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# OPTIMIZATION OF HETEROGENEOUS BATCH EXTRACTIVE DISTILLATION WITH NON NEGLIGIBLE HEAT EFFECTS.

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## **Abstract:**

Optimization of batch distillation has been treated extensively in the literature. However, batch heterogeneous distillation has been less considered and even less in extractive mode. The performance of the optimization scheme is illustrated through the separation of chloroform – methanol mixture with water considering non negligible heat effects. The resulting design is compared to the corresponding case in which heat effect is ignored.

The objective function maximizes the overall profit and the optimization variables are the entrainer flowrate, temperature of entrainer feeding, the reflux ratio composed by an optimal proportion of both decanted phases during the chloroform distillation stage and the reflux ratio during the methanol distillation stage. Recovery and purity of chloroform methanol and water are set as constraints during the calculation. The optimization relies upon a genetic algorithm procedure and the simulation of the process is coded in two different modes: considering a short-cut model with constant molar overflow assumption for the negligible heat effect process and taking into account a differential mass balance model computing the molar overflow variation inside the column through the energy balance.

Two different alternatives are compared, taking into account negligible (case I) and not heat effects (case II). Profitability for case II is about 35 % higher compared to case I. The optimal temperature for feeding the heterogeneous entrainer (water) was around 28°C allowing a reduction of 18.4% of entrainer, a lower chloroform-entrainer reflux to the column top (14%) during the chloroform withdrawal and lesser reflux ratio for the recovery of methanol. Besides, better recovery (+3.4%, +1.3%) and purity (+0.2%, +0.5%) of chloroform and methanol were obtained, respectively. This optimal policy allows the feeding of heterogeneous entrainer near to the normal environmental temperature reducing the extra energy spending to heat the entrainer until its boiling temperature.

**Keywords:** batch extractive distillation, heterogeneous entrainer, heat effects, optimization, genetic algorithm

# OPTIMIZATION OF HETEROGENEOUS BATCH EXTRACTIVE DISTILLATION WITH NON NEGLIGIBLE HEAT EFFECTS.

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## 1. Introduction

Batch distillation becomes invaluable when it is necessary to take care of 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 often used in batch azeotropic distillation, its application has been extended to extractive mode only recently[1,2]. The main interest of heterogeneous batch extractive distillation (HBED) is that the resulting ternary diagram can exhibit more than one heterogeneous azeotropic mixture. The continuous feeding of the heterogeneous entrainer allows the binary heterogeneous azeotrope being a saddle of the residue curve map to be drawn as top vapor of the distillation column. 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 tasks for HBED were considered in this work:

- (T<sub>1</sub>) Startup of the column at infinite reflux. The unstable node located at the ternary heterogeneous azeotrope reaches the column top.
- (T<sub>2</sub>) Filling the top decanter along with continuous feeding of the entrainer ( $F_E$ ) using a reflux ratio equals to unity. the saddle binary heterogeneous azeotrope replaces the ternary heterogeneous azeotrope.
- (T<sub>3</sub>) Operation at a given reflux ratio ( $R'$ ) together with ( $F_E$ ) until molar purity of the partially miscible original component in the distillate drops below 0.99.
- (T<sub>4</sub>) Off cut product distillation using a  $R_{\text{offcut}}=1$  in order to diminish the molar composition of immiscible original composition into the boiler less than 0.001.
- (T<sub>5</sub>) Separation between the homogeneous original component and the entrainer at a given reflux ratio ( $R''$ ) without ( $F_E$ ) feeding.

A stochastic optimization method, genetic algorithm real-coded in MATLAB, is used along with the simulation of the HBED. Simulation is performed considering a differential mass balance inside the column with the typical assumptions: theoretical plates, negligible pressure drop and liquid hold-up on the trays. Top decanter is considered as a total condenser with a significant liquid hold-up. Hence, both decanted phases are refluxed as boiling liquid. Several parametric studies have demonstrated that reflux ratio ( $R'$ ) and the entrainer flowrate are the variables having a key incidence over the overall profit of the HBED. 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 (T<sub>3</sub>) because independency between all tasks is not real at all [3]. The effect of the entrainer feeding temperature ( $T_E$ ) has not been published hitherto. It implicates the inclusion of energy balance in the process modeling. Hence, this work is devoted to optimization of HBED through the solution of an overall profit function taking

