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Optimisation of heterogeneous batch extractive distillation

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Abstract

This paper considers the optimisation of batch extractive distillation, using heterogeneous entrainers for the first time. The objective function includes the maximum of overall profit and the optimisation variables are the entrainer flowrate and the reflux ratio that is an optimal combination of both decanted phases. Simulation and optimization is performed within MATLAB, by using a genetic algorithm coupled to a short-cut model of the distillation column. The performance of the optimisation scheme is illustrated through the separation of chloroform – methanol mixture with water considering either a constant or a piecewise constant policy for both optimization variables.

Keywords: batch extractive distillation, heterogeneous entrainer, genetic algorithm

1. Introduction

Batch distillation becomes irreplaceable when it is necessary to treat small quantities of materials with a great diversity in composition. Azeotropic and extractive distillation processes are the most used processes for separating azeotropic or close boiling mixture, always involving the addition of an auxiliary entrainer. Although heterogeneous entrainer has been widely used in batch azeotropic distillation, it has only been recently considered for batch heterogeneous extractive distillation (BHED) of the chloroform – methanol mixture with water [1]. Continuous feeding of the heterogeneous entrainer allows the residue curve map saddle binary heteroazeotrope to be drawn at the top of the column. Besides, unlike to the homogeneous entrainer, the heterogeneous entrainer can be fed at the column top and the process takes place with an extractive section only. The following operating steps for BHED were considered in this work: (T1) start-up of the column at infinite reflux, (T2) filling the top decanter along with continuous feeding of the entrainer F_E (T3) total reflux operation keeping the continuous feeding of the entrainer (F_E) until the unstable node is replaced by the saddle binary heterogeneous azeotropic mixture (T4) operation at a given *R'* together with F_E until the still is depleted of the immiscible key component (T5) separation between the remain homogeneous component and the entrainer at *R"* without F_E. The top decanter is considered as a total condenser with a significant liquid hold-up. Both decanted phases can be refluxed and also supplement the entrainer feeding at the column top.

A stochastic optimisation method, genetic algorithm real-coded in MATLAB, is used along with the simulation of the BHED considering the short-cut modelling with the typical assumptions: theoretical plates, negligible pressure drop and liquid hold-up on the trays and constant molar overflow. The global optimization problem is decomposed into a series of independent single optimizations, each one related to an operating task and considering the same objective function. Preliminary parametric studies have demonstrated that the reflux ratio (R') and the entrainer flowrate (F_E) are the variables having a key incidence over the overall profit of the BHED. Mujtaba pointed that the optimal overall profit in homogeneous BED is mainly determined by assuring optimal values for F_E and R' in the task (T4) [2]. If unlimited capacity in the boiler is taken into account, optimization of task (T3) is not necessary because the operating time for setting the binary heterogeneous mixture chloroform - water at the top of the column logically decreases when F_E increases. Hence, this work is devoted to optimization of task (T4) related to the withdrawal of the heterogeneous key component to improve an overall profit function. A constant value and, also, a piecewise constant policy considering two intervals of time for F_E and R' will be considered. We solve the optimisation problem considering all combinations for F_E and R'.

2. Optimization problem formulation

2.1 Case of study: Separation of chloroform – methanol azeotropic mixture

Optimisation problem formulation concerns to the separation of azeotropic mixture chloroform – methanol which is widely used for separating bioactives substances from biological sources. Water was shown to be an effective heterogeneous entrainer [1]. Thermodynamic and topological features of the resulting ternary system are shown in Figure 1 including the univolatility curve chloroform – methanol (α_{12}). Thermodynamic calculations were done by using Simulis®Thermodynamics, a thermodynamic property server available in Microsoft Excel [3]. NRTL was chosen as thermodynamic model with literature binary coefficients [1]. As explained [1], because the univolatility line α_{12}=1 ends at the chloroform – water edge, the saddle binary hetero-azeotrope chloroform – water can be drawn as a vapour overhead at the column if water is fed continuously at the column top generating two liquid – liquid phases into the decanter after condensation. The heavy chloroform-rich phase ($x^{II} = x_D$) can be drawn as distillate product whereas the water – rich phase (x^I) or a mixture composed by both decanted liquid phases can be refluxed toward the column top.

