly decreases but still remains above that of the fresh feed. What is more important, B and D do not accumulate in the subsequent charges.

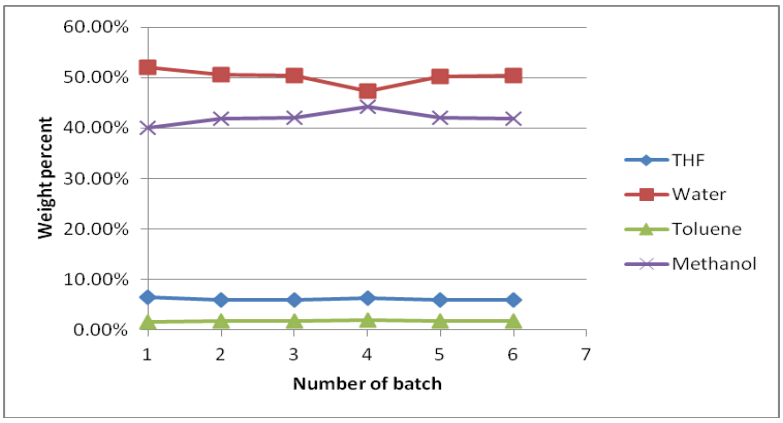

Figure. 3. Variation of the charge composition as a function of the serial number of batch (base case)

The volume of fresh feed (Figure 4) considerably decreases for Batch 2, as the recycled material from Batch 1 is mixed with the fresh feed. After that it remains practically constant except for a temporary increase for Batch 4, which is due to the fact, that the final hold-up of Batch 3 is not recycled. The effect of the recycled of methanol-rich material can be seen on the increase of the mass of methanol product, which is directly proportional to the income.Both the incineration and operational costs vary in a narrow region except a temporary increase for Batch 4 (Table 1). The evolution of income obviously follows that of the amount of methanol product. The tendency of the evolution of the profit is very similar to that of the income. It considerably increases for Batch 2. It is the maximal for Batch 4 (in spite of the fact that the costs are also the highest for this batch.) The influence of the amount of fore-cut incinerated ($V_{D,1a}$) on the profit was also investigated (Table 2). The highest profit is achieved by the base case (based on industrial experiences; $V_{D,1a}$ varies between 3.3 and 3.7 m^3). When nothing ($V_{D,1a}$=0) or only 1 m^3 is incinerated from the fore-cut, the concentration of THF and toluene in the charge considerably increases, therefore

methanol of prescribed purity cannot be produced (under the given parameters) after Batch 3 or 4, respectively. (Though the concentration of methanol increases, but that of water decreases to a higher extent.) In these cases the whole amount of fore-cut of the last batch still producing methanol of prescribed purity must be incinerated which drastically diminishes the profit. These results show that there is a minimum volume of fore-cut to be incinerated, below which the 6-batch process could not be performed. It must be still noted in all other cases both the second fore-cut and after-cut of the last batch have appropriate composition for recycling to a later production and therefore they need not be incinerated. In the cases, where the 6-batch process is feasible, incineration cost increases, while operation cost slightly decreases with increasing $V_{D,1a}$. The income has a maximum value.

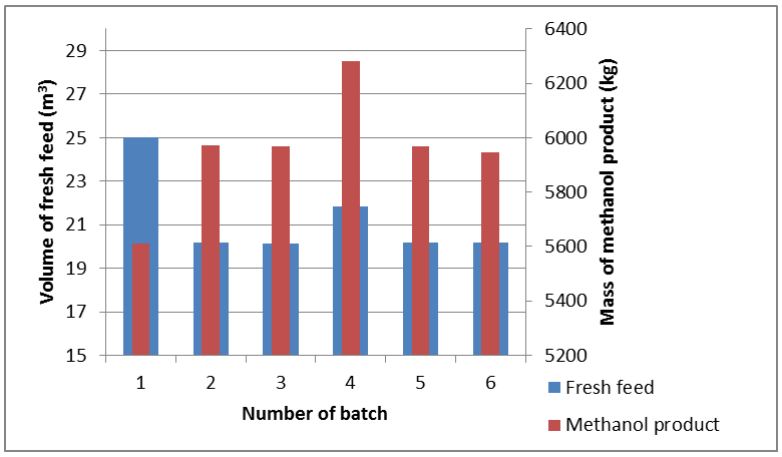

Figure 4. Evolution of the volume of fresh feed and the mass of methanol product (base case)

