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Optimisation of a Batch Extractive Distillation Process with Off-Cut Recycle

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The recovery of methanol from an industrial waste solvent mixture (acetone (A) – methanol (B) – THF (C) –water (D) – toluene (E)) by a batch (BD) and batch extractive distillation (BED) process was simulated and optimised. For both processes a production cycle consists of six consecutive batches. The first fore-cut is incinerated; the second fore-cut, the after-cut and the hold-up are recycled to the next batch in order to decrease the loss of methanol. The optimization of both processes was performed by a genetic algorithm (GA) coupled with a professional flow-sheet simulator performing the dynamic simulation. The optimization of the batches was performed consecutively, with the objective function being the profit of the actual batch. The optimization variables were the reflux ratios of the steps (fore-cuts, main cut), duration of fore-cut withdrawals and for the BED the flow rate and duration of entrainer (water) feeding. The effects of the recycling of the off-cuts on the charge composition and on the optimal values of the parameters were studied, and the optimised BD and BED processes were compared.

1. Introduction

For the separation of pharmaceutical waste solvent mixtures, batch distillation (BD) is a frequently applied method. In BD, an arbitrary number of cuts (fractions) can be taken. The main component to be recovered is produced in the main cut(s). The polluting components and azeotropes having
-lower boiling point than the main component are removed in the fore-cuts,
-higher boiling point than the main component are withdrawn in the after-cuts.
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.
For the separation of azeotropic mixtures a special (e.g. extractive) distillation method must be applied. In batch extractive distillation – BED (Yatim et al, 1993), an entrainer is fed continuously into the column, changing the relative volatilities favourably. BED is usually applied to extract pollutants of moderate concentration from the main component to be recovered. In this case the main component is extracted from beside the pollutants of low concentration forming minimum azeotropes with it. These pollutants can be removed in fore-cuts, and by using BED, it is possible to reduce the loss of the main component with the fore-cuts. However, the high amount of entrainer fed renders the separation of the main component from it more difficult.
Hegely et al. (2013a) studied the recovery of methanol from a waste solvent mixture containing THF(C) and toluene (E) as main pollutants. The recovery of methanol (B) is disturbed by the azeotropes B–C (30 mass % B, 59.5 °C) and B–E (71.5 % B, 63.6 °C). The influence of water (D) as a potential entrainer on the relative volatilities was investigated. We stated that by BED using water as entrainer C and E can be

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removed in the fore-cuts more efficiently (with lower B loss) than by BD. The laboratory and industrial-size experiments gave also much higher recovery for the BED than for the BD. Hegely et al. (2013b) investigated the effects of off-cut recycle for six-batch BD and BED processes, but only the volume of the first fore-cut was optimised. Hegely and Lang (2014) performed the optimization of processing only one batch by BD and BED by a genetic algorithm (GA), using multiple optimization variables. The highest profit was reached by the optimized BED process.
The aim of this paper is to optimise the whole six-batch production process, instead of only one batch, both for BD and BED. The effect of the off-cut recycle on the charge composition and on the optimal values of the operational parameters is studied. Optimization variables are reflux ratios and termination criteria of the operation steps, and the parameters of water feeding (flow rate and duration). The optimization is performed by a genetic algorithm with ChemCAD performing the dynamic simulation. The individual batches are optimized consecutively, by maximizing the profit of the batch.