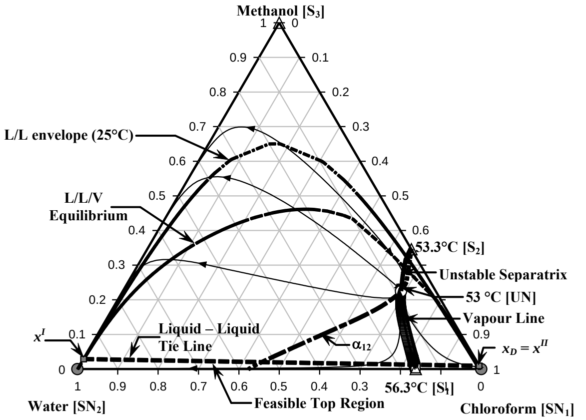

Figure 1. Chloroform – methanol - water residue curve map

2.2 Modelling of heterogeneous BHED by short-cut model

Dynamic behaviour of BHED is described by the following differential and algebraic equations:

- Boiler mass balances: $\frac{dB}{dt} = F_E - D$ (1)

$$\frac{dx_B}{dt} = \frac{F_E}{B}(x_{FE} - x_B) + \frac{D}{B}(x_B - x^{II}) \qquad \text{where } D = (1-\alpha)(1-\omega)V \tag{2}$$

- Extractive liquid profile inside the extractive column section (differential mode proposed by Lelkes et al. [4]; column with significant height)

$$\frac{dx_i}{dh} = \frac{V}{L}(y_i - y_i{*}) \tag{3}$$

y_i^* is determined applying the modified Rachford-Rice procedure for a three-phase mixture as the vapour phase selected as a reference phase.

$$\sum_{1}^{c=3} \frac{z_i(K_{ij} - 1)}{1 + \sum_{1}^{Phases=3} \beta_j(K_{ij} - 1)} = 0 \tag{4}$$

β_i is the molar amount of each phase, z_i is the molar phase composition and K_{ij} is the equilibrium coefficient. The operating vapour composition y_i can be expressed in terms of R' and F_E/V as:

$$y_i = (\frac{R'}{R'+1} + \frac{F_E}{V})x_i + \frac{1}{R'+1}x^{II} - \frac{F_E}{V}x_{FE} \tag{5}$$

Usually, BHED involves a reflux combination of the whole water-rich entrainer phase L^I along with a portion "α" of the chloroform rich-phase L^{II}. The proportion of L^I and L^{II} inside the decanter is determined by the liquid – liquid splitting ratio ω. Therefore, the total reflux liquid $L_R = L^I + \alpha L^{II}$. The reflux ratio can be determines as:

$$R' = \frac{\omega + \alpha(1-\omega)}{(1-\alpha)(1-\omega)} \tag{6}$$

2.2 Objective function and constraints

Optimization problem will deal with the maximization of the overall profit of the process and it can be formulated as following:

$$\underset{F_E(T_2,T_3,T_4),\alpha(T_4),R''(T_5)}{min}\{-OP\} = C_1 * D_1 + C_2 * D_2 - C_S * S - C_f * (t_{total}) \tag{7}$$

St. $x_{D\,chloroform}(T_4) \geq 0.99$

$x_{D\,methanol}(T_5) \geq 0.99$

$Re_i > 0.90$

Where Re_i is the recovery yield for component i. If one phenotype of the population doesn't fulfil any constraint, the associated OP takes the mandatory value of 10^6. C_1 (3.012 \$/mol), C_2 (0.5085 \$/mol) and C_S (0.001 \$/mol) are the prices of the products chloroform; methanol and the make-up of water, respectively. C_f (0.0027 \$/min) is the total operating cost of a real bench column. Optimisation using some market product prices revealed a non sensitive effect for a given C_f. It was also assumed that the possible off-cut product (ternary heteroazeotrope) is not a commercial product and it can be recycled to the next batch. The optimization variables are the ratio (F_E/V) for tasks T2 T3 and T4 and the reflux policies *R'* for task T4 and *R"* for task T5. The aim of the optimization is searching an optimal value of (F_E/V) along with a comparison between a constant reflux ratio and a piecewise constant reflux policy considering two time intervals. If off-cut operation is required, reflux ratio is set at unity in order to reduce the chloroform molar content into the boiler lower than 0.01.