into account the heat effects and comparing with the corresponding case in which heat effects are ignored. We solve the optimization problem considering the entrainer flowrate ( $F_E$ ) and its temperature ( $T_E$ ) and top external reflux ratios ( $R'$  and  $R''$ ) as the key operating variables having a direct incidence over the economical profit of the HEBD. Liquid top reflux ( $R'$ ) during the chloroform removal comprises the whole amount of water-rich phase mixed with a portion  $\alpha$  of the distillate phase from the top decanter. The decanter water-rich phase amount refluxed to the column top enables to keep constant the decanter light phase level [1]. Indeed,  $\alpha$  is the optimization variable instead of  $R'$ . A constant value for optimization variables will be considered because they are the simplest reflux policies commonly used in plant practice.

**2. Optimization problem formulation**

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

Optimization problem formulation concerns to the separation of azeotropic mixture chloroform – methanol which is widely used for separating bioactives substances from biological sources. Water was used in practice as 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 ( $\alpha_{12}$ ). Thermodynamic calculations were done by using Simulis Thermodynamics®, a thermodynamic property server available in Microsoft Excel [4]. NRTL was chosen as thermodynamic model and the binary coefficients published elsewhere [1]. Because the univolatility line  $\alpha_{12}=1$  ends at the edge chloroform – water, the saddle binary heteroazeotrope chloroform – water can be drawn as a vapour overhead at the column if water is fed continuously at the column top, giving rise to two liquid – liquid phases into the decanter after condensation [1]. 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.

