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# Optimization of heterogeneous batch extractive distillation

**Alien Arias BARRETO<sup>1</sup>, Ivonne RODRIGUEZ-DONIS<sup>1</sup>, Vincent**

**GERBAUD<sup>2,3\*</sup>, Xavier JOULIA<sup>2,3</sup>**

<sup>1</sup> *Instituto Superior de Tecnologías y Ciencias Aplicadas (INSTEC), Ave. Salvador Allende Luaces, Plaza, Ciudad de la Habana,, Cuba*

<sup>2</sup> *Université de Toulouse, INP, UPS, LGC (Laboratoire de Génie Chimique), 4 Allée Emile Monso, F-31432 Toulouse Cedex 01 – France*

<sup>3</sup> *CNRS, LGC (Laboratoire de Génie Chimique), F-31106 Toulouse Cedex 01 – France*

\* Corresponding author: Vincent.Gerbaud@ensiacet.fr

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## Abstract

Heterogeneous extractive batch distillation of the chloroform – methanol minimum boiling temperature azeotropic mixture is studied with water as a heterogeneous entrainer. The continuous feeding of water allows recovering 99% molar chloroform after condensation of the saddle binary heteroazeotrope water – chloroform. Unlike a homogeneous process, the reflux composition is different from the heteroazeotrope water – chloroform in the vapor overhead. Besides, the distillate recovery is improved by refluxing a portion  $\alpha$  of the chloroform-rich distillate phase along with the water-rich entrainer phase. A genetic algorithm is coupled to a constant molar overflow model to study seven operation policies. Optimization parameters are the entrainer flowrate  $F_E/V$ , the portion  $\alpha_{T3}$  of distillate-rich phase refluxed to the column during chloroform distillation, the reflux policy  $R_{T5}$  during methanol distillation. The optimization maximizes a profit function, penalized with recovery yields constraints whereas purity targets are used as Task ending events. All optimized solutions achieve higher than 90% molar recovery yields and 99% molar purity for both products chloroform and methanol. Results are confirmed by rigorous simulation showing the good performance of coupling simplified model and genetic algorithm as a first approach. The two piece-wise parameter values operation policies for all three parameters increases profit by 41.8% and reduces total time by 43.8% compared to single value parameter policy. The parameter influence study ranks  $R_{T5}$  first,  $\alpha_{T3}$  second and  $F_E/V$  last. Keeping  $F_E/V$  constant and using two piece-wise  $\alpha_{T3}$  and  $R_{T5}$  value operation is recommended to increase profit.

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

## Notations

### Roman letters

$A$	most volatile initial component (-)
$A_{ij}$	NRTL binary parameter
$A_z$	azeotrope (-)
$B$	least volatile initial component (-)
$c$	cost contribution (\$/unit)
$D$	distillate flowrate (mol.s <sup>-1</sup> )
$E$	entrainer (-)
$F_E$	entrainer feed flowrate (mol.s <sup>-1</sup> )
$h$	column height (m)
$K$	equilibrium constant (-)
$L$	internal liquid flowrate (mol.s <sup>-1</sup> )
$n$	constraint number (-)
$OP$	optimal profit (\$)
$P$	weighting factor for equality constraint (-)
$Q$	weighting factor for inequality constraint (-)
$R$	reflux ratio (-)
$s$	saddle singular point (-)
$sn$	stable node singular point (-)
$t$	time (s)
$T$	temperature (°C)
$T_j$	Task j
$U$	holdup (mol)
$un$	unstable node singular point (-)
$V$	internal vapor flowrate (mol.s <sup>-1</sup> )
$x$	liquid molar fraction (-)
$y$	vapor molar fraction (-)
$z$	overall molar fraction (-)

### Greek letters

$\alpha$	portion of the product-rich phase refluxed to the column
$\alpha_{AB}$	A – B relative volatility
$\alpha_{ij}$	NRTL binary parameter
$\beta$	molar amount of each phase
$\omega$	liquid – liquid split ratio in the decanter

### Superscript

I	entrainer lean phase in the decanter
II	entrainer rich phase in the decanter
VL	vapor liquid
LL	liquid liquid
$j$	tray number
*	equilibrium

### Subscript

$l$	refers to the top liquid stream
2	refers to the top vapor stream
$A$	component A
$B$	component B
$cond$	condenser
$D$	distillate
$dec$	decanter
$ext$	extractive profile map
$FE$	entrainer
$i$	component i
$j$	tray j
$k$	constraint k
$l$	phase l
$minim$	minimum condition value
$min$	minimum boiling
$N$	boiler
$obj$	objective
$rcm$	residue curve map
$R$	reflux stream
$RS$	rigorous simulation
$S$	still
$SM$	simplified model
$Top$	column top

## 1. Introduction

Solvent recovery often involves azeotropic or low relative volatility and including close boiling mixtures for which non-conventional distillation techniques must be used. In the pharmaceutical and specialty chemical industries, such separations are a major issue in batch operated distillation columns. The most common non-conventional distillation alternatives involve changing the operating pressure or adding of a so-called entrainer. Design of pressure swing batch distillation process has been recently revisited with precise feasibility criteria based on thermodynamic properties of ternary diagrams<sup>1-3</sup> but, the pressure option is economically attractive only for mixtures very sensitive to pressure. Adding an entrainer to the mixture is then more frequent. The entrainer is always loaded initially into the still in azeotropic batch distillation<sup>4-7</sup> whereas the entrainer is fed continuously in extractive batch distillation at some tray of the column or into the still<sup>8-13</sup>, inducing various column configurations among which the rectifier configuration<sup>14,15</sup> and the inverse/stripper distillation<sup>16,17</sup> are well understood, much less the middle vessel configuration<sup>15</sup>. When the entrainer is partially miscible with one component of the initial mixture, the process is qualified as heterogeneous azeotropic batch distillation<sup>18-22</sup> or heterogeneous batch extractive distillation<sup>23-25</sup>. The reflux policy alternatives are then more numerous and the process is often simpler as the rectifying section is usually not required<sup>26</sup>.

In azeotropic batch distillation, the first distillate (resp. bottom) product in a rectifying (resp. stripping) is the unstable/lowest boiling (resp. stable/highest boiling) node of the distillation region where the feed composition lies. Except for curved distillation boundaries<sup>5</sup>, product are removed in increasing (resp. decreasing) temperature order. However, in extractive batch distillation, a saddle/intermediate boiling point of the distillation region of the ternary diagram can be drawn as a top (or bottom) product where a non monotonously increasing or decreasing temperature order may occur. For heterogeneous extractive batch distillation (HEBD), Van Kaam et al.<sup>25</sup> demonstrated experimentally and by simulation that the same behavior holds: continuous feeding of water during the batch distillation of the chloroform –

methanol azeotrope shifted the top composition from the ternary unstable heteroazeotrope to the binary saddle heteroazeotrope chloroform – water, enabling to recover chloroform in the distillate.

Relying upon the properties of ternary diagrams, in particular singular points location and stability, and univolatility curves<sup>27</sup>, feasibility rules have been published for batch azeotropic distillation<sup>6,7</sup>, heterogeneous batch azeotropic distillation<sup>18-21,28</sup> and batch extractive distillation<sup>10,14,29-31</sup>. Optimization of homogeneous batch distillation has been devoted much attention as shown in the next section but that is not the case for heterogeneous batch distillation optimization, which we focus on. Key differences between homogeneous and heterogeneous distillation exist. The main one is that compositions of the vapor overhead, compositions of the liquid reflux and composition of the distillate are all similar in homogeneous distillation and they are all different in heterogeneous batch distillation. The composition of the top vapor is near to the heteroazeotropic mixture (ternary or binary), the distillate composition corresponds to the key component – rich phase and the liquid reflux to the column top match either the entrainer-rich phase composition or a combination of the entrainer-rich phase with a portion “ $\alpha$ ” of the entrainer-lean phase. The reflux of the entrainer-rich phase is necessary for drawing the heterazeotrope at the column top. However as the distillation proceeds, the top vapor composition moves away from the heteroazeotrope if the entrainer-lean phase is not refluxed as well, eventually shortening the process and lowering the product recovery for a given purity. Therefore, optimization of heterogeneous batch distillation must deal with determining the optimal proportion “ $\alpha$ ” of the distillate – rich phase refluxed along the entrainer-rich phase, although it may increase the operation time. Optimization of heterogeneous batch distillation has been published once in the literature<sup>32</sup> but only with the reflux of the entrainer-rich phase. This is the first time that  $\alpha$  is considered as an optimization variable.

The paper is organized as follow: an overview of batch distillation optimization published in the literature is presented. Then, a finite difference model for the HEBD column is presented. Next, the optimization problem is defined: objective function, constraints and optimization variables. Based on the

separation of the chloroform – methanol azeotrope with water by HEBD, seven cases with various operating parameter policies are optimized and compared.

## **2. Background on batch distillation optimization**

The optimization of batch distillation processes has been intensively studied in the literature. For a conventional batch distillation column, the overall objective is to determine the optimal strategy based on a given objective function and satisfying several constraints. In particular, the goal is to determine the optimal reflux policy to obtain a specified quality of product. For batch extractive distillation, less work is recorded and the problem becomes systematically multivariable as both the entrainer flow rate and the reflux policy become optimization variables.

The optimization problems studied in the literature go from the simplest to the most complex ones. In addition to the type of process structure or of operation mode, those problems differ by the types of thermodynamic mixtures handled, often 2 or 3 components forming an ideal zeotropic homogeneous mixture, more rarely an azeotropic or a low relative volatility mixture. Even rarer are optimization of mixtures with vapor-liquid-liquid equilibrium.