Genetic algorithm real-coded in MATLAB is used as optimization method. The initial population was set at 50, the selection rate is 0.8 and the mutation rate is 0.01. The optimization is stopped if no improvement of the objective function is achieved after 10 generations. Bounds for the optimization variables are: $1.4 \leq (F_E/V) \leq 2$ and $0.4 \leq \alpha \leq 0.9$ for chloroform recovery and $1 \leq R'' \leq 10$ for the separation of methanol – water. Those bounds for (F_E/V), α and *R"* were taken from previous study according to the purity product constraints [1]. Optimisation by genetic algorithm comprises a large evaluation of the objective function including the solution of the dynamic model. Use of short-cut model allows a good approximation of the optimal operation conditions with less computational effort and time. The optimal results obtained by simplified method is validated by rigorous simulation using ProSim Batch for all optimal cases.

3. Results and discussion

Optimization of the BHED was performed considering several cases:

- Case I: (F_E/V), α and *R"* constant;
- Case II: constant (F_E/V) and piecewise constant α for two time intervals
- Case III: piecewise constant (F_E/V) and α for two time intervals.

Operating conditions for simulation of the separation of chloroform (1) – methanol (2) with water (3) are: initial charge (20 mol), composition charge (x_1=0.2704/ x_2=0.6714/ x_3=0.0582), decanter holdup (1 mol), vapour flow (0.016 kmol/hr) and column pressure (1.013 bar). Real mixture to be separated contains a little amount of water.

Table 1 displays the optimal values for (F_E/V), α and the respective *R'* for cases I, II and III along with the objective function for simplified model OP_{SM} and rigorous simulation OP_{RS} and the total operating time. Profitability for cases II and III are similar and they are about 24 % higher compared to case I. Case III, implementation of piecewise constant policy for F_E together with α during the withdrawal of chloroform, is the best option because chloroform can be drawn with high purity without increasing the time compared to case II and maintaining the recovery yield. But case II will be preferred for a simpler control of the BHED.

Table 1. Summary of the optimization results

case	F_E/V	α	*R"*	time (h)	OP_{SM}	OP_{RS}
I	1.74	0.823	8.2	9.15	20.74	19.1
II	1.78	0.5751, 0.8468	7.8	8.16	25.23	21.9
III	1.67, 1.85	0.6159, 0.8866	7.7	8.3	25.86	22.04

Simulation results using the short-cut model are presented in table 2, setting the constraint purities as ending criteria for the concerned task. The optimized variables provided the specified purity and recovery requirements, in particular enabling to achieve significant recovery of the products while maintaining their purity, thus demonstrating the interest of the BHED process. They were in agreement with the experimental validation done in ref. [1].

For all three cases, better than 0.99 molar fraction of chloroform is achieved in the heavy liquid phase into the decanter at the end of task T2 by filling the decanter while feeding the entrainer. Therefore, typical operation at total reflux and $F_E>0$ (task T3) was not necessary. On the other hand, the off-cut operation task is almost negligible for case I. In our study, the cost of the raw material has not been included. It would lower the OP and improve the case I performance and lower the cases II and III.

Table 2. Simulation Results of each operating tasks (short-cut model)

	case I	Rigorous simulation	case II	Rigorous simulation	case III	Rigorous simulation
time decanter filling (h)	0.13		0.13		0.13	
x_{D1} in decanter (task T2)	0.9945		0.9967		0.9981	
time of task T3 (h)	0		0		0	
switch time in task T4 (h)	-	-	0.55	*0.55*	0.685	*0.685*
time of task T4 (h)	2.02	*1.93*	1.3	*1.33*	1.57	*1.52*
x_{D1} in chloroform tank I	0.9911	*0.99*	0.9931	*0.99*	0.9981	*0.99*
chloroform recovery (%)	91.5	*99.6*	93.7	*99.8*	93.0	*99.81*
off-cut time (h)	0.02	*0*	0.25	*0*	0.18	*0*
time of task T5 (h)	7.0	*7.06*	6.7	*6.88*	6.6	*6.3*
x_{D2} in methanol tank II	0.9901	*0.99*	0.9901	*0.99*	0.99	*0.9901*
methanol recovery (%)	94.0	*95.1*	96.8	*96.0*	96.3	*96.6*

Table 2 also presents the rigorous simulation using BatchColumn® [3] with column features taken from literature [1]: assumptions of negligible liquid hold-up and pressure drop inside the column were considered. Distillation column was considered having 45 theoretical plates with the entrainer fed at the column top. Figure 2 displays the trajectory of the composition into the still for all studied cases involving steps T2, T3 and T4. The break point for changing α and F_E/V is pointed for cases II and III as well.