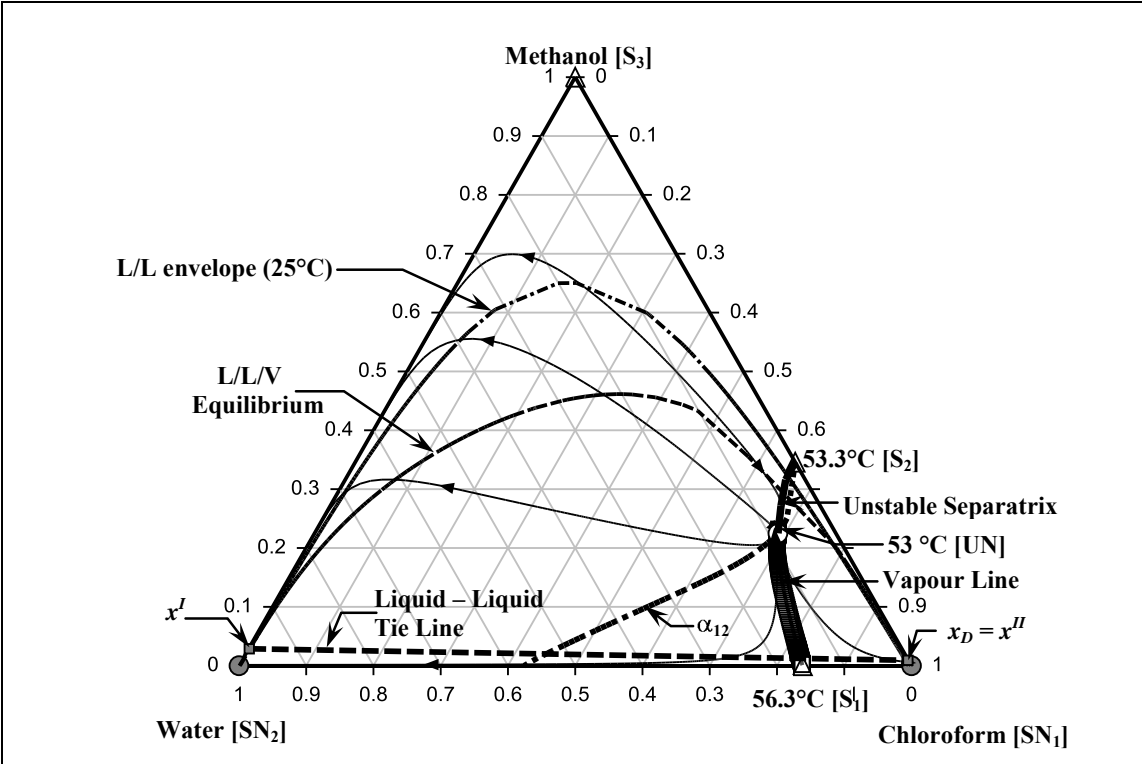


Figure 1. Residue curve map of ternary mixture chloroform – methanol – water

## 2.2 Modeling of HBED with non negligible heat effects

Schematic representation of the heterogeneous extractive distillation process in a rectifying batch column configuration is given in Figure 2. Unlike to the homogeneous extractive distillation, the heterogeneous entrainer is fed at the column top.

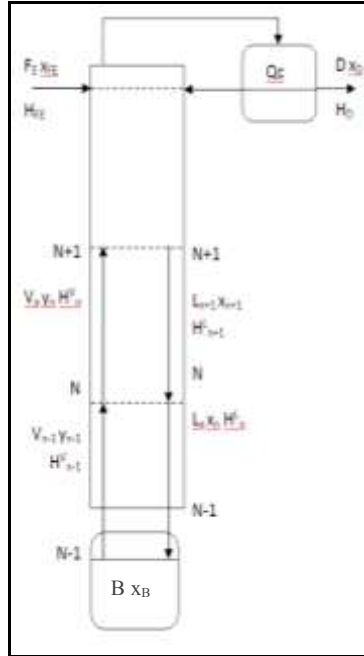


Figure 2. Column configuration of heterogeneous batch extractive distillation (HBED)

The dynamic behavior of HBED can be described by a set of differential and algebraic equations as follow

- Boiler mass balances: (J'ai TRANSFORME EN WORD 2003 et les equations sont pas jolies)

$$\frac{dB}{dt} = F_E - D \quad (1)$$

$$\frac{dx_B}{dt} = \frac{F_E}{B} (x_{FE} - x_B) + \frac{D}{B} (x_D - x_B) \quad (2)$$

where  $D = (1-\alpha)(1-\omega)V$

- Finite difference of mass and energy balances for the extractive section are:

$$L_{n+1}x_{n+1} + Dx_D = V_n y_n + F_E x_E \quad (3)$$

$$L_n H_n^L + DH^D + Q_C = V_{n-1} H_{n-1}^V + F_E H_{FE} \quad (4)$$

Defining  $R_{n+1} = \frac{L_{n+1}}{D}$  and  $Q_{cond} = H^D + \frac{Q_C}{D}$  for including in equations (3) and (4) become:

$$x_{n+1} = \frac{\left(R_{n+1} + 1 - \frac{F_E}{D}\right)}{R_{n+1}} y_n + \frac{F_E}{R_{n+1} D} x_E - \frac{1}{R_{n+1}} x_D \quad (5)$$

$$R_n = \frac{Q_{cond} - \frac{F_E}{D} (H_{FE} - H_{n-1}^V) - H_{n-1}^V}{H_{n-1}^V - H_n^L} \quad (6)$$

The liquid mole fraction and the reflux can be approximated by a first-order Taylor series expansion:

$$x_{n+1} = x_n + \left. \frac{dx}{dh} \right|_{h=n} \Delta h \quad (7)$$

Taking  $\Delta h = 1$ , substituting equations (5) in (7) and assuming  $H_{n-1}^V = H_n^V$  leads to:

$$\frac{dx}{dh} = \frac{\left(R_n + 1 - \frac{F_E}{D}\right)}{R_n} y_n + \frac{F_E}{R_n D} x_E - \frac{1}{R_n} x_D - x_n \quad (8)$$

Vapor phase in equilibrium is determined applying the modified Rachford-Rice procedure for a three-phase mixture as the vapor phase selected as a reference phase.  $\beta_i$  is the molar amount of each phase,  $Z_i$  is the molar composition and  $K_{ij}$  is the equilibrium coefficient.

$$\sum_1^{c=3} \frac{z_i (k_{ij} - 1)}{1 + \sum_1^{p \text{ phase} = 3} \beta_j (k_{ij} - 1)} = 0 \quad (9)$$

