



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>
Eprints ID : 19581

To link to this article : DOI:10.1016/j.compchemeng.2017.09.004
URL : <http://dx.doi.org/10.1016/j.compchemeng.2017.09.004>

To cite this version : Stojkovic, Marija and Gerbaud, Vincent and Shcherbakova, Natalya *Cyclic operation as optimal control reflux policy of binary mixture batch distillation*. (2018) Computers and Chemical Engineering, vol. 108. pp. 98-111. ISSN 0098-1354

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Cyclic operation as optimal control reflux policy of binary mixture batch distillation

Marija Stojkovic, Vincent Gerbaud*, Nataliya Shcherbakova

Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France

A B S T R A C T

We revisit the maximum distillate optimal control problem of batch distillation of non-ideal binary zeotropic mixtures. The direct method with full discretization is used. The problem formulation is based on full column dynamics and the distillate flow rate is used as control variable instead of the reflux. The purity constraint is handled as a new state variable, the purity deviation. Literature simulations showed that the cyclic reflux policy (bang-bang type control) performs better than variable reflux (singular type control) or constant reflux policy for small amount of light product in the load. For the first time, a cyclic reflux policy is found as the optimal control solution. The results are confirmed by rigorous simulation of the batch distillation, as the cyclic policy improves by 13% the product recovery over the variable reflux policy. Influence of the relative volatility, vapour flow rate, plate hold-up and initial load is discussed.

Keywords:

Non-ideal binary mixture
Batch distillation
Optimal control
Maximum distillate problem
Direct method

Nomenclature

$u(t)$	Distillate flow rate (control variable) [mol/h]
V	Vapour flowrate (constant) [mol/h]
$L(t)$	Liquid flow rate [mol/h]
$x(t)$	Mole fraction of the light component in the liquid phase
$y(t)$	Mole fraction of the light component in the vapour phase
N	Total number of plates
$U_0(t)$	Tank liquid hold-up [mol]
$U_i, i=1, \dots, N-1$	Liquid hold-up on the plates (constant) [mol]
$U_N(t)$	Reboiler liquid hold-up [mol]
$R(t)$	Reflux ratio [mol/h]
$x_{D,spec}$	Desired purity specification
$p(t)$	Purity deviation
$\sigma_{sepdiff}$	Degree of separation difficulty
t_f	Overall time of the process [h]
n_{cycle}	Total number of cycles

1. Introduction

Our study is motivated by the problem of industrial solvents regeneration. For example, in France, the solvent regeneration has a strong potential: according to a 2011 French national environmental agency ADEME, only 18% of waste solvent is partially regenerated, while 82% is incinerated (Gerbaud and Rodriguez-Donis, 2010). Typically, the concerned binary mixtures are non-ideal, and suitable processes (such as azeotropic or extractive distillation) are required (Van Dongen and Doherty, 1985; Bernot et al., 1991; Rodriguez-Donis et al., 2001; Kim et al., 2001; Gerbaud et al., 2006). In the solvent regeneration industry, the batch operation mode gives the flexibility enabling to handle various solvent lots over the year. In practice, batch operation reflux and heating policies are mostly set based on a valuable know-how which might not be optimal though.

Over a century, many works have focused on operating strategies for the conventional batch column configuration. Kim and Diwekar (2001) reviewed the three operating modes for a batch rectifier, namely constant reflux rate with variable distillate composition, variable reflux rate with constant distillate composition, and finally optimal reflux rate with optimal reflux composition. They defined the last operating mode as the one leading to the most profitable operation. Compared with other operating modes, their optimal reflux rate was also a policy of increasing reflux policy and it led to the shortest batch time. Sorensen (1999) and earlier Jorgensen and Toftegard (1987) discussed the cyclic operation and its practical implementation in batch distillation. It consists in

* Corresponding author.