### **2.1. Formulation of a batch distillation optimization problem**

Three categories of batch distillation optimization problems are found in the literature <sup>33</sup>:

1. Problem of maximum distillate which aims at maximizing the quantity of distillate recovered with a given purity in a given time.
2. Problem of minimum time which aims at minimizing the total operation time to produce a given quantity of distillate with a given purity.
3. Problem of maximum profit which aims at optimizing an economic cost function which includes many contributions like the total operation time, the quantity of distillate, its purity...

The third criterion is often set based on a linear combination or a ratio of the first two criteria. Finally, depending on the criterion, the various problem constraints can be stated differently.

## 2.2. Batch distillation optimization variables

The most used variable of action or of control is the reflux as it is often sought to set an optimal reflux policy enabling to obtain the various specifications of purity, time or quantity. Other optimization variables can be taken into account such as the heat duty to the boiler<sup>34</sup>, the plate and tank holdup values<sup>35</sup>, the recycling flows<sup>9,36</sup>, the column configuration (rectifier, stripper, middle vessel, extractive)<sup>37-39</sup> and the operating conditions<sup>40</sup>. For batch extractive distillation, the entrainer flow rate and the Task at which the entrainer is fed should also be considered<sup>38,41-43</sup>.

Most optimization variables are time dependent, conferring to the problem an infinite dimension. To transform it into a finite size problem, discretization techniques with respect to time can be used. The time horizon is then cut out in a finite number of intervals: 2<sup>44</sup>, 4<sup>45</sup>, 5<sup>34</sup>, 6<sup>46</sup>, 7<sup>35</sup> or 40<sup>47</sup>. This choice comes from a compromise between precision from the discretization and computing time. Several schemes of parameterization can then be considered: Lagrange polynomials to describe a constant profile (order 1) or linear per part (order 2); exponential functions<sup>48</sup> or a combination of Lagrange - exponential function<sup>49</sup>. Two types of discretization with respect to time can be distinguished: the parameterization of all variables or the parameterization of the optimization variables only. In the first case, integration of the DAE system modeling the batch distillation process is avoided, but the size of the problem becomes very large. In the second case that we choose, the size of the problem is more reduced, but using of an efficient DAE integrator is necessary to handle to the complexity of the DAE set of equation. In both cases, new values of the optimization variables are generated for each interval of time considered.

Finally, optimization variables of integer type are sometimes considered, primarily in process design: number of theoretical stages, feed plate position, as well as a sequence of the batch Tasks. They require a particular treatment in the methods of optimization (MINLP)<sup>50</sup>. In particular cases, the number of stages



is regarded as a continuous variable that is then transformed into an integer using appropriate computer functions <sup>46</sup>.

### **2.3 Solving methods of batch distillation optimization problems**

The methods of resolution of batch distillation optimization problems depend on the type of optimization variables and of the choice of the criterion, with or without explicit constraints. The presence or not of integer variables brings the optimization problem into a different mathematical world (Mixed Integer Non Linear Programming vs. Non Linear Programming). The MINLP undoubtedly represents currently the highest degree of mathematical sophistication and is used for the design of distillation process <sup>50,51</sup>.

When only continuous/real variables are present, as it is in our case, various methods can be employed: dynamic programming <sup>52</sup>, Pontryagin maximum principle <sup>53,54</sup>, increased Lagrangian <sup>55</sup>, generalized reduced gradient <sup>56</sup> and Sequential Quadratic Programming SQP <sup>45</sup>. All these optimization techniques are deterministic methods. The use of SQP seems to be from now on a standard to deal with nonlinear problems of optimization and it is available in most commercial libraries (IMSL, GAMS, MATLAB, etc...). Besides, a study of various commercial SQP was published to compare their performances according to various criteria such as the problem size, the accuracy of the solution or the computing time <sup>57</sup>. But stochastic methods of optimization are also becoming popular, among which Genetic Algorithm based methods <sup>40,58</sup> and simulated annealing methods <sup>47</sup> can be quoted.

The choice of a deterministic or a stochastic method depends on their characteristics. In the first case, convergence towards an optimum requires a good starting point and often the knowledge of the gradients of the criterion and constraints which are explicit. In the second case, mathematical implementation is much simpler, without gradient or any good initial point, but it requires a large number of calls to the objective function which requires in its turn to simulate the process and it can only handle constraints implicitly in the objective function. Finally, to soften the disadvantages of each one of these methods, the use of a stochastic method as initialization of a deterministic method seems to be a compromise worth consideration <sup>59</sup>. Recent studies comparing both methods have preferred stochastic methods: it found the

most profitable operation for the separation of water – acetonitrile mixture<sup>60</sup>; it achieved most of the path towards the optimum when optimizing a water – pyridine mixture with toluene by heterogeneous batch distillation<sup>32</sup>.

### **3. Materials and methods**

#### **3.1. Process analysis of the separation of chloroform – methanol with water by heterogeneous extractive batch distillation.**

We consider the separation of the minimum boiling azeotropic mixture chloroform (A) – methanol (B) which is widely used for separating bioactives substances from biological sources. Van Kaam et al.,<sup>25</sup> computed residue curve maps and univolatility line to evaluate fourteen entrainers (E) and found that half enabled the recovery of methanol and half enabled the recovery of chloroform in the distillate, in agreement with the general feasibility criterion for extractive distillation recently published<sup>30,31</sup> The most efficient and least toxic entrainer came out to be water with which experiments and simulation proved that chloroform could be separated in a heterogeneous extractive batch distillation column with molar purity better than 0.991 and a molar recovery of 89.1%.

Insert here figure 1

The thermodynamic and topological features of the ternary diagram are shown in Figure 1, including the univolatility curve chloroform – methanol ( $\alpha_{AB}$ ). Thermodynamic calculations were done by using Simulis Thermodynamics®, a thermodynamic property server available in Microsoft Excel<sup>61</sup>. The NRTL thermodynamic model is chosen with binary coefficients validated before<sup>25</sup> and reported in table 1.

Insert here table 1

In a non extractive distillation process, the ternary heteroazeotrope being the unstable node [ $un_{rcm}$ ], it would be recovered in the distillate. In extractive distillation when water is fed continuously at the column top, the saddle binary heteroazeotrope chloroform – water [ $s_{ext}$ ] can be drawn as a vapor overhead at the column because the univolatility line  $\alpha_{AB}=1$  ends at the chloroform – water edge. This is in

accordance with the general feasibility criterion of homogeneous extractive distillation<sup>30,31</sup> that depends on the residue curve shape and on the volatility order region defined by the univolatility line. For the heterogeneous process here, one should consider that the criterion concerns the overhead vapor rather than the distillate composition as in the homogeneous process investigated by Rodriguez-Donis et al.<sup>30</sup>. Then the criterion can be formulated as: “the saddle heteroazeotrope is drawn overhead if temperature decreases along a residue curve starting at the entrainer (water) and nearing the saddle heteroazeotrope (azeo<sub>water –chloroform</sub>), in the volatility order region (ABE) where chloroform (A) is the most volatile compound”.

After condensation, the saddle heteroazeotrope splits in two liquid phases into the decanter with a split ratio  $\omega$ . The water – rich phase ( $x^I$ ) is refluxed toward the column top with a portion  $\alpha$  of the heavy chloroform-rich phase ( $x^II=x_D$ ). The remaining portion  $(1-\alpha)$  is withdrawn as distillate product.

As already observed in heterogeneous batch distillation<sup>19,28</sup>, refluxing part of the distillate-rich phase ( $\alpha$  is positive) Van Kaam et al.<sup>25</sup> in their experiments enabled to keep the top vapor close to the desired heteroazeotrope, which enables to get high purity chloroform during the whole process, although it increases the process time.

Figure 2 sketches the column with the decanter. Because water is fed at the top there exists only an extractive section in the column, an advantage of the heterogeneous process versus the homogeneous extractive batch distillation where a rectifying section is usually necessary<sup>14,30,31</sup>.

Insert here figure 2

Van Kaam et al.<sup>25</sup> ran the following Tasks having a ternary mixture chloroform – methanol – water as initial charge into the still:

- Task 1 (T1): infinite reflux operation is commonly carried out to obtain the steady state inside the column and the unstable ternary heteroazeotrope at the column top. Notice that if a binary mixture chloroform – methanol had been initially into the still, the binary homoazeotrope would have been obtained at the column top, as usual.

- Task 2 (T2): Under infinite reflux operation, thanks to the continuous feeding of the heterogeneous entrainer at the column top, the ternary unstable heteroazeotrope is replaced in the vapor overhead by the binary saddle heteroazeotrope chloroform – water. Notice that for a binary mixture chloroform – methanol had been initially into the still, the binary homoazeotrope at the top would have been also replaced by the binary saddle heteroazeotrope chloroform – water.

- Task 3 (T3): Distillation of the chloroform-rich phase with a given reflux policy is ran, while continuously feeding the entrainer. At the end of this step, the chloroform content into the still must be as low as possible. For the present work, the stop event is  $x_{D,\text{chloroform}} < 0.99$  in the distillate tank. The reflux combines all the water-rich phase and a portion  $\alpha$  of the chloroform-rich phase.

- Task 4 (T4): Entrainer feeding is stopped. An offcut is withdrawn to eliminate further the chloroform from the column. For the present work, the stop event is  $x_{\text{Still, chloroform}} < 0.001$ .