Usually, HBED involves the reflux of the whole water-rich phase  $L^I$  along with a portion “ $\alpha$ ” of the chloroform rich-phase  $L^{II}$ . The proportion of  $L^I$  and  $L^{II}$  inside decanter is determined by the liquid – liquid splitting ratio  $\varpi$ . Therefore, the liquid external reflux liquid at the top decanter is  $L_R = L^I + \alpha L^{II}$  and the reflux ratio can be determines as:

$$R = \frac{\varpi + \alpha(1 - \varpi)}{(1 - \alpha)(1 - \varpi)} \quad (10)$$

**PROBLEM IT IS R' in the text and in the tables**

For enthalpy calculation, saturated vapor is the reference state, for both phases

$$H_n^V = \sum_{i=1}^{NC} y_{i,n} h_{i,n}^V \quad (11)$$

$$H_n^L = \sum_{i=1}^{NC} [x_{i,n} (h_{i,n}^V - \lambda_{i,n})] \quad (12)$$

where

$$h_{i,n}^V = \int_{298}^{T_n} C_p dt$$

$T_n$  is the equilibrium temperature and  $\lambda_{i,n}$  c'est soit lambda  $\Lambda$  majuscule, soit  $\Delta H_{\text{vap}}$  is the vaporization heat for the compound  $i$  at the height  $h$ .  $C_p$  and  $\lambda$  coefficients were taken from Component Plus® database [4]

### 2.3 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:

$$\text{MAX}_{F_E(T_2, T_3), T_E(T_2, T_3), \alpha(T_3), R''(T_5)} OP = C_1 * D_1 + C_2 * D_2 - C_S * S - C_f * (t_{\text{total}}) \quad (13)$$

subject to the constraint s:

$x_D \geq 0.99$ , for chloroform in  $T_3$  and methanol in  $T_5$

Recovery yield for all components:  $Re > 90\%$

$C_1$  (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. Optimization using some market product prices revealed a non sensitive effect for a given  $C_f$ . It is assumed that the off-cut product (ternary heteroazeotrope) drawn in step 4 is not a commercial product and it can be recycled to the next batch. Table 1 displays the operating conditions for simulation of the separation of chloroform (1) – methanol (2) with water (3). Real mixture to be separated contains a little amount of water.

Table 1  
Input data for optimisation of HBED

Parameters	value
Initial charge (mol)	20
Initial charge composition *	(0.2704/0.6714/0.0582)
Decanter holdup (mol)	1
vapor flow (Kmol/hr)	0.016
Column pressure (bar)	1.013

\*(chloroform/methanol/water)

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 not improvement of the objective function is achieved after 10 generations. Optimization by genetic algorithm requires many evaluation of the objective function and thus of calculation of the dynamic model. Use of a differential model as above allows a good approximation of the optimal operation conditions with less computational effort and time. The main results of the simulation are amount and composition in each product tank and the total operating time until the specified average purity of distillate cannot be maintained anymore (stop criterion). If one phenotype of the population doesn't accomplishes any constraint, the associated OP is increased by  $10^6$ .



The optimization variables are the ratio of (entrainer/vapor) flowrate ( $F_E/V$ ), the temperature of the entrainer feeding ( $T_E$ ) for task 2 and 3, the reflux of the chloroform-rich phase  $R'(f(\alpha))$  for task 3 and the reflux ratio  $R''$  for task 5. The aim of the optimization is searching an optimal value for all variables in order to compare the optimization results obtained with and without heat effects. Bounds for the optimization variables are:  $1.2 \leq (F_E/V) \leq 2$  and  $0.4 \leq \alpha \leq 0.9$  for chloroform recovery and  $4 \leq R'' \leq 10$  for the separation of methanol – water. In the case of taking into account energy balance  $25^\circ\text{C} \leq T_E \leq 80^\circ\text{C}$  was set. The variable range for  $(F_E/V)$ ,  $\alpha$ ,  $T_E$  and  $R''$  were taken from previous study according to the purity product constraints [1]; in particular the  $F_E/V$  limit of 1.2 corresponds to the minimal value for the process to be feasible [1].