E-mail address: vincent.gerbaud@ensiacet.fr (V. Gerbaud).

an alternation of three tasks: a reflux drum filling situated below the condenser, total distillate removal into a tank and total reflux from the reflux drum with varying hold-up. Bai et al. (2010) applied Sorensen's strategy by focusing on the influence of the reflux drum hold-up and of the plate hold-up dynamics on operation time. They showed by simulation and experiments how these hold-up dynamics impact the optimal product yield for a given number of cycles. Earlier, Sorensen and Skogestad (1994) proposed an optimal reflux policy based on cycles, and noticed that the number of cycles increases as the batch time decrease. Sorensen (1999) developed a heuristic equation using gPROMS tool for finding the total number of cycles in order to study the cyclic operating policy for a batch distillation column configuration. She found that a cyclic operating policy could significantly reduce the total operating time for mixtures with a low amount of light key component. But clearer guidelines for other mixtures were difficult to formulate, because they depend on the mixture, on the column number of plates and on the product purity and recovery specifications. Jiang and Bai (2012) simulated the cyclic total reflux batch distillation without reflux drum and demonstrated its higher performance compared to constant reflux operation when the initial load contains a low amount of product. Hasebe et al. (1999) and Noda et al. (2001) studied the optimal operating policy, which minimizes the energy consumption in a total reflux column assuming negligible hold-up and constant vapour flow rate. They showed that a higher performance was achieved by optimizing the reflux flow rate, thereby adjusting reboiler and reflux drum hold-up's with time. Finally Bildea et al. (2015) published a review on cyclic distillation technology, where they noted that cyclic operation can be easily implemented in old distillation columns by changing internals.

Mujtaba (2004) reviewed the optimal control problem definition for batch distillation, dividing all problems to belong to one of the three following groups: time minimization, distillate maximization, and profit maximization. He found that the inequality constraint for all groups must be relative to the distillate purity, with the exception of the time minimization problem where one have to add the amount of distillate. Further, he stressed that the control variable chosen should always be the reflux ratio with linear bounds imposed on it, with the exception of the time minimization problem where the final time is to be added to the list of the controlled variables.

Optimal control of batch distillation is challenging in practice compared to 'classical control' due to 1) strong control loop interactions; 2) large measurement delay in composition analyzers (>10 min); 3) frequent occurrence of disturbances. There were many attempts to solve the batch distillation optimal control problem with simplified models (Diwekar et al., 1987; Jorgensen and Toftegard, 1987). Nearly 30 more papers addressing the maximum distillate problem, the minimum time problem or the maximum profit problem have been discussed in the review by Kim and Diwekar (2001). Among them, Coward (1967a, 1967b) applied Pontryagin's maximum principle to the minimum time problem in binary batch distillation with a constant boilup rate to achieve a fixed quantity and purity in terms of minimum batch time. Hold-up on the column internal plates was neglected by Coward. Indeed, the optimal control problem of batch distillation can be written in a standard optimal control form and solved by using Pontryagin's Maximum Principle (PMP). The associated Hamiltonian H is affine with respect to the control variable, u ; $H = H_0 + u \cdot H_1$ and u is bounded between a lower and an upper bound. According to PMP, along the optimal solution the Hamiltonian takes its maximal value among all possible values of the control function. One has to distinguish between two possibilities: either the maximal value of H is reached in interior part of the control interval or on the bounds. In the first case the optimal control is called singular, it can be computed from the extremality condition $dH/du = 0$, which in the affine

case reads $H_1 = 0$. Otherwise, the corresponding control is said to be of bang type (Bonnard and Chyba, 2003). A detailed analysis of the batch distillation optimal control problem is found in Stojkovic et al. (2017) where it was verified that the Hamiltonian found has the right properties.