- Task 5 (T5): Separation of the zeotropic mixture methanol – water remained into the still with a given reflux policy where methanol, then the most volatile component, is drawn as the second distillate cut. For the present work, the stop event is  $x_{D,\text{methanol}} < 0.99$  in the distillate tank.

Task 1 and 2 are distinct for the purpose of illustrating the extractive effect. Then, the decanter is bypassed during Task 1 and filled during Task 2, simultaneously to the feeding of the heterogeneous entrainer at the column top. But, in practice they can be merged and we experienced in our former study<sup>25</sup> that time, entrainer consumption and energy are reduced. This is done in the optimization cases investigated here using the simplified modeling

## **3.2. Modeling of heterogeneous extractive batch distillation based on Constant Molar Overflow assumption**

### **3.2.1. Simplified modeling**

The dynamic behavior of HBED can be described by a set of differential and algebraic equations. Typical simplifying assumptions are liquid and vapor constant molar overflow (CMO:  $L^j=L$  and  $V^j=V$ ) inside the

column, no energy balance, negligible liquid hold-up on the column plates but not in the decanter, negligible pressure drop and equilibrium stages.

- Boiler mass balances:

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

$$\frac{dx_{i,N}}{dt} = \frac{F_E}{U_N} (x_{i,FE} - x_{i,N}) + \frac{D}{U_N} (x_{i,N} - x_{i,D}) \quad (2)$$

- Extractive liquid profile inside the extractive column section can be approximated by a first-order Taylor series expansion considering the distillation column having a significant height  $h$ . Therefore, the liquid composition at each height  $h=j$  can be computed by:

$$x_{i,j-1} = x_{i,j} + \Delta h \left. \frac{dx_{i,j}}{dh} \right|_{h=j} \quad (3)$$

The differential model can be solved from bottom to top, taking the composition inside the boiler as initial value for each time step. The total height in the column is  $h=45$ . Taking  $\Delta h = 1$ , the differential model matches with a tray by tray model.

The differential part of equation (3) can be described according to the differential model proposed by Lelkes et al.<sup>10</sup>:

$$\frac{dx_i}{dh} = \frac{V}{L} (y_i - y_i^*) = \frac{1}{\frac{R}{R+1} + \frac{F_E}{V}} (y_i - y_i^*) \quad (4)$$

Where  $y_i$  is the operating vapor composition and  $y_i^*$  is the equilibrium vapor composition.

$y_i^*$  is determined applying the modified Rachford-Rice procedure for a three-phase (liquid – liquid – vapor) mixture with the vapor phase selected as a reference phase.

$$\sum_{i=1}^c \frac{z_i (K_i^{VL} - 1)}{1 + \sum_{j=1}^{Phases=3} \beta_j (K_i^{VL} - 1)} = 0 \quad (5)$$

$\beta_i$  is the molar amount of each phase considering that the molar total amount of all phases equals to unity,  $z_i$  is the overall liquid molar composition and  $K_i^{VL}$  is the vapor – liquid equilibrium constant.

Assuming that the distillate is withdrawn from the liquid phase II ( $x_D = x^H$ ), the operating vapor composition  $y_i$  is computed from the external mass balance for the extractive section on position  $j$  and expressed in terms of external reflux ratio  $R = \frac{L_R}{D}$  and  $F_E/V$  as:

$$y_i = \left( \frac{R}{R+1} + \frac{F_E}{V} \right) x_i + \frac{1}{R+1} x_{i,D} - \frac{F_E}{V} x_{i,FE} \quad (6)$$

- In the condenser, total condensation is assumed. The liquid hold-up inside the decanter ( $U_{dec}$ ) and its overall composition ( $x_{dec}$ ) are determined by a mass balance around the decanter (see Figure 2):

$$\frac{dU_{dec}}{dt} = V - (L^I + L^H) = V - (L_R + D) \quad (7)$$

$$\frac{dx_{i,dec}}{dt} = \frac{V}{U_{dec}} (y_{i,2} - x_{i,dec}) + \frac{L_R}{U_{dec}} (x_{i,dec} - x_{i,R}) + \frac{D}{U_{dec}} (x_{i,dec} - x_{i,D}) \quad (8)$$

- The liquid-liquid split ratio  $\omega$  and the composition of each liquid phase inside the decanter are computed using the modified Rachford-Rice equation for liquid – liquid equilibrium.

$$\sum_{i=1}^c \frac{x_{i,dec} (1 - K_i^{LL})}{1 - \omega + \omega K_i^{LL}} = 0 \quad (9)$$

Where:  $K_i^{LL} = \gamma_i^H(T, \mathbf{x}^H) / \gamma_i^L(T, \mathbf{x}^L)$  and  $\omega = L^I / (L^I + L^H)$

The composition of each phase can be computed as:

$$x_i^H = \frac{x_{i,dec}}{1 - \omega + \omega K_i^{LL}} \quad \text{and} \quad x_i^L = K_i^{LL} x_i^H \quad (10)$$

Therefore, the liquid external reflux liquid and the composition at the column top is:

$$L_R = L^I + \alpha L^{II} = \omega V + \alpha(1 - \omega)V \quad (11)$$

$$x_{i,R} = \frac{L^I x_i^I + \alpha L^{II} x_i^{II}}{L_R} \quad (12)$$

With  $\alpha$  being the proportion of the distillate rich phase  $L^{II}$  that is refluxed to the column.

The distillate flow rate is:

$$D = (1 - \alpha)(1 - \omega)V \quad (13)$$

and the reflux ratio can be determined as:

$$R = \frac{\omega + \alpha(1 - \omega)}{(1 - \alpha)(1 - \omega)} \quad (14)$$

The optimization of heterogeneous extractive batch distillation is based on the simplified model above, implemented in Matlab, including NRTL equation, and connected to the genetic algorithm tool from the global optimization toolbox in Matlab.

The initial load is 20 moles with composition 0.2704 in chloroform, 0.6714 in methanol and 0.0582 in water as considered by Van Kaam et al.<sup>25</sup>, taken from a real liquid waste from solvent extraction process widely used for separating bioactives substances from biological sources. The distillation column is considered as operating under atmospheric pressure and having 45 theoretical plates with the entrainer fed at the column top, thus defining a unique extractive section. The decanter liquid hold-up is 1 mole. The entrainer is supposed to be at its boiling temperature.

The general software architecture of the simulation through the simplified modeling follows the inherent sequence of each operating Task of batch extractive distillation process:

Task 1: Start-up liquid profile of the column is computed from the initial condition of the charge into the still using eq. (3) - (6) at total reflux and  $F_E=0$ . No decanter is included.

Task 2: Decanter filling is simulated for the selected value of  $F_E/V$ . Reflux ratio ( $R_{T2}$ ) is set at unity indicating that a half of the condensed vapor is refluxed  $L_R = 0.5V$ , and the remaining is used to fill the decanter. Eq. (1) and (2) are used to compute the boiler hold up and composition time evolution, considering that a pseudo distillate filling the decanter exists  $D = 0.5V$  and  $\mathbf{x}_D = \mathbf{y}_2$ . The punctual still composition  $\mathbf{x}_N(t)$  is the starting point for determining the column liquid profile by eq. (3) - (6) under  $R_{T2}=1$ . Eq. (6) and (7) are then used to calculate the decanter hold-up and composition time evolution, setting  $\mathbf{x}_R = \mathbf{y}_2$  and  $D=0$ , as there is no real distillate withdrawn in this Task. The stop event is set when the decanter hold up specification is reached ( $U_{dec} = 1\text{mole}$ ). At this time  $t_2$ , the required purity of chloroform rich phase ( $x_{\text{chloroform}}^{\text{II}} \geq 0.99$ ) is verified applying eq. (8) and (9) for the final composition  $\mathbf{x}_{dec}$  into the decanter.

Task 3: Withdrawal of chloroform is simulated with the selected value of  $F_E/V$  and  $\alpha(R_{T3})$ . Constant or piece-wise policy can be defined for the optimization variables  $F_E/V$  and  $\alpha$ . The final still content after Task 2 is used as Task 3 starting point. Every time step  $t$ , the values  $D$  and  $\mathbf{x}_D$  calculated previously at  $(t-dt)$  are used in eq. (1) and (2) to update the boiler amount  $U_N(t)$  and composition  $\mathbf{x}_N(t)$ . Similarly, the liquid composition profile is computed using the equations (3) - (6) from the boiler up to the column top so as to determine the new top vapor  $\mathbf{y}_2(t)$  composition. Thus, the decanter amount  $U_{dec}$  and composition  $\mathbf{x}_{dec}$  are updated from eq. (7) and (8) whereas eq. (10) - (12) are the used to determine the new values of  $\omega$ ,  $\mathbf{x}^{\text{I}}$ ,  $\mathbf{x}^{\text{II}} = \mathbf{x}_D$ ,  $L_R$  and  $\mathbf{x}_R$  to be used in the next time iteration. Simulation of Task 3 ends when  $x_{D,\text{chloroform},T3} < 0.99$ .

Task 4: off cut Task is performed only when  $x_{N,\text{chloroform},T3} > 0.001$ . An intermediate distillate product is drawn with  $F_E/V = 0$  and  $R_{T4} = 5$  until  $x_{N,\text{chloroform},T4} \leq 0.001$ .

Task 5: Withdrawal of methanol is simulated at  $F_E/V = 0$ . The reflux ratio  $R_{T5}$  can be fixed as a constant value or follow a piece-wise policy. The ending event is  $x_{D,\text{methanol},T5} = 0.99$ .