### 3- Results and discussion

Optimization of the HBED was performed considering two cases: (I) negligible heat effect and (II) non-negligible heat effect. Table 2 displays the optimal values for  $(F_E/V)$ ,  $\alpha$  and  $R''$  for the scenarios I and II and  $T_E$  for the case II. Value of the objective function OP and total operating time is also shown in Table 2. Case II provides the best optimal results. Profitability for case II is 34.28 % higher than compared to case I. The optimal temperature for feeding water is close to 28 °C. Cooling the entrainer increases the liquid flowrate inside the column also intensifying the internal reflux ratio. In consequence, recovery and purity of all components are improved. The positive effect of a cooler entrainer feeding is lower  $(F_E/V)$  ratio and chloroform-rich phase ( $\alpha$  value) for the heterogeneous extractive distillation tasks T2 and T3. In the task T5 separation of methanol – water requires a smaller reflux ratio ( $R''$ ). Overall, the operating time is higher than for case I because of the longer duration of task 5.

Table 2  
Summary of the optimization results

case	$F_E/V$	$T_E(^{\circ}\text{C})$	$\alpha$	$R''$	Total Time (min)	OP (\$)
I	1.74	100	0.85	8.4	596	25.36
II	1.30	27.7	0.76	7.3	665	38.59

The simulation results for each optimal operating case are summarized in Table 3. The first operating task concerning to the filling of decanter takes more time for case II because the partial condensation of the top vapor. However, this task has no significant contribution in the total operating time. At the end of the first task, the composition of the chloroform in the organic phase reaches the specified purity. Task T3 separation of chloroform by HBED takes 10 minutes more than case I but provides a higher purity and recovery. However, off-cut task T4 is also necessary for case II because the content of chloroform into the boiler at the end of HBED T3 doesn't match with the specification (less than 0.001). Task T5 final separation of methanol requires a lower reflux ratio but a longer duration (almost one hour more) for case II. However, this optimal operating condition allows a higher recovery and purity for methanol as second distillate product and the water retained inside the boiler at the end of the distillation process.

### 4. Conclusions

Multivariable optimization of heterogeneous batch extractive distillation was carried out by using genetic algorithm, an optimiser tool implemented in MATLAB. Total profitability was

selected as the objective function taking into account the main variables of each operating tasks involved in HBED. Flowrate of the entrainer feeding, reflux of the chloroform-rich phase, portion of distillate refluxed and the reflux ratio for separating methanol are the typical operating variables for optimizing HBED. Entrainer feeding temperature has been considered as a new optimization variable through the integration of energy and mass balance. Two different alternatives have been developed taking into account negligible (case I) and non negligible heat effects (case II). Profitability for case II is about 35 % higher compared to case I. The optimal temperature for feeding the heterogeneous entrainer (water) was around 28°C allowing a reduction of 18.4% of entrainer, a lower chloroform-entrainer reflux to the column top (14%) during the chloroform withdrawal and lesser reflux ratio for the recovery of methanol. Besides, better recovery (+3.4%, +1.3%) and purity (+0.2%, +0.5%) were obtained, respectively. This optimal policy allows the feeding of heterogeneous entrainer near to the normal environmental temperature reducing the extra energy spending to heat the entrainer until its boiling temperature.

*Table 3  
Simulation Results of each operating tasks for optimal operating values*

Operating Parameters	Case I	Case II
<b>Task 2</b>		
time (min)	8	12
$x_{D1}$ in decanter (task 2)*	(0.995/0.005/0.000)	(0.995/0.005/0.000)
<b>Task 3</b>		
time (min)	145	155
$x_{D1}$ in chloroform tank*	(0.992/0.006/0.002)	(0.994/0.005/0.001)
chloroform recovery (%)	91.49	94.62
end still composition*	(0.008/0.185/0.806)	(0.005/0.155/0.839)
<b>Task 4</b>		
off-cut time (min)	13	5
<b>Task 5</b>		
time (min)	430	493
$x_{D2}$ in methanol tank*	(0.000/0.991/0.009)	(0.000/0.996/0.004)
methanol recovery (%)	94.27	95.49
$x_{D3}$ in water in still*	(0.000/0.099/0.901)	(0.000/0.054/0.946)
water recovery (%)	91.27	96.38

\*(chloroform/methanol/water)

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