Confirmed later by others (Robinson, 1970), the optimal reflux policy found by Coward was an increasing reflux policy to maintain a constant purity operation. In any case, it performed much better than a constant and unique value reflux policy. The increasing reflux policy will be later observed in the optimal control policy pattern and be called a singular arc in reference to the optimal control framework explained above. Aside from that preference for a variable optimal reflux policy regarding the minimum time problem, Hansen and Jorgensen (1986) found that an optimal control policy of the boilup rate performed better than an optimal reflux policy. Solving the maximum distillate problem under fixed purity, Farhat et al. (1991) found that a stepwise constant reflux policy achieved a better recovery in a shorter time than a reflux increase policy for the distillate withdrawal periods, followed by a large reflux policy for the off-cuts periods. Regarding the problem of maximizing the total profit, Low and Sorensen (2004) proposed for a multiproduct batch distillation, an optimal operation that consisted in sequences of constant reflux for each product distillation task. Other optimization variables were the number of plates, each task period and the constant boilup vapour flow rate. But other authors recommended earlier to use a variable reflux policy for that problem type (Logsdon and Biegler, 1993).

Then Diwekar (1992) solved the optimal control problem of batch distillation by using a short-cut method based on a quasi-steady-state model for each of the three problem categories listed by Mujtaba. They used this model in an algorithm combining Pontryagin's Maximum Principle and non-linear problem techniques. This formulation reduced the dimensionality of the problem and the computational effort, and it allowed to set bounds on variables such as the reflux ratio. Comparing the optimisation results with those obtained in open literature, Diwekar reached the same conclusions about the optimal operation, namely that an increasing reflux policy is the optimal one. Raducan et al. (2005) took a step further in defining the optimal control problem as they studied the free time optimal control problem. They were the first to describe the reflux ratio optimal control to be of 'bang-bang' type. But they did not refer to a cyclic zero reflux—total reflux policy that was studied by Sorensen, but to a 'bang-bang' shape around an optimal increasing reflux function due to piecewise step approximation. Their simplified mathematical model consisted in a one-plate distillation process. A zero reflux—total reflux policy shall occur in the optimal control patterns and it will be called through the paper a bang type optimal control policy, in accordance with standard optimal control analysis (Bonnard and Chyba, 2003).

In the present paper, we investigate the optimal control problem in order to find the optimal reflux policy for a maximum distillate problem. Although it is a fifty years old problem solved in many ways in the literature, new contributions are added in several other aspects:

- Our study is limited to binary mixtures of various relative volatilities with a single distillation task under constant average product. Behind the simplicity of such a separation, compared to literature works dealing with the distillation of multicomponent mixtures to product multiple product, it requires extensive computational effort because the distillation column model includes the full column dynamics, unlike most literature work that used simplified models.
- A new optimal control formulation is proposed in two ways. First, the optimal design problem is formulated with respect to a 'desired purity deviation', defined not as an inequality constraint

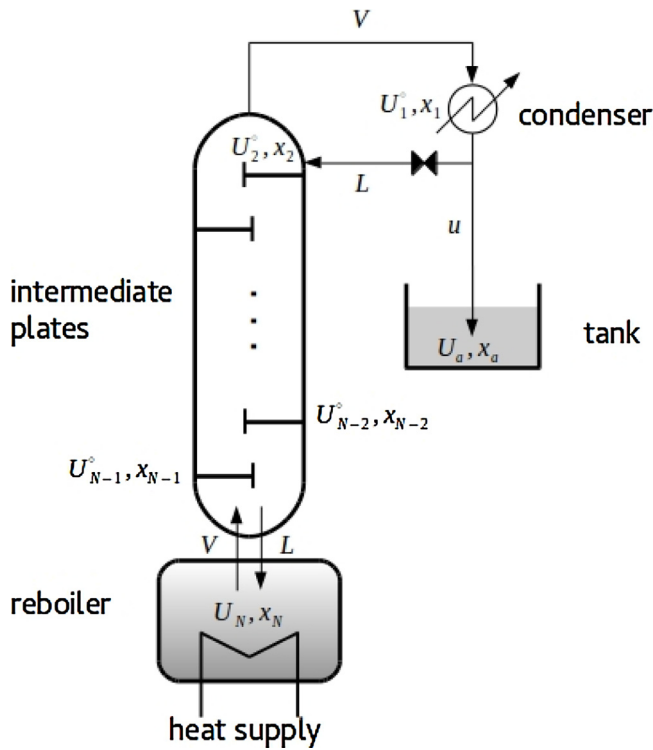


Fig. 1. Batch rectifier model for the optimal control problem.

as is usual but implemented as an additional state variable. Second, the distillate flow rate is used as the control parameter, where almost all authors have used the reflux ratio instead.