2. The separation process

The fresh charge contains 0.07 mass % A (acetone), 37.14 % B, 4.89 % C, 56.34 % D and 1.56 % E. The boiling points of the components and azeotropes, with the azeotropic compositions were given by Hegely and Lang (2014).
The BD separation of one batch consists of the following separation steps (Hegely et al., 2013a):
- Step 0: heating-up of the column under total reflux. At the end of heating-up, the condensate is rich in B and C, compositions and temperatures start to stabilize.
- Step 1: taking the first fore-cut, which contains a high amount of C and E in addition to B. The first fore-cut is incinerated.
- Step 2: taking the second fore-cut, which contains more B and less pollutant than the first fore-cut. The aim of both fore-cuts is the removal of organic pollutants. The second fore-cut is recycled to the next batch in order to decrease the loss of B.
- Step 3: taking the main-cut that is the product B in high purity.
- Step 4: taking the after-cut, which is aqueous B. The aim of this step is to remove B from the still residue, so that the residue can be sent to biological purification. As the after-cut contains a considerable amount of B, it is recycled to the next batch.
In the BED process, the steps are the same as presented above, except Step 0, which can be divided into two parts:
- Step 0a: heating-up without water feeding. The step ends as the vapour reaches the top of the column.
- Step 0b: heating-up with water feeding. Water is fed continuously to the column causing a decrease in $x_{D,B}$ and an increase in $x_{D,C}$.
Water feeding can be stopped at the end of Step 0b or it can be still continued during Steps 1 and 2, as well. In the latter case, the loss of B in the fore-cuts can be further reduced, but this dilutes the mixture from which B is to be recovered and can also increase the amount of the fore-cuts increasing the cost of incineration and energy.
Both for BD and BED, six consecutive batches are processed in two cycles (1-3 and 4-6). The state-task network of both processes was presented by Hegely et al. (2013b). The bottoms 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 within a cycle remains in the column, that is, it is recycled to the next charge, as well.
The column has 25 theoretical plates (excluding the condenser and reboiler). The top pressure of the column is atmospheric, the pressure drop: 0.25 bar. The volume of the charge is always 25 m^3 (20 °C). The hold-up of the condenser: 0.45 m^3, that of the column: 0.05 m^3/plate. The prescribed purity of B is 99.5 mass%. The duration of Step 0 (for BD) was 360 min. For BED Step 0a was 160 min long, after which water feeding (of 15 °C) was started. Step 0b was 200 min long. The termination criteria for Steps 1 and 2 are optimization variables (Cr_1 and Cr_2), while the criterion for Step 4 is based on industrial experiences:
- Step 1: $x_{D,C}<Cr_1$ (mass fraction of C in the distillate)
- Step 2: $x_{D,C}<Cr_2$
- Step 3: $x_{MC,A}<99.52$ mass%
- Step 4: $x_{SR,B}<0.25$ mass% (mass fraction of B in the still residue)

3. Optimization method

The six batches were optimized consecutively, that is, each batch was optimized separately for the charge composition obtained by mixing fresh feed and the material recycled from the previous batch. The mass of

fresh feed was calculated so as to always obtain a charge of 25 m^3. A constraint was added in order to ensure the recyclability of the second fore-cut to the next batch: the C/B and E/B ratios in the second fore-cut cannot exceed those of the traditional batch distillation process applied in the plant (0.1068 and 0.1203,).

The objective function (OF) to be maximized is the profit of the processing of the individual batches. It is defined as:

$$OF = p_B m_{MC} - c_{inc} m_{FC1} - c_{st} \frac{\dot{Q}_{st}}{r_{st}} t - c_{cw} \frac{Q_{cond}}{cp_{cw} \Delta T_{cw}} - c_{bio} m_{SR} \quad (1)$$

where m_{MC} is the mass of the main-cut, m_{FC1} is that of the first-fore-cut, m_{SR} is that of the still residue. p_B is the price of methanol (0.46 \$/kg), c_{inc} is the cost of incineration (0.21 \$/kg), c_{st} is cost of heating steam of 3 bar (57.6 \$/t), r_{st} is its heat of condensation (2,263.5 MJ/t), $\dot{Q}_{st}$ is the heat duty (1,800 MJ/h) and t is the duration of the whole process. Q_{cond} is total heat withdrawn by the cooling water, cp_{cw} is the specific heat of the cooling water and ΔT_{cw} is the increase in its temperature. c_{cw} is the cost of cooling water and c_{bio} is the cost of biological purification, which are neglected. (These are not debited to the solvent recovery plant). Therefore, operation cost is the term related to the heating steam.

The optimization variables were the reflux ratios of the steps: R_1 (1^{st} fore-cut), R_2 (2^{nd} fore-cut), R_3 (main-cut), the termination criteria of Steps 1 and 2 (Cr_1 and Cr_2), and for BED, additionally, the flow rate (F_{water}) and duration (t_F, even integer) of water feeding. The lower and upper bounds for all reflux ratios were 0.6 and 15. The lower bound of both termination criteria was 0.05 mass%, the upper bounds were 40 % (Step 1) and 10 % (Step 2). However, the value of Cr_1 also acted as an upper bound for Cr_2. The ranges of the variables connected to water feeding were: flow rate: $0 \leq F_{water} \leq 3{,}000$ kg/h; duration: $0 \leq t_F \leq 1{,}000$ min. (Water feeding was always stopped at the end of Step 2, even if t_F had been longer.)