The main results of the simulation using the simplified modeling are operating times ( $t_2, t_3, t_4, t_5$ ), distillate information of key products chloroform and methanol and the off-cut at the end of each Task ( $\mathbf{x}_{D,T3}, D_{T3}, D_{T4}, \mathbf{x}_{D,T5}$  and  $D_{T5}$ ) and the amount of water ( $U_{N,final,H2O}$ ) into the still at the end of the process. All these results are further sent to the genetic algorithm tool in order to evaluate the objective function and the constraints of each individual of the current population.

### 3.2.2. Rigorous model

Rigorous (standard MESH equations) simulation is performed with Prosim BatchColumn commercial software<sup>62</sup>. The number of theoretical trays of the column is taken as  $N=45$  and the same conditions selected for simplified simulation were kept. Negligible liquid hold-up and pressure drop inside the column are assumed, hypothesis that were achieved in the packed batch distillation column in which experimental separation of chloroform – methanol using water was performed and published elsewhere<sup>24</sup>. Therefore, consideration of energy balance is the main key difference between simplified and rigorous simulation. For the sake of comparison, the rigorous simulation using ProSim Batch is started for all studied cases with the boiler and decanter filled with the optimized values (composition and liquid holdups) at the end of the decanter filling Task 2 described in the section above and computed by simplified modeling. Task 3, Task 4 (if necessary) and Task 5 are also simulated using ProSim Batch and setting as stop condition the purity of chloroform and methanol in Task 3 and 5, same stop conditions of simplified simulation. Task 4 is only simulated if the molar composition of chloroform into the still at the end of Task 3 is higher than 0.001.

### 3.3. Batch distillation optimization problem definition

We consider a batch distillation optimization aiming at maximizing a profit function ( $OP$ ) while respecting constraints on the product recovery yield, whereas purity is used as Task ending event. It is a nonlinear optimization problem under constraints. The classical formulation with equality constraints  $g_k$  and inequality constraints  $h_k$  is:

$$\begin{aligned}
& MIN \quad -OP(\mathbf{x}) \\
& g_k(\mathbf{x}) = 0 \quad k = 1, \dots, n_g \\
& h_k(\mathbf{x}) \leq 0 \quad k = 1, \dots, n_h
\end{aligned} \tag{15}$$

### 3.3.1. Objective function and constraints

The optimization problem deals with maximizing the economical profit  $OP$  with positive contribution from the product sales per batch (\$/mole), and pay-off given by the solvent consumption cost (\$/mole), the total operating cost (\$/time) and the further disposal of non recovery amount of key components.

$$MIN \quad \{-OP(x)\} = \sum_{i=1}^2 R_i * M_i^0 * c_i - m_{water} * c_3 - time_{Total} * c_4 - \sum_{i=1}^2 (1 - R_i) * M_i^0 * c_i \tag{16}$$

Subject to chloroform and methanol recovery yield (%):

$$90 - R_i \leq 0 \tag{17}$$

The corresponding factor  $c_i$  are reported in Table 2. The incomes is determined considering the recovery yield  $R_i$  of each component, the molar amount in the initial charge  $M_i^0$  and the typical sale price ( $c_1$  and  $c_2$  in Table 2). The water cost  $c_3$  is computed on the basis of the consumed water, namely the fresh water minus the recovered water at the end of Task T5. The total time is the summation of the time of each operating steps. Cost associated to further disposal and treatment of non recovery amount of methanol and chloroform is considered proportional to the sale prices.

Insert Table 2

The formulation of the optimization problem includes no consideration about distillate purity of key components. Instead 0.99 and 0.001 chloroform molar purity is used as a stop event for the distillation Tasks T3 and T4 respectively. A 0.99 methanol molar purity is used as a stop event for the distillation Task T5. In this work, only inequality constraints are defined, with respect to chloroform and methanol molar recovery which should be higher than 90%.

### 3.3.2. Optimization variables

Optimization variables are chosen among all the available degrees of freedom for each Task of the batch distillation process. For the HEBD process, we select: (i) the entrainer flowrate  $F_E/V$  that is kept constant in Task T2 (merged with T1) and T3; (ii) the portion  $\alpha$  of distillate-rich phase refluxed to the column along with all the entrainer-rich phase during Task T3. Note that according to equation 14, the reflux policy for Task T3 depends on the liquid – liquid split ratio in the decanter, and on the  $\alpha$  policy.; (iii) the piece-wise reflux policy  $R_{T5}$  for Task T5 (methanol production with no decanter).

The  $F_E/V$  variation range is selected after the preliminary results of Van Kaam et al.<sup>25</sup>. Indeed, extractive distillation with the 2.1-2b diagram (Figure 1) requires a minimum entrainer flow rate that was evaluated by Van Kaam et al.<sup>25</sup> as  $(F_E/V)_{minim} = 1.0$  for the chloroform – methanol – water mixture under infinite reflux. These authors did the feasibility analysis and simulation with  $F_E/V = 1.2$  but they needed a larger value in their experiments to expel the methanol from the top vapor and achieve the expected chloroform purity in the distillate. Those authors also investigated the  $\alpha$  range between 0.4 and 0.9. The reflux range, for which exists a minimum feasible value in connection to the still path from an initial load composition (see<sup>25</sup>), was set between 1 and 10.

Optimization variables and ranges are shown in Table 3 for all cases.

Insert Table 3

Case I is the basic one, with constant reflux policies in Tasks T3 ( $\alpha_{T3}$ ) and T5 ( $R_{T5}$ ). Case II proposes a two piece wise reflux policy ( $R_{1,T5}$  and  $R_{2,T5}$ ) for methanol production Task T5. Case III proposes a two piece wise reflux policy ( $\alpha_{1,T3}$  and  $\alpha_{2,T3}$ ) for chloroform production Task T3. Case IV proposes a two piece wise reflux policy ( $\alpha_{1,T3}$  and  $\alpha_{2,T3}$ ) for chloroform production Task T3 and a two piece wise reflux policy ( $R_{1,T5}$  and  $R_{2,T5}$ ) for methanol production Task T5. Case V proposes a two piece wise entrainer flowrate ( $F_E/V_{1,T2-T3}$  and  $F_E/V_{2,T3}$ ) and a two piece wise reflux policy ( $\alpha_{1,T3}$  and  $\alpha_{2,T3}$ ) for chloroform production Task T3. Case VI proposes a two piece wise entrainer flowrate ( $F_E/V_{1,T2-T3}$  and  $F_E/V_{2,T3}$ ) and a two piece wise reflux policy ( $R_{1,T5}$  and  $R_{2,T5}$ ) for methanol production Task T5. Case VII considers two

piece wise policies for the three optimization variables: ( $F_E/V_{1,T2-T3}$  and  $F_E/V_{2,T3}$ ), ( $\alpha_{1,T3}$  and  $\alpha_{2,T3}$ ) and ( $R_{1,T5}$  and  $R_{2,T5}$ ).

### 3.3.3. Optimization methods

Based on the literature survey above and on our own experience, we solve the optimization problem by using a Genetic Algorithm stochastic method, available in Matlab global optimization toolbox<sup>63</sup>. Preliminary sensitivity analysis was performed for the key parameters of genetic algorithm such as the initial population, the selection rate and the mutation rate. Results are summarized in Table 4 for the reference. As expected, stricter values for the initial population, selection rate and mutation rate increase the evaluation number of objective function that is proportional to the computational time for obtaining similar optimal value of the selected optimization variables ( $F_E/V$ ,  $\alpha$  and  $R_{T5}$ ) and the objective function. Therefore, the initial population is set at 50, the selection rate is 0.8 and the mutation rate is 0.01 in the remaining of the paper (last column in Table 4). These parameters provided a good compromise between performance of genetic algorithm and computation time. The genetic algorithm works as follows: individuals of the initial population characterize the manipulated variables and they are sent to the simplified model also coded in Matlab. Then the genetic algorithm retrieves the results required to evaluate the objective function and constraints for each individual. The optimization is stopped if no improvement of the penalized objective function is achieved after 10 generations.

The constraints are introduced into the objective function by penalty terms. The optimization problem aims then at finding the minimum of the following  $Profit_{penalized}$  penalized Profit function:

$$Profit_{penalized} = Profit + \sum_k (P_k \times (g_k)^2) + \sum_k (Q_k \times (h_k)^2) \quad (18)$$

$$\text{with } P_k(x) = \begin{cases} 0 & \text{if } g_k(x) = 0 \\ P_k^0 & \text{if } g_k(x) \neq 0 \end{cases} \quad \text{and} \quad Q_k(x) = \begin{cases} 0 & \text{if } h_k(x) \leq 0 \\ Q_k^0 & \text{if } h_k(x) > 0 \end{cases}$$

and  $P_k^\circ$  and  $Q_k^\circ$  are weighting factors equal to the non penalized function value divided by the squared tolerances on the constraints. The tolerance on the recovery yield constraints is 1%. Therefore, any failure to reach the constrained value of 90% molar recovery is penalized by  $1/(0.01)^2$  in the profit function.

#### 4. Results

Table 5 displays the optimal values for  $(F_E/V)_{T2-T3}$ ,  $\alpha_{T3}$  and  $R_{T5}$  for all cases, along with the duration of each Task and the switch time when the piece-wise policy for optimized variables is defined. The objective function of the optimized solution with the simplified model  $OP_{SM}$  and computed with the optimized parameters by rigorous simulation  $OP_{RS}$  are also reported along with the total operating time. Table 6 displays holdup, compositions and recoveries with the optimized parameter values used in simulation with the simple model and with the rigorous simulation model for each case. Figure 3 shows the still path of Task T3, T4 and T5 computed by both models as well, along with selected liquid composition profiles in the column.