- Unlike some literature work, the distillate flow rate policy and by consequence the reflux policy is not predefined. It requires more computation but it leaves free the solver to find piece-wise constant reflux, variable reflux parts, and quasi-cyclic policies, depending on the separation difficulty.

The paper is organized as follow. Section 2 describes the batch process, details about the mixtures characteristics and thermodynamic models, and introduces a degree of separation difficulty. Section 3 details the mathematical model of the batch column, its formulation as an optimal control problem of maximising the total distillate in a fixed time with a prescribed desired purity. Solving strategies and the rigorous simulation model used to validate the optimal control policy are also covered in Section 3. Section 4 presents the influence of several parameters on the optimal control solution and discusses the new findings in perspective with literature works. The optimal control policy is validated with the rigorous model of batch column and is compared to the standard increasing reflux policy.

2. Materials

2.1. Process setup

With reference to the conventional batch distillation column shown in Fig. 1, the process model is studied here. Table 1 contains the process data used in the numerical resolution of the optimal control problem discussed in the next Section. The batch operation consists in heating the reboiler initially loaded with $U_{N,load}$ mol of liquid mixture of given composition in light component $x_{N,init}$ and filling the column plates upwards with the condensed vapour from the plate below. At the end of this task, the column contains $U_{a,init}$, $U_{i,init}$, ($i = 1, \dots, N$) mol of liquid in the accumulator tank on each

Table 1
Process data for simulation and optimal control.

Number of plates	$5 \leq N \leq 14$
Initial accumulator tank hold-up	$U_{a,init} = 0.1 \text{ mol}$
Initial plates hold-ups	$U_{i,init} = 0.1 \text{ mol } i = 1, N - 1$
Initial reboiler hold-up	$U_{N,init} = 10 \text{ mol}$
Initial reboiler composition (light component)	$x_{N,init} = 0.10$
Desired product composition	$x_{D,spec} = 0.95$
Vapour flowrate	$V = 11 \text{ mol/h}$
Reflux ratio	$R \in [0, +\infty)$
Relative volatility of the mixtures at $x_{D,spec}$	$\alpha = \{7; 2.23; 1.48\}$

Table 2
Parameters for the simple VLE thermodynamic model.

Mixture	a	b
n-hexane (68.7 °C)–p-xylene (138.4 °C)	7.0	0.0
Methanol (64.6 °C)–water (100 °C)	7.15	-0.33
Benzene (80.1 °C)–ethylenediamine (116 °C)	9.0	0.6

plate (including condenser and reboiler) which sum up to $U_{N,load}$. Then the column runs under the total reflux until the steady state is reached with molar compositions $x_{i,ss}$, $i = 1, \dots, N$ kept constant to the fourth digit. The optimal control is applied in the next phase of the process.

2.2. Mixture data

Three real zeotropic binary mixtures are chosen according to their relative volatility and their VLE is displayed in Fig. 2. For each, two models are compared. The UNIQUAC model with binary interaction parameters taken from DECHEMA (Gmehling and Onken, 1982) is used in the simulation of the optimal control policy with the BatchColumn simulator whereas the simple model is used in this work for all the optimal control problems and is described by the equation below (Doherty and Malone, 2001):

$$y = \frac{ax}{1 + (a-1)x} + bx(1-x) \quad (1)$$

where x and y are the liquid and vapour mole fractions respectively, and a and b are thermodynamics constants given in Table 2 for the mixtures studied.