For the first batches, the reflux of the after-cut (R_4) was also considered as optimization variable. However, the sensitivity analysis of this variable revealed that its value has a negligible influence on OF. Therefore, we used the value of R_4 obtained for the first batch (5.41 for BD and 4.72 for BED) for every batch.

By BED, the location of water feeding was fixed as the top plate of the column on the basis of previous simulation experience. The optimality of this location can be explained by two facts. First, the more trays the extractive section has, the more efficient the entrainer feeding. Second, feeding the water into the condenser (which was also considered) highly increases the water content of the distillate, resulting in a greater amount of first fore-cut, thus, higher incineration cost, and less methanol recovered.

The optimization was performed by a real-coded elitist GA written in VBA under Excel. GA was chosen as OF can only be evaluated by simulation, that is, with a black box approach. The parameters of the GA: mutation probability: 5 %, population size: 30, crossover probability: 70 %. The number of generations was 100 for BD and 178 for BED. OF changed less than 1 % during the last 26 and 46 generations. OF is evaluated by dynamic simulation using different modules of the flow-sheet simulator ChemCAD. The failure to reach the specified purity of B (99.5 mass %), is penalized by changing the value of OF onto -10,000 \$. For the calculations, an equilibrium-based column model is used, and the phase equilibria are described by the UNIQUAC model.

4. Results

4.1 Batch distillation

The composition of the charge (x_{ch}), the optimal values of the optimization variables, the different costs and the profit calculated for the consecutive batches are shown in Table 1. The recycling changes the charge composition (Figure 1) from batch to batch. The B content is slightly higher than in Batch 1, that of C is lower (except in Batch 4). On the other hand, E accumulates in the recycled material, leading to a significant increase of the E content of the charges. The concentration of A is almost constant. Batch 4 is different from the other batches, as the hold-up from Batch 3 is not recycled. The absence of the hold-up (containing mostly water) results in the increased concentration of methanol, but that of organic pollutants, as well. Hence the charge of Batch 4 has increased B and E contents, and a C content similar to that of Batch 1. This high E content is also transferred to Batch 5, as E appears in the recycled material in a concentration higher than from Batches 1-2.

The optimal values of the operational parameters (Figure 2) are also influenced by the change of the charge composition. R_3 is almost the same for all the batches, even if it slightly increases for Batches 4-6. The values for Batches 2 and 3 are very similar, just as the charge compositions are. Compared to Batch 1, the decreased C and increased E content results in the following changes. Both R_1 and Cr_1 decrease,

the result is a slight increase in the mass, to avoid a too high E content in the second fore-cut. Both R_2 and Cr_2 increase. The increase of Cr_2 can be explained by the fact that at the end of the second fore-cut, the C content of the distillate is always higher than that of E, so less C in the charge allows a higher Cr_2. For these batches, incineration and operation costs are higher than for Batch 1, but an increased income results in higher profit.