Insert Table 5

Insert Table 6

Insert figure 3

General remarks arise from the analysis of Table 5 and 6 and Figure 3:

- The optimization with the simplified model always matches the recovery constraints in chloroform and methanol for all cases and, therefore, did not penalize the objective function value relevant for each case. The product purities are achieved as well because they are used as Task ending events for Task T3 and T5.
- Concerning the decanter filling Task T2, results are almost identical for all cases, despite different  $F_E/V$  values (see Table 6). Duration equals 8 min and the final composition is almost identical (Figure 3). That analysis prompted us to use the final amount and composition into the still and into the decanter of Task T2 as initial conditions for the rigorous simulation in both vessels as can be seen in Figure 3. It also enabled easy comparison of the simplified and rigorous models for Tasks T3 to T5.

- In most cases, the operating time of each Task computed by rigorous simulation is smaller than that obtained by simplified simulation. But the recovery yield for chloroform and water is higher by rigorous simulation. The likely reason could be that the energy balance is taken into account in the rigorous simulation. Liquid profiles computed by simplified modeling and rigorous simulation are displayed in Figure 3 for several boiler compositions. They look alike, hinting at the low incidence of the inclusion of energy balance. A closer look shows that the ending point of the liquid profile at the column top ( $sn_{extr}$ ) is located closer to the water apex in the case of rigorous simulation mainly when the half time of Task 3 is overtaken. It implies a different decanter split ratio and withdrawal of chloroform is carried out under a higher entrainer reflux, providing a better recovery yield and distillate purity for this component. Conversely, the recovery yield for methanol is smaller for rigorous simulation, in particular for cases I, II and VI where methanol is more diluted into the still at the beginning of Task 5 with methanol composition around 0.87, 0.83 and 0.83 respectively (see  $x_{final,T3}$  in Figure 3).
- Off-cut operation step T4 is not necessary in the rigorous simulations because the chloroform content into the still is already below the composition of 0.001 required to proceed to Task 5, as the location of  $sn_{extr}$  allows already good recovery of chloroform.
- For all cases in Figure 3, the still path moves towards the water – methanol edge during Task 3, in a direction imposed by the summation of the entrainer feeding vector  $+E$  and the distillate withdrawal vector  $-D$ . Good agreement is obtained between the simplified model results (continuous lines) and rigorous simulation results (symbols). After the off-cut Task 4, the composition is indistinguishable from the water – methanol edge and methanol production Task 5 proceeds along that triangle edge.
- Coupling of the simplified model with a genetic algorithm allows a good estimation of optimal operating conditions with less computational effort and time than trial and error. It can therefore be used as a first approach for the optimal analysis of heterogeneous batch extractive distillation and then, further corroboration can be performed by using rigorous simulation.

Insert figure 4

- In all cases, the computed value of  $OP_{RS}$  is higher than  $OP_{SM}$  (Table 5). However, figure 4 shows that they share the same trend. Case VII involving two constant piece-wise policy for all optimization variables gives the optimal profit compared to the worst case I (+41.8% and +30.1%, respectively). The second best option is case IV. However,  $OP_{RS}$  of case IV and VII are almost identical within 0.2% although the simplified model shows a greater difference of 5.5%). That happens because the cost function naturally favors chloroform and methanol sales ( $c_1$  and  $c_2$  in Table 2) and the simplified model case VII shows higher chloroform and methanol than case IV whereas the rigorous model shows similar recoveries (Table 6).

- The cost associated to the make-up of fresh water is negligible in the total cost of the process because the high recovery of water into the still at the end of the process and the lowest price  $c_4$  (see Table 2)

#### 4.1. Analysis of the basic case with constant parameter values

The simplest operating mode, represented by case I with constant variables value, shows the lowest profit as expected because it has the longest operating time as well as not so good chloroform and methanol recovery yields. Hence, total time almost reaches 10 hrs, which may not be easy to implement for operation in most European countries subjected to 7 to 8 hrs working shifts. The optimal entrainer flow rate  $F_E/V$  equals 1.75, quite above the  $(F_E/V)_{minim} = 1.0$  which again confirm the experimental observation that a significant entrainer flowrate is needed to achieve high purity chloroform, namely 0.99. As discussed, a high chloroform recovery is connected to the ability to keep the overhead vapor composition near the binary heteroazeotrope which is favorable for a split ratio to produce high purity chloroform. The optimal solution shows that it is achieved by using a reflux policy that returns  $\alpha = 0.881$  of the chloroform-rich phase from the decanter, corresponding to an effective average reflux of 7.55 during Task 3 (Table 5). With such a reflux, Task T3 is a high consuming operation time and a large amount of entrainer had to be fed, namely 106 moles (Table 6). At the end of Task T3, very little chloroform is left, as the recovery shows (Table 6 and Figure3).

For reasons discussed before, rigorous simulation is started from the composition after Task 2 and shows qualitatively the same features than the simplified model simulation (table 6). For case I, the stop event of Task T3 is the optimized total time, namely 189 min. Then, the rigorous model simulation leads to a better chloroform purity and the chloroform recovery at the end of Task T3 is greater by several percent. Those features prevent from simulating an off-cut time because the chloroform molar composition is already below 0.001 in the still, and methanol production Task T5 can proceed immediately after Task 3 with the optimized reflux value and a stop event set as methanol purity equal to 0.99. The energy balance effect, taken into account in the rigorous simulation, has sped the light component, methanol removal as T5 time is reduced by 48 min. However, methanol production result is mitigated because the methanol recovery is almost 5% below the simple model recovery. Note in Figure 3 that the still composition at the beginning of Task 5 is located closer to water vertex and the stipulated recovery of methanol was not achievable by rigorous simulation using the lowest value of  $R_{T5}$  constant policy.

#### 4.2. Analysis of piece-wise parameter value cases

Case II considers a two value reflux policy during methanol recovery. The total time is reduced by 36%, boosting the profit by 22%. The effect is most pronounced for Task 5 where a smaller average reflux values  $R_{T5}$  enable to operate in lesser time (41% compared to case I). The greatest recovery yield of methanol is provided by this case because of the highest reflux ratio after the switch time in Task 5 compared to cases IV, VI and VII. For Task 3, the smaller  $\alpha_{T3}$  value leads to a smaller average reflux and T3 time is reduced by 32%, while keeping chloroform recovery above 91% molar. That helps reducing the still content at 80 moles at the end of Task 3, 24% less than for case I. The increase of the boiler content during batch extractive distillation is one of its major drawbacks of the process and the initial charge can be included as an optimization variable in order to accomplish a geometrical constraint related to the maximum capacity of the still<sup>41</sup>. The selectivity and the molar volume of the entrainer should be considered as criteria during the entrainer selection.



Case III considers two reflux values during T3 through a two piece-wise  $\alpha_{T3}$  value operation but a constant reflux policy  $R_{T5}$  is retained for Task 5. The two  $\alpha$  values correspond to significantly smaller average refluxes (table 5) compared to  $\alpha$  constant policy (cases I, II and VI). Operating at low reflux enables to withdraw chloroform distillate faster and T3 time is reduced by 60%, also maintaining the still content at the end of Task 3 below 55 moles, almost 50% less than case I. This has been already noticed from the feasibility analysis of Van Kaam et al.<sup>25</sup> who recommended to start Task T3 at low reflux for diminishing operation time, then to increase it so as to prevent the still composition to enter the unfeasibility region and to accomplish the recovery yield constraint. Regarding Task T5, time is much longer than case I, because of the highest reflux value  $R_{T5}$  reaching almost 9. Recovery yield of methanol overpass the set minimum value and it was also validated for rigorous simulation. Those factors explain why this case is positioned as second worst alternative in Figure 4.

Case IV combines both  $\alpha_{T3}$  and  $R_{T5}$  two values operation under constant  $F_E/V$ . The intervals of  $\alpha_{T3}$  (0.5551 – 0.8318) and  $R_{T5}$  (3.3001 - 6.6360) contain the smallest two values compared to the others two piece-wise policy, case III, V, VI and VII. As expected the benefits observed for cases II and III sum up. As a consequence, the overall profit is +34% greater than case I whereas the operation time is reduced by 43%. The liquid content into the boiler is the second smallest one, only increasing 2.7 times the initial charge. Recovery of chloroform and methanol are well fulfilled and case IV remains the second best profitable alternative behind case VII.

Case V investigates a two entrainer flowrate value  $F_E/V$  operation with a two piece-wise  $\alpha_{T3}$  value operation as in case III but reflux ratio  $R_{T5}$  is kept constant. Compared to case III, profit is slightly higher (6.3%) and parameter values are close. Time is reduced for Task 5 but increased for Task 3 along with the still content. Recovery is higher for Task 3 but lower for Task 5. Case V has an intermediate position in the profit trend displayed in Figure 4.

Case VI confirms the poor interest of running a two entrainer flowrate value  $F_E/V$  operation under constant  $\alpha_{T3}$  while maintaining a clear interest for running a two reflux  $R_{T5}$  operation. Compared to case II

(two reflux  $R_{T5}$  operation), the advantages of  $R_{T5}$  are similar in Task 5 with a 38.4% reduction of T5 time. The two  $F_E/V$  values bring no improvement because the shift happens at the last minute of T3 operation. The longer T3 operation occurs because of a greater  $\alpha_{T3}$  value. That enables a better chloroform recovery (+4.1%) than case II, which is the main reason for the +5% boost in profit. That boost is not significant, especially as the rigorous simulation predicts a -0.1% profit drop. The methanol recovery yield obtained from rigorous simulation fails to reach the fixed constraint, as compared to case II, reflux ratio  $R_{T5}$  is smaller after the switch time in Task 5.