The VLE agree with each other and with the experimental data found in the DECHEMA series (not shown for clarity). As the driving force $x - y$ is reduced as one goes from mixture 1 (n-hexane–p-xylene), 2 (methanol–water) and 3 (benzene–ethylenediamine), Fig. 2 shows that the separation by distillation will be more difficult. The first mixture exhibits an almost ideal behaviour; with a constant relative volatility equal to seven. The second one has a decreasing volatility near pure methanol and the third one is an illustration of a mixture with a pinched VLE near pure ethylenediamine.

Additionally from the VLE diagrams, the minimal total number of plates required for feasible separation can be found by graphical method. Setting a desired purity $x_{D,spec} = 0.95$ in light key component (respectively n-hexane, methanol, benzene) and an initial load composition of 0.1 in the light component, the McCabe Thiele construction displayed in Fig. 2 at total reflux gives a minimum number of plates N_{min} equal to 3, 4 and 6 for mixture 1, 2 and 3 respectively. They compare well with the values obtained by using Fenske's formula for minimum number of theoretical plates. Fenske's equation values are 3 (2.64), 4 (3.84) 5 (4.33), using average relative volatility of 7, 3.76 and 3.27 respectively.

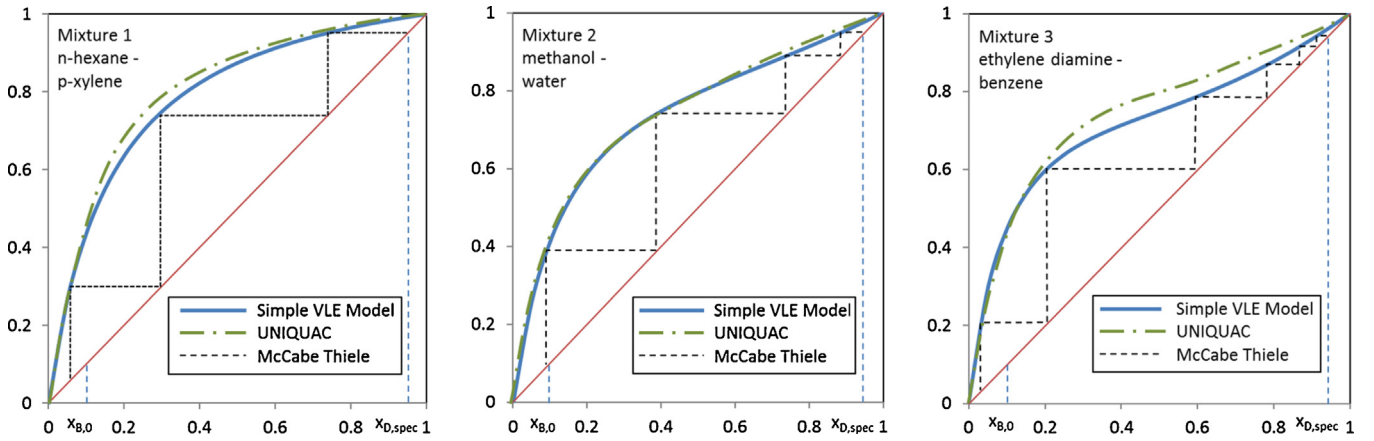


Fig. 2. Vapour – liquid equilibrium and McCabe Thiele drawing at total reflux for three binary mixtures of decreasing mean relative volatility.

2.3. Degree of separation difficulty

Table 1 also reports relative volatility values for the three mixtures {7; 2.23; 1.48} that corresponds to the relative volatility value at the desired distillate purity $x_{D,spec} = 0.95$. Together with the calculation of the minimum number of theoretical plates, they illustrate the intuition that mixture 1 with a high and constant relative volatility is easier to separate by distillation than mixture 2, itself easier than mixture 3 with a pinch in the composition range near the distillate product.