Table 1: Optimization results for the consecutive batches of the BD process

Process	BD						BED					
Batch	1	2	3	4	5	6	1	2	3	4	5	6
x_{ch}, mass %												
A	0.07	0.065	0.066	0.071	0.065	0.065	0.07	0.066	0.066	0,071	0.067	0.067
B	37.14	38.29	38.23	40.31	38,79	37.82	37.14	37.55	37.61	39.99	38.04	37.52
C	4.89	4.51	4.54	4.89	4.51	4.47	4.89	4.46	4.48	4.81	4.46	4.45
D	56.34	55.29	55.32	52.78	54.68	55.89	56.34	56.42	56.30	53.46	55.73	56.45
E	1.56	1.85	1.84	1.95	1.95	1.76	1.56	1.51	1.55	1.66	1.71	1.52
R_1	6.22	5.01	5.07	6.11	5.56	5.06	7.74	7.65	7.34	8.63	6.39	6.78
R_2	3.07	4.33	4.75	1.68	5.28	4.94	3.41	3.86	3.43	2.69	5.96	4.12
R_3	3.05	3.06	3.06	3.22	3.11	3.16	3.48	3.54	3.66	3.64	3.61	3.28
Cr_1, mass% C	17.5	16.4	16.1	17.4	13.5	16.2	18.7	18.9	18.9	22.2	16.4	18.3
Cr_2, mass% C	2.62	3.09	3.15	2.31	3.14	3.34	3.83	3.57	3.58	2.72	4.19	3.89
F, kg/h	-	-	-	-	-	-	283	462	428	678	545	374
t_F, min	-	-	-	-	-	-	574	500	498	554	470	488
Income, $	2,597	2,666	2,678	2,754	2,738	2,669	3,003	3,040	3,018	3,209	3,076	2,996
Incineration cost	492	511	513	533	555	500	390	343	347	329	370	357
Operation cost	1,638	1,651	1,666	1,669	1,719	1,667	1,820	1,854	1,840	1,977	1,910	1,783
Profit	467	504	499	552	464	502	793	843	831	903	796	836

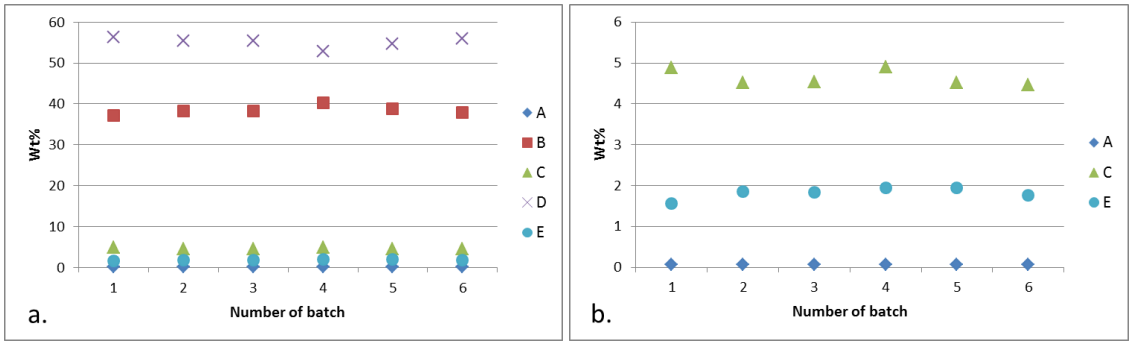

Figure 1: Variation of the charge composition for BD: a. all components, b. organic pollutants

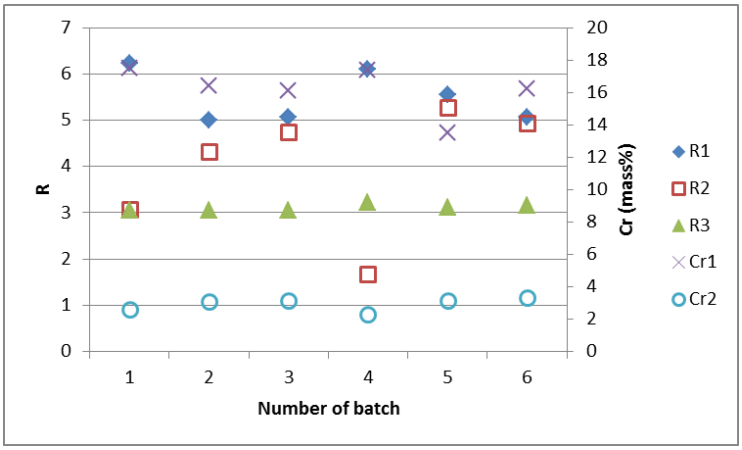

Figure 2: Variation of the optimal values of the optimization variables for BD

The optimal values for Batch 4 are similar to those for Batch 1, with the following exceptions. R_3 is slightly higher, because of the high concentration of organic pollutants in the charge. R_2 is much lower, and Cr_2 is slightly lower, resulting in an increased amount of the second fore-cut, necessary because of the organic pollutants. Although the incineration cost is increased, the higher B content makes this batch the most profitable, even if it contains a high amount of C and E.
On the other hand, Batch 5 is the least profitable, due to its unfavourable charge composition: the concentration of E is still high, but that of B is already lower. R_1 is between the values obtained for Batches 2-3 and 4. In order to avoid a high E content in the second fore-cut, R_2 is high, and Cr_1 is much lower than for the other batches. This also means a high amount of first fore-cut. Cr_2 is similar to the one applied for Batches 2-3. Although the income is high, the increased incineration and operation cost reduces the profit.
Similarly to the charge composition, the optimal values for Batch 6 are very similar to those for Batches 2-3. An increased Cr_2 can be explained by the fact that the C and E content of the charge is lower.