Table 1. The evolution of costs and that of the income (in $, base case)

No. batch	1	2	3	4	5	6	Total
Incineration	578	547	560	613	566	562	3,426
Operation	1,733	1,753	1,759	1,806	1,761	1,759	10,571
Income	2,585	2,752	2,750	2,895	2,750	2,740	16,472
Profit	275	452	431	476	423	418	2,475

Table 2. The influence of the amount of fore-cut incinerated on the profit (in $, traditional batch distillation)

Case	$V_{D,1a}$ =0 m^3	$V_{D,1a}$ =1 m^3	$V_{D,1a}$ =2 m^3	$V_{D,1a}$ =3 m^3	Base	$V_{D,1a}$ =4 m^3	No recycle
Incineration	1,674	2,171	2,009	2,990	3,426	3,954	4,994
Operation	5,654	7,602	11,332	10,807	10,571	10,385	10,243
Income	7,176	9,914	15,061	16,081	16,472	16,451	15,532
Profit	-153	141	1,722	2,285	2,475	2,112	295

The same investigation concerning the effect of taking different amounts of first fore-cut was performed for BED, as well (Table 3). By the BED production, the base case means a first fore-cut between 2.65-2.97 m^3, which is lower than that of the traditional BD. Another important difference is that the minimum volume of the first fore-cut is higher, the 6-batch process is not feasible with $V_{D,1a}$ = 2 m^3, that is the BED process is more sensitive to the accumulation of organic pollutants in the charge. By BED, the profit is greater in all cases, except $V_{D,1a}$ = 4 m^3. If the cases with feasible 6-batch process ($V_{D,1a}$ > 2 m^3) are compared, it can be seen that both operational costs and incomes are higher by BED, but the stronger increase in incomes results in higher profits. The higher A recovery of BED is explained by the fact that the volume of the second fore-cut is significantly lower and its methanol content is higher, that is, the methanol loss in the fore-cuts is reduced. The optimal case of BED shows an 18 % profit increase compared to that of the traditional batch distillation. At the same time, the volume of incinerated material decreases from 22.7 to 20 m^3 (-12 %), contributing to pollution reduction. The water fed into the column appears in the first fore-cut as a slight increase of water concentration compared to the BD production, but the majority of the water increases the amount of the final residue, subject to biological purification.

Table 3. The influence of the amount of fore-cut incinerated on the profit (in $, BED)

Case	$V_{D,1a}$ =0 m^3	$V_{D,1a}$ =1 m^3	$V_{D,1a}$ =2 m^3	Base	$V_{D,1a}$ =3 m^3	$V_{D,1a}$ =4 m^3	No recycle
Incineration	1,236	1,215	2,120	2,798	3,018	3,963	4,431
Operation	3,797	3,746	7,602	11,145	11,033	10,819	10,756
Income	5,040	5,291	10,865	16,812	16,972	16,524	16,098
Profit	7	330	1,142	2,869	2,921	1,743	911

4. Conclusion

The influence of recycling off-cuts for the batch distillation and batch extractive distillation regeneration of a four component (methanol - THF - water - toluene) waste solvent mixture of a pharmaceutical plant was studied by rigorous dynamic simulation made with the CCDCOLUMN simulator. The evolution of the charge composition, of the amount of fresh feed and that of the methanol product were determined for 6 consecutive productions of batch rectification, where the first fore-cut is incinerated, whilst the second fore-cut, the after-cut and (excepted batches 3 and 6) the (column and condenser) hold-up are recycled. In the batch extractive distillation separation process, water as entrainer was fed into the top of the column during the heating-up period. The profit of the production was calculated on the basis of operational and incineration costs and the price of methanol. The influence of the amount of the first fore-cut on the profit of the whole production process was also investigated. For the traditional batch distillation, the highest profit was achieved when taking of the first fore-cut was continued until the THF concentration in the distillate fell below 20 wt% (incineration of cca. 15 vol% of the charge). By using batch extractive distillation the optimal incinerated volume was 12 vol% of the charge. For both separation processes, a minimum volume of first fore-cut must be taken to avoid the accumulation of THF and toluene in the charge, which would render the 6-batch process infeasible, although this volume is higher for the batch extractive distillation. The batch extractive distillation provided higher profits than the traditional one, except for one case. Moreover, the volume of incinerated material is also lower by 12 %, leading to reduction in air pollution.

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