Case VII is the best alternative among all studies cases (Figure 4). Compared to case VI, it shows an important improvement of the profit when both  $F_E/V$  and  $\alpha_{T3}$  follows two piece-wise policy at the same time. The profit increases by +41.8% and total time is reduced by 43.8% compared to case I. Notice that optimal values for  $F_E/V$  and  $R_{T5}$  are very similar to case VI but the switch time for  $F_E/V$  now takes place in the middle of the duration of Task 3. The two  $\alpha_{T3}$  values operation is responsible for the smaller T3 duration and the increase in profit. Comparing to the second best case IV, the middle value of  $F_E/V$  of case VII is very close to the constant  $F_E/V$  computed for case IV. Again, the lower second value for  $\alpha_{T3}$  reduces the T3 duration and improves profit, together with higher recovery yields for chloroform and methanol.

However, practical implementation of the optimal parameter will favor second best case IV over the best case VII because variation of the entrainer flow rate in case VII may not be easy to control on an industrial column. According to the rigorous simulation results, both cases give similar profit.

### 4.3. Analysis of the parameter influences

Now, considering all cases, Figure 4 clearly shows that the most efficient parameter to play with for increasing the profit is  $R_{T5}$ . It can be deduced comparing the cases I vs II, III vs IV and V vs VII wherein the definition of two piece-wise constant policy for  $R_{T5}$  improves the objective function by 14%, 15.2% and 14.6%, respectively for each couple of cases.

Those four cases II, IV, VI and VII exhibit the best profits (see Figure 4) and HEBD run within less than 7 hrs, a much suitable scheduling in European countries than the remaining three cases I, III and V all above 9 hrs.

Second in influence comes parameter  $\alpha_{T3}$ , the portion of the chloroform-rich phase that is refluxed to the column along the entrainer-rich phase because it reduces significantly the operating time for chloroform withdrawal. Influence of  $\alpha_{T3}$  can be evaluated by comparison of cases I vs III, II vs IV and VI vs VII. For each couple of case, a two piece-wise constant policy for  $\alpha_{T3}$  enables to increase the profit by 5.7%, 6.9% and 7.05% respectively.

Third, the entrainer flowrate  $F_E/V$  has the lowest influence on profit as shows a comparison of cases II vs VI, III vs V and IV vs VII, only improving the profit by 3.6%, 3.7% and 4.3, respectively for each couple of cases. For the rigorous model simulation the benefit of piece wise  $F_E/V$  policy is even not convincing at all: case V has a better  $OP_{RS}$  profit than case III, case VI has a slightly lower one than case II and case VII and IV are almost identical.

Overall, one would suggest keeping  $F_E/V$  constant near 1.8. Concerning  $\alpha_{T3}$  and  $R_{T5}$ , a two piece-wise value operation is recommended, respectively for reducing Task 3 time and still content and for reducing Task 5 time, while keeping the high purity and recovery on both products chloroform and methanol. These recommendations match with the optimal operating strategy illustrated by case IV, simpler to run in industrial practice than case VII.

## **5. Conclusion**

Heterogeneous extractive batch distillation of the chloroform – methanol minimum boiling temperature azeotropic mixture has been studied with water as a heterogeneous entrainer. The ternary diagram belongs to the 2.1-2b class and requires a minimum entrainer flowrate to be feasible. With the continuous feeding of water, the unstable ternary heteroazeotrope is replaced by the saddle binary heteroazeotrope water –

chloroform in the vapor overhead. Condensation of the vapor enables to remove the chloroform-rich phase and obtain better than 0.99 molar purity chloroform. The water-rich phase is totally refluxed to the column, along with a portion  $\alpha$  of the chloroform-rich phase in order to improve chloroform recovery as was suggested in the literature<sup>25</sup>. Unlike to homogeneous extractive distillation, the reflux at the column top implies that a portion  $\alpha$  of the distillate chloroform-rich phase is refluxed along with the water-rich phase in order to assure both high purity and recovery by maintaining longer the top vapor closer to the heteroazeotrope.

The column behavior is first modeled with a simplified tray by tray model based on constant molar overflow and zero tray holdup hypotheses. Coded in Matlab and coupled with the genetic algorithm from Matlab global optimization toolbox, it allows investigating seven cases with different parameter policies, including constant and piece-wise policies. The optimization parameters are the usual entrainer flowrate  $F_E/V$  and reflux policy  $R_{T5}$  for the methanol production, and for the first time the portion  $\alpha_{T3}$  of distillate-rich phase refluxed to the column along with all the entrainer-rich phase during the chloroform production Task. The optimization aims at maximizing a profit function, with recovery yields constraints introduced as penalties and purity target used as Task ending event.

All optimized solutions achieve higher than 90% molar recovery yields and purity higher than 0.99 for both products chloroform and methanol. Results are also confirmed by rigorous simulation and in agreement with earlier experiments<sup>25</sup> demonstrating the good performance of coupling simplified model and genetic algorithm as first approach.

Regarding the operation policy, the two piece-wise parameter values policies for all three parameters increases profit by 41.8% and total time is reduced by 43.8% compared to the constant single value parameter case. The most efficient parameter to play with for increasing the profit is  $R_{T5}$ , the reflux during the methanol production Task, reducing significantly the total operation time. Second in influence comes parameter  $\alpha_{T3}$ , the portion of the chloroform-rich phase that is refluxed to the column along the entrainer-rich phase because it halves the operating time for chloroform withdrawal. Finally the entrainer flowrate

$F_E/V$  has the least influence. Therefore keeping  $F_E/V$  constant near 1.8 and using two piece-wise value operations  $\alpha_{T3}$  and  $R_{T5}$  is recommended to achieve the best profit.

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## **Table Caption**

Table 1. Thermodynamic model parameters

Table 2. Economical cost functions taken into account in the objective function

Table 3. Optimization variables, ranges and constraints

Table 4. Parameter sensitivity analysis on the GA optimization results

Table 5. Summary of optimization results

Table 6. Comparison of simulation from the optimal solution parameter values, using simple and rigorous model

## **Figure Caption**

Figure 1. Chloroform (A) – Methanol (B) – Water (E) residue curve map (class 2.1-2b)

Figure 2. Batch rectifying column configuration for heterogeneous extractive distillation.

Figure 3. Comparison of still path computed by the simplified model and rigorous simulation.

Figure 4. Profit ranking of optimized cases.

Table 1. Thermodynamic model parameters

<b>Vapor – Liquid – Liquid equilibrium and Liquid – Liquid equilibrium</b>			
<b>Binary Coefficients for NRTL model</b>	$A_{ij}$ [cal/mol]	$A_{ji}$ [cal/mol]	$\alpha_{ij}$
chloroform – methanol	2736.86	-1244.030	0.0950
chloroform - water	3303.40	3533.100	0.2000
methanol - water	-253.80	845.206	0.2994

Table 2. Economical cost functions taken into account in the objective function

cost function	object	value	basis
$c_1$	Chloroform	+ 3.82 \$.mol <sup>-1</sup>	Chloroform in product
$c_2$	Methanol	+ 0.59 \$.mol <sup>-1</sup>	Methanol in product
$c_3$	Water	- 0.007 \$.mol <sup>-1</sup>	(fresh – recovered) water
$c_4$	Overall operating cost	- 0.0161 \$.min <sup>-1</sup>	Total time
$c_5$	Offcut	< 0 see text	Lost chloroform and methanol

Table 3. Optimization variables, ranges and constraints

<b>Case</b>	<b>Optimized variable<sub>Task</sub> and [range]</b>
I	$F_E/V_{T2-T3}$ [1.4-2.0]; $\alpha_{T3}$ [0.40-0.95]; $R_{T5}$ [1.0-10.0]
II	$F_E/V_{T2-T3}$ [1.4-2.0]; $\alpha_{T3}$ [0.40-0.95]; $R_{1,T5}$ [1.0-5.0]; $R_{2,T5}$ [5.0-10.0]
III	$F_E/V_{T2-T3}$ [1.4-2.0]; $\alpha_{1,T3}$ [0.40-0.70]; $\alpha_{2,T3}$ [0.70-0.95]; $R_{T5}$ [1.0-10.0]
IV	$F_E/V_{T2-T3}$ [1.4-2.0]; $\alpha_{1,T3}$ [0.40-0.70]; $\alpha_{2,T3}$ [0.70-0.95]; $R_{1,T5}$ [1.0-5.0]; $R_{2,T5}$ [5.0-10.0]
V	$F_E/V_{1,T2-T3}$ [1.4-1.7]; $F_E/V_{2,T3}$ [1.7-2.0]; $\alpha_{1,T3}$ [0.40-0.70]; $\alpha_{2,T3}$ [0.70-0.95]; $R_{T5}$ [1.0-10.0]
VI	$F_E/V_{1,T2-T3}$ [1.4-1.7]; $F_E/V_{2,T3}$ [1.7-2.0]; $\alpha_{T3}$ [0.40-0.95]; $R_{1,T5}$ [1.0-5.0]; $R_{2,T5}$ [5.0-10.0]
VII	$F_E/V_{1,T2-T3}$ [1.4-1.7]; $F_E/V_{2,T3}$ [1.7-2.0]; $\alpha_{1,T3}$ [0.40-0.70]; $\alpha_{2,T3}$ [0.70-0.95]; $R_{1,T5}$ [1.0-5.0]; $R_{2,T5}$ [5.0-10.0]