4.2 Batch extractive distillation

For BED, the composition of the charge, the optimal values of the optimization variables, the different costs and the profit calculated for the consecutive batches are shown in right hand side of Table 1. The effect of recycling on the charge composition (Figure 3) is similar to that of BD. The B content is slightly higher than in Batch 1, whilst that of C is lower. Unlike by BD, E only accumulates for Batches 4-5, where it is the result of absence of hold-up from the recycled material, leading to increased B and E content. The lower E contents by BED can be explained by the fact that water increases more the volatility of E, than that of C.

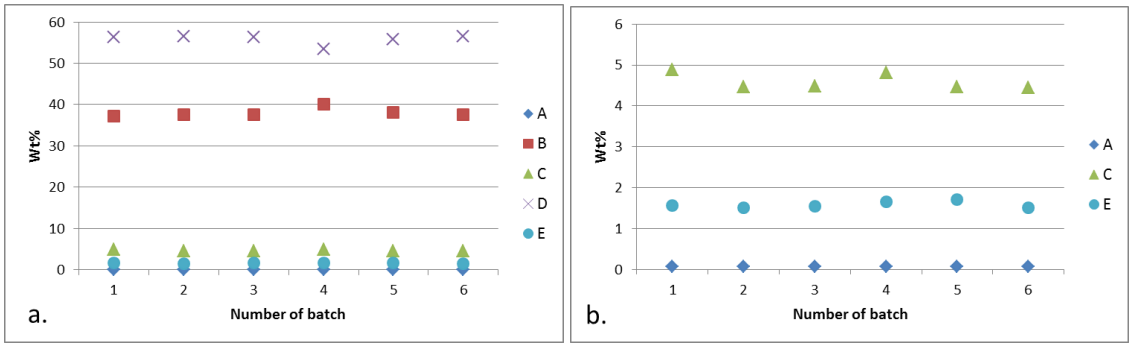

Figure 3: Variation of the charge composition for BED: a. all components, b. organic pollutants

The optimal values of the operational parameters change in the following way (Figure 4). R_3 is almost the same for all the batches, except for Batch 6, where it has a lower value. As in the case of BD, the values for Batches 2 and 3 are very similar, just as the charge compositions are. These values are also similar to the ones obtained for Batch 1, except Cr_2, which is lower, because of the reduced concentration of organic pollutants, and the parameters of water feeding. F_F is higher; t_F is lower for Batches 2-3. The profit of Batches 2 and 3 are higher than that of Batch 1, mainly because of the reduced incineration cost.
The optimal values for Batch 4 are significantly different from those for Batches 1-3 (except R_3). R_1 and Cr_1 are higher. The increase of R_1 reduces the loss of B, but also increases operation time. On the other hand, the increase of Cr_1 reduces both operation time and incineration cost. A similar change is observed for the second fore-cut: both R_2 and Cr_2 are lower. The result is an increased mass of second fore-cut, which is necessary to avoid a too high C/B or E/B ratio. Batch 4 has the highest profit, because of the high income (increased B content) and low incineration cost, although the operation cost is also elevated.
Considering the pairs R_1-Cr_1, R_2-Cr_2, Batch 5 shows a change in the opposite direction: the first two variables decrease (lower than for Batches 1-3), the last two one increase (higher than for Batches 1-3). The result is the taking of more first and less second fore-cut. This can be explained by the high E and moderate C content of the charge. The mass of the first fore-cut has to be increased to avoid a high E content in the second fore-cut. On the other hand, Cr_2 can be increased, and the mass of the second fore-cut decreased, as the change to the main-cut is always determined by the concentration of C, not that of E. The increase of R_2 makes the operation cost higher, thus reducing the profit. Note that the same trends can be observed both by BED and BD in the case of Batches 5-6.
The optimal values for Batch 6 are between those for Batch 5 and for Batches 2-3 (except R_3). The charge composition is very similar to that of Batch 2, and even though the values of the parameters are different, the profit is almost identical. By Batch 6, less methanol and more first fore-cut is produced, but this is