Start-up of the batch column is done at total reflux without F_E (task T1). The filling-up of decanter (task T2) shows identical still path for all reflux policies. The filling of the decanter (cross line in Figure 2) was performed until the boiler compositions were similar to those computed by the short-cut method taking about 0.13 hr for all cases. Then the chloroform-rich phase was drawn as distillate until its average purity was 0.99 (task T4). The operating total time for task (T4) agree well to those determined by short-cut method. In all three cases, the recovery yield of chloroform was higher 99.5% and no off-cut step was necessary. Due to this significant chloroform recovery yield, less difference of OP (approximately 15%) was obtained by rigorous simulation between case I and the other cases than for the short-cut model optimization (Table 1).

Figure 2 displays the trajectory of the still during the withdrawal of chloroform-rich phase (task T4). Good agreement was obtained between short-cut model results (continuous lines) and rigorous simulation results (symbols). Rigorous simulation of the separation of methanol – water (task T5) led to similar results of R”, time, methanol purity and methanol recovery for all three cases (Table 2).

Finally, the entrainer water recovery yield was higher than 98%, with a molar purity around 0.988 retained into the still at the end of the process. These results indicating that optimal operation of BHED is mostly determined by operating variables associated to the separation of chloroform, F_E/V and the portion of chloroform rich phase (α) in the top reflux ratio R'.

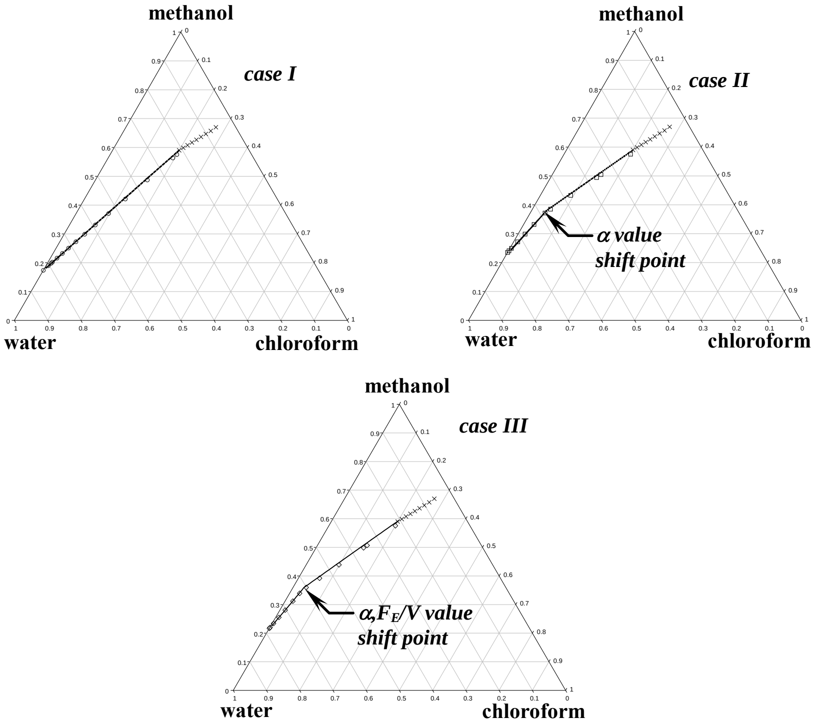

Figure 2. Comparison of still path computed by short-cut model and rigorous simulation.

4. Conclusions

Optimal operating values for reflux ratio and entrainer flowrate have been determined using the genetic algorithm implemented in MATLAB and connected to a short-cut model for simulation of batch heterogeneous extractive distillation. Three operating alternatives have been considered, combining either a constant or a piecewise variation with two time intervals for both optimization variables; the entrainer flowrate F_E/V and the amount (α) of the chloroform-rich phase returned to the column top from decanter along with the entrainer phase reflux.

The best profitability were achieved with piecewise constant F_E/V and α, with a 25% better OP than for constant F_E/V and α. Constraints of purity and recovery for both distillate products were met for all operating alternatives. Good agreement of rigorous simulation results taking the optimal conditions demonstrated the convenience of using the short-cut model along with genetic algorithm in order to accelerate the preliminary optimization analysis. Perspectives concern the incorporation of the energy balance to study the effect of the entrainer and decanter temperature.

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