Table 4. Parameter Sensibility analysis on the genetic algorithm optimization results

Parameter varied	Reference Set	Initial Population	Initial Population	Selection rate	Mutation rate	Final set
Initial population	100	10	50	100	100	50
Mutation rate	0.05	0.05	0.05	0.05	0.01	0.01
Selection rate	0.5	0.5	0.5	0.8	0.5	0.8
$\alpha$	0.8817	0.701	0.8812	0.8826	0.8814	0.8815
$F_E/V$	1.721	1.674	1.711	1.763	1.755	1.755
$R_{T5}$	7.548	6.893	7.361	7.578	7.7891	7.8507
Objective function (\$)	15.681	10.267	15.220	15.142	15.26	15.38
Recovery yield Chloroform (%)	92.71	90.04	92.12	92.56	91.98	92.7
Recovery .yield Methanol (%)	90.93	88.14	90.02	90.91	90.4	90.7
Objective function evaluation number	1282	160	882	813	985	762

Table 5. Summary of optimization results

Task	T1+T2		T3 CHCl <sub>3</sub> removal			T4	T5 CH <sub>3</sub> OH removal		Full process		
	$F_E/V_{T2}$	Duration (min)	$F_E/V_{T3}$	$\alpha_{T3}$ (mean $R_{T3}$ )*	Duration (min)		Duration (min)	$R_{T5}$	Duration (min)	Total duration (min)	OP <sub>SM</sub>
I	1.7550	8	1.7550	0.8815 (7.55)	189.0	11	7.8507	390.0	598.0	15.38	18.23
II	1.8543	8	1.8543	0.8312 (5.07)	127.0	14	3.4520 8.5570	180.0 50.0	379.0	18.76	22.34
III	1.8027	8	1.8027	0.6109 (1.69) 0.8485 (5.74)	40.1 36.1	8	8.9896	490.0	582.2	16.67	19.92
IV	1.8101	8	1.8101	0.5551 (1.39) 0.8318 (5.07)	30.1 64.1	9	3.3001 6.6360	190.0 40.0	322.2	20.69	23.67
V	1.6710	8	1.6710 1.8530	0.6158 (1.72) 0.8867 (7.94)	41.0 53.0	5	8.2200	440.0	547.0	17.72	20.33
VI	1.6982	8	1.6982 1.9510	0.8501 (5.82)	144.2 1.1	8	3.5299 7.6502	190.0 50.0	401.3	19.74	22.14
VII	1.7001	8	1.7001 1.9530	0.5681 (1.43) 0.8050 (4.26)	32.1 40.1	4	3.5308 7.6490	210 40	334.2	21.81	23.61

\* for Task T3,  $R_{T3}$  depends on  $\alpha_{T3}$  (see equ. 8)

Table 6. Comparison of simulation from the optimal solution parameter values, using simple and rigorous model

Simulation using the optimal solution parameter values	Case I $F_E/V_{T2-T3}; \alpha_{T3}; R_{T5}$		Case II $F_E/V_{T2-T3}; \alpha_{T3}; R_{1,T5}; R_{2,T5}$		Case III $F_E/V_{T2-T3}; \alpha_{1,T3}; \alpha_{2,T3}; R_{T5}$		Case IV $F_E/V_{T2-T3}; \alpha_{1,T3}; \alpha_{2,T3}; R_{1,T5}; R_{2,T5}$		Case V $F_E/V_{1,T2-T3}; F_E/V_{2,T3}; \alpha_{1,T3}; \alpha_{2,T3}; R_{T5}$		Case VI $F_E/V_{1,T2-T3}; F_E/V_{2,T3}; \alpha_{T3}; R_{1,T5}; R_{2,T5}$		Case VII $F_E/V_{1,T2-T3}; F_E/V_{2,T3}; \alpha_{1,T3}; \alpha_{2,T3}; R_{1,T5}; R_{2,T5}$	
	Simple model	Rigorous model	Simple model	Rigorous model	Simple model	Rigorous model	Simple model	Rigorous model	Simple model	Rigorous model	Simple model	Rigorous model	Simple model	Rigorous model
T1+T2 filling time (min)	8	N.A.	8	N.A.	8	N.A.	8	N.A.	8	N.A.	8	N.A.	8	N.A.
$x_{dec}$ CHCl <sub>3</sub>	0.9938	See text	0.9928	See text	0.9925	See text	0.9928	See text	0.9908	See text	0.9926	See text	0.9927	See text
CH <sub>3</sub> OH	0.0020		0.0039		0.0040		0.0038		0.0030		0.0040		0.0040	
H <sub>2</sub> O	0.0042		0.0033		0.0035		0.0034		0.0062		0.0034		0.0033	
T3 total time (min)	189.0	189.0	127.0	119.0	76.2	68.0	94.2	67.0	94.0	77.0	145.3	135.0	72.2	63
T3 switch time (min)	-	-	-	-	40.1	41.0	30.1	30.0	41.0	41.0	144.2	0.0	32.1	32
tank I (mol)	5.05	5.22	4.97	5.36	5.17	5.36	5.14	5.36	5.27	5.36	5.19	5.37	5.29	5.36
$x_{D,tankI}$ CHCl <sub>3</sub>	0.9904	0.9931	0.9912	0.9900	0.9902	0.9900	0.9918	0.9900	0.9910	0.9900	0.9914	0.9900	0.9916	0.9900
CH <sub>3</sub> OH	0.0056	0.0061	0.0047	0.0053	0.0055	0.0053	0.0046	0.0053	0.0045	0.0053	0.0044	0.0053	0.0044	0.0053
H <sub>2</sub> O	0.0040	0.0008	0.0041	0.0047	0.0043	0.0047	0.0036	0.0047	0.0045	0.0047	0.0046	0.0047	0.0040	0.0047
CHCl <sub>3</sub> recovery (%)	92.7	96.7	91.3	99.3	94.8	99.3	94.5	99.3	96.7	99.3	95.4	99.4	97.1	99.3
Final still content (mol)	106.0	105.6	80.8	76.6	54.1	50.0	53.7	50.3	59.0	53.5	82.7	78.6	49.8	48.1
T4 off-cut time (min)	11	none	14	none	8	none	9	none	5	none	8	none	4	none
T4 off cut distillate (mol)	0.489		0.622		0.356		0.400		0.222		0.274		0.1778	
$x_{off-cut}$ CHCl <sub>3</sub>	0.6940		0.6880		0.6910		0.6930		0.6890		0.6938		0.6930	
CH <sub>3</sub> OH	0.2020		0.2070		0.2030		0.2020		0.2070		0.2021		0.2020	
H <sub>2</sub> O	0.1040		0.1050		0.1060		0.1050		0.1040		0.1041		0.1050	
T5 total time (min)	390	342	230	212	490	438	230	190	440	399	240	211	250	202
T5 switch time (min)	-	-	180	158	-	-	190	172	-	-	190	161	210	186
tank II content (mol)	12.27	11.63	13.1	12.25	12.6	12.90	12.5	12.49	12.2	12.79	12.4	12.00	12.84	12.45
$x_{D,tankII}$ CHCl <sub>3</sub>	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH <sub>3</sub> OH	0.9901	0.9900	0.9905	0.9900	0.9918	0.9900	0.9920	0.9900	0.9919	0.9900	0.9916	0.9900	0.9918	0.9900
H <sub>2</sub> O	0.0099	0.0100	0.0095	0.0100	0.0082	0.0100	0.0080	0.0100	0.0081	0.0100	0.0084	0.0100	0.0082	0.0100
CH <sub>3</sub> OH recovery (%)	90.7	85.8	96.9	90.3	93.6	95.1	92.6	92.1	90.7	94.3	92.3	88.5	96.6	92.9
Final still content (mol)	94.4	94.0	68.8	64.3	41.3	37.1	41.6	37.8	46.7	40.7	71.1	66.6	37.3	35.5
H <sub>2</sub> O still composition	0.9867	0.9851	0.9932	0.9859	0.9792	0.9914	0.9762	0.9808	0.9733	0.9897	0.9853	0.9819	0.9663	0.9829
H <sub>2</sub> O recovery (%)	99.1	99.2	98.7	99.1	97.1	98.4	96.9	98.6	98.3	98.6	98.4	99.1	97.8	98.3

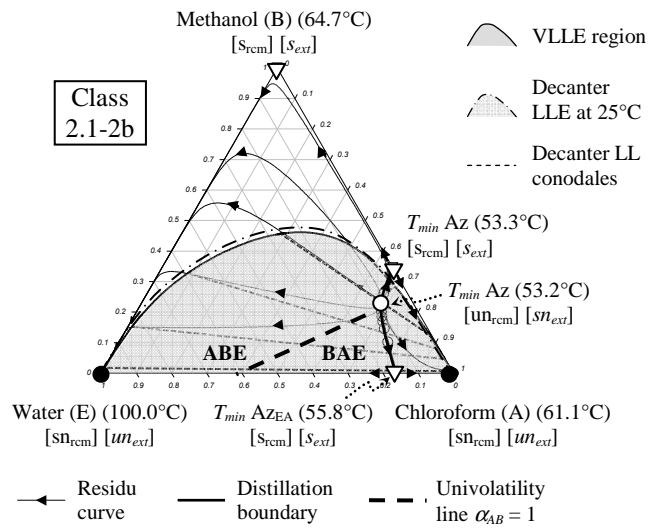


Figure 1. Chloroform (A) – Methanol (B) – Water (E) residue curve map (class 2.1-2b)