balanced by faster production. This shows that different values of the parameter pairs R_1-Cr_1 and R_2-Cr_2 can lead to almost the same profit, as the effects of the variables in these pairs compensate each other.
The flow rate of water feeding is high for Batches 4-5 which a have high concentration of organic pollutants, but contrary to the expectation, it is lowest for Batch 1. It must be noted that preliminary calculations showed that the results are not very sensitive to the change of the flow rate. The duration of water feeding is longer for the batches with high C content. Water feeding is always stopped before the end of Step 1. For higher C content, Step 2 starts circa 30 min after the end of water feeding, for lower C content, the difference is circa 60 min.

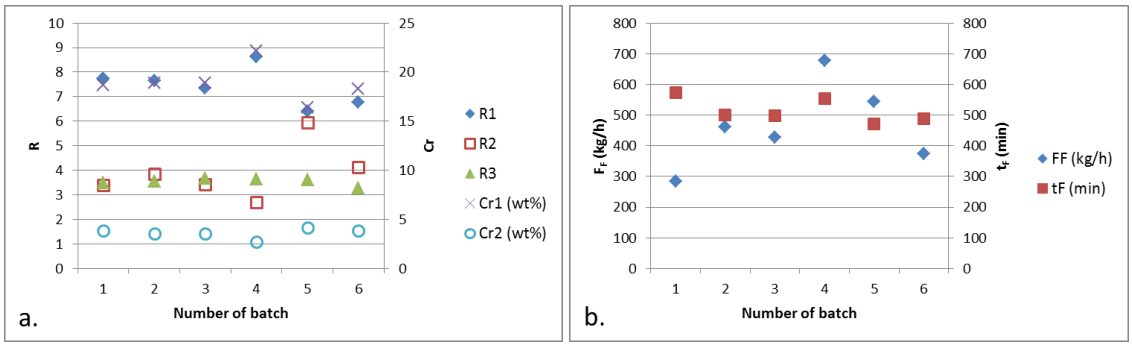

Figure 4: Variation of the optimal values of the optimization variables for BED: a. reflux ratios and termination criteria, b. parameters of water feeding

R_3 is always higher for BED than for BD, which can be explained by a slightly more difficult separation of methanol and water, because the water feeding dilutes the mixture in the still. R_1 is also always higher, probably in order to limit the water content of the distillate. R_2 is higher for BED for higher E contents (Batches 1, 4 and 5); otherwise, it is lower. Both Cr_1 and Cr_2 are always higher by BED than by the same BD batch, which means that less fore-cut has to be taken, and that the loss of methanol is reduced.
The income and the operation cost are always higher by BED, while the incineration cost is always lower. The final result is that BED produces significantly more profit than BD (5,002 $ instead of 2,988 $).

5. Conclusions

A traditional (BD) and an extractive (BED) batch distillation process with off-cut recycle were optimized by a genetic algorithm (GA) coupled with a professional flow-sheet simulator performing the dynamic simulation. The production cycles consist of six batches. The optimization of the batches was performed consecutively, with the objective function being the profit of the actual batch. The optimization variables were the reflux ratios of the steps (fore-cuts, main cut), duration of fore-cut withdrawals, and for the BED the flow rate and duration of entrainer (water) feeding. Due to the recycling off-cuts, toluene accumulated in the charge by BD, although this did not cause a reduction of profit. By BED, the accumulation only appeared for two batches. The recycle also increased the methanol content of the charges. The changes in the composition resulted in the change of the optimal values of the optimization variables, with the toluene content having the most significant influence. The most drastic changes in the composition, and thus the values of parameters occurred, when the hold-up of the column was not recycled, resulting in increased concentration of methanol and organic pollutants in the next charge. By BED, water feeding was always stopped shortly before the end of the first fore-cut. Though both six-batch production processes were feasible and economical, the BED gave significantly (64.7 %) higher profit, thanks to the increased recovery and reduced incineration cost.

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