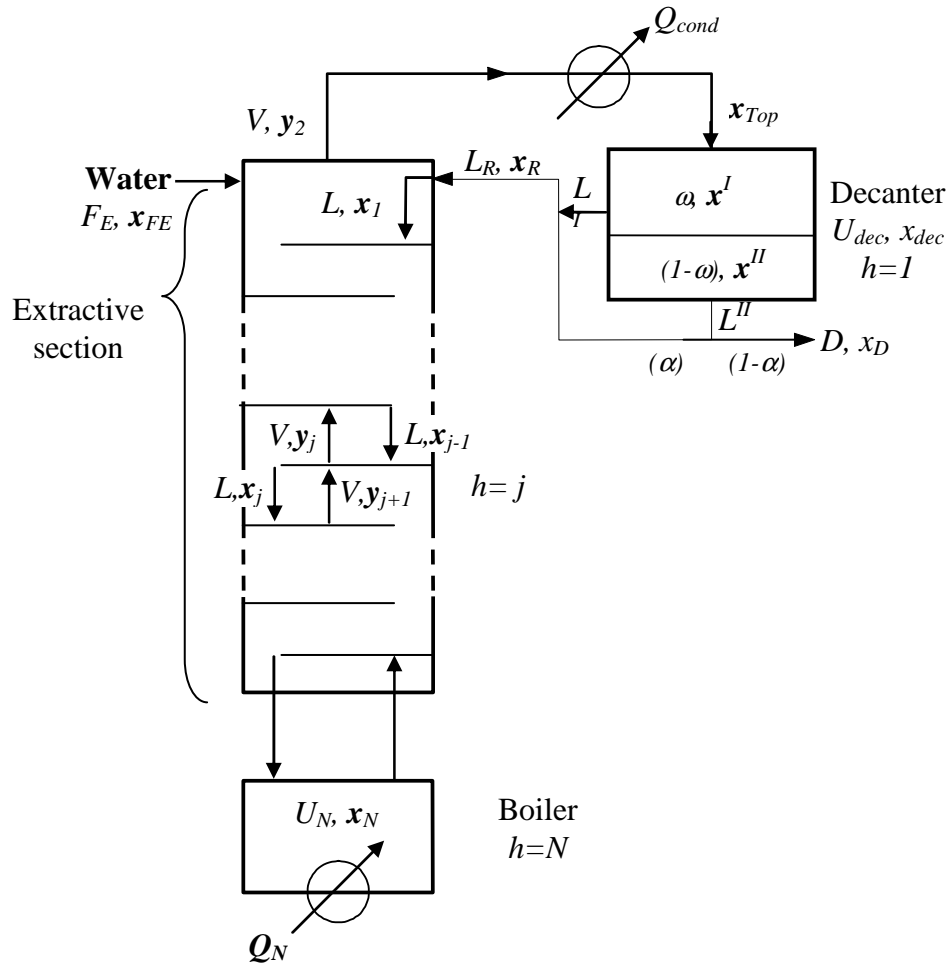


Figure 2. Batch rectifying column configuration for heterogeneous extractive distillation.

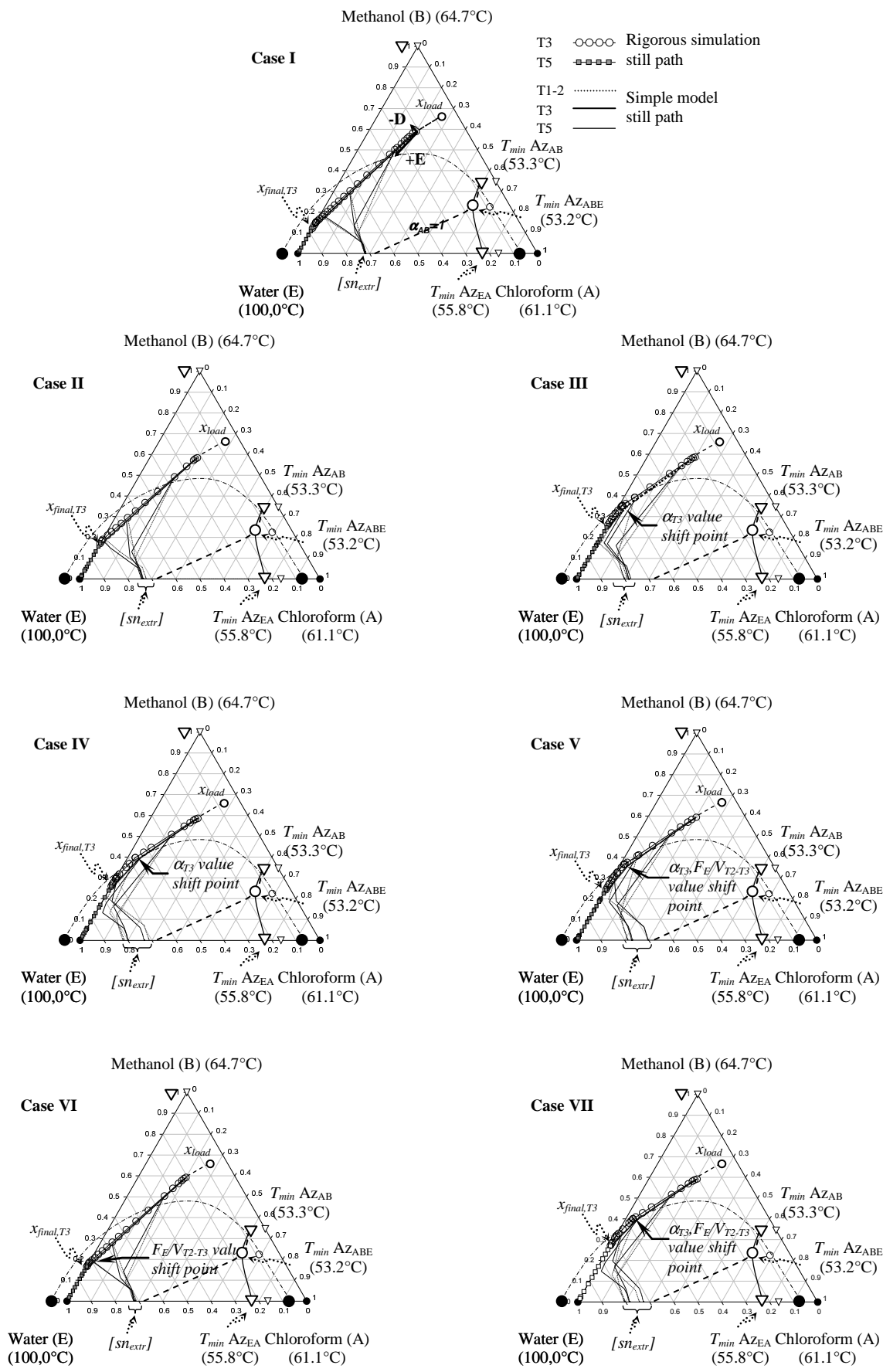


Figure 3. Comparison of still path computed by the simplified model and rigorous simulation.



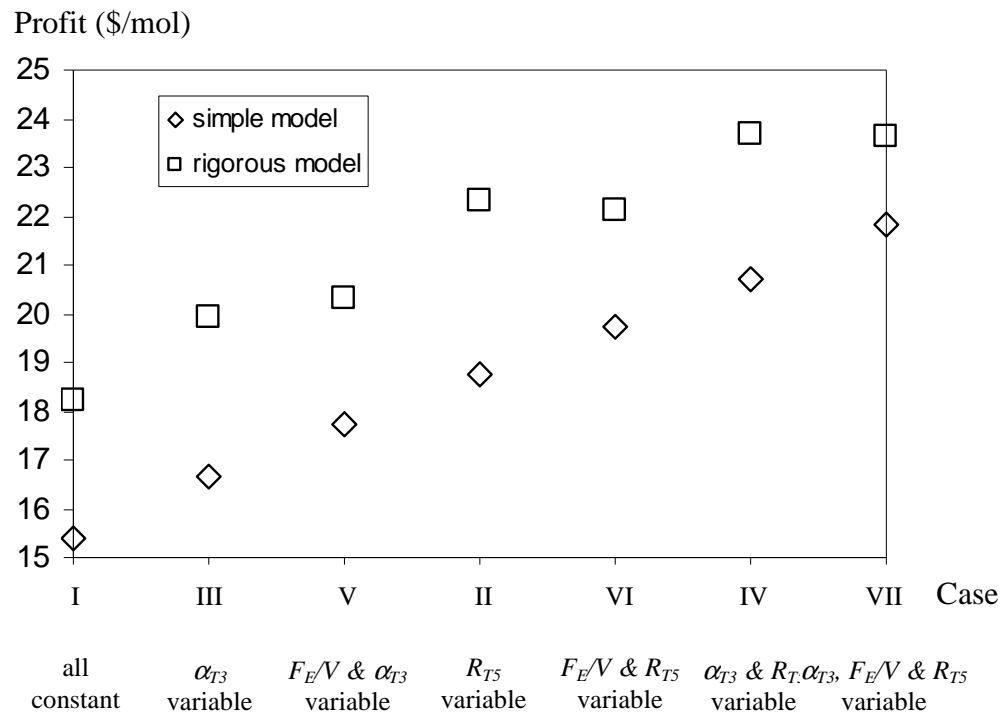


Figure 4. Profit ranking of optimized cases.