The degree of separation difficulty is another elegant way to compare batch distillation operation for different mixtures in different column configurations for given initial load. Christensen and Jorgensen (1987) proposed to use q , the ratio of the average minimum number of theoretical plates from Fenske's equation to the total number of plates. It should vary between 0 and 1. However, we experienced that the separation was feasible with less plates than Fenske's equation N_{min} , inducing $q > 1$. Hence, inspired by Betlem et al. (1998) for a maximum distillate optimal control problem, like us, the following expression is proposed for computing the separation difficulty:

$$\sigma_{sep.diff} = \frac{(x_{D,spec} - x_{N,init})}{(1 - x_{D,spec})} \frac{1}{\left(\alpha^{\left(\frac{N}{N_{min}}\right)} - 1\right)} \quad (2)$$

This formula shows that the difficulty of separation increases when the relative volatility α decreases, when the product purity/quality $x_{D,spec}$ increases or the initial load composition $x_{N,init}$ is low in product. Betlem's formula was discarded in the present study. It differs from Eq. (2) about the exponent of α and was not adopted since it assumed that the separation difficulty increases when the number of plates increases, which is in contradiction with the usual belief in distillation. In that equation the choice of the relative volatility value α is debatable when, like mixture 2 and 3, it is not constant over the whole range of composition. Hence, the relative volatility value at the desired distillate purity $x_{D,spec} = 0.95$ is used in Eq. (2).

3. Methods

3.1. The maximal distillate problem: an optimal control formulation

Our study is focused on the maximal distillate problem, which can be formulated as follows: for a batch column of given configuration charged with a binary mixture, find the best distillation policy

allowing to maximize the final product of a prescribed purity in a fixed interval of time. In order to provide a rigorous mathematical formulation of such an optimal control problem at the end of this section, a system of differential equations describing the column dynamics, the final product purity constraint, as well as initial and final states of the column need to be specified.

In order to write down the mathematical model of the batch column presented in Fig. 1, assumptions of equimolar overflow, total condensation and constant liquid hold-ups on all plates are adopted. The vapor and the liquid phases, kept at thermodynamic equilibrium according to Eq. (1), are assumed to be perfectly mixed. The vapor hold-up on the plates and the pressure drop along the column are neglected. Heat balance is neglected but a comparison with a detailed model including heat balance will be made in Section 4.5. Under these assumptions, the dynamics of the batch column given in Fig. 1 with a distillate flow rate u can be described by the system of ordinary differential equations (Mujtaba, 2004):

$$\frac{dx_a}{dt} = \frac{u}{U_a} (x_1 - x_a), \quad \frac{dx_1}{dt} = \frac{V}{U_1} (y_2 - x_1), \quad \text{accumulator} \quad (3.1)$$

tank and condenser

$$\frac{dx_i}{dt} = \frac{1}{U_i} (L(x_{i-1} - x_i) + V(y_{i+1} - y_i)), \quad U_i = \text{const}, \quad (3.2)$$

$i = 2, \dots, N-1$ plates

$$\frac{dx_N}{dt} = \frac{1}{U_N} (L(x_{N-1} - x_N) - V(y_N - x_N)), \quad \text{reboiler} \quad (3.3)$$

$$\frac{dU_a}{dt} = u, \quad (3.4)$$

$$\frac{dU_N}{dt} = -u \quad \text{liquid hold - ups in the tank and in the reboiler}$$

As Fig. 1 shows, the plates are enumerated from the top to the bottom (1 for condenser, N for the reboiler), x_i, y_i are the mole fractions of the light component in the liquid and in the vapour phases related by the VLE condition given by Eq. (1), U_i denote the liquid hold-ups along the column and U_a the accumulator tank hold-up. The vapour flow rate is a constant parameter $V = \text{const}$, while liquid and distillate flow rates vary in time and verify $u(t) + L(t) = V$. In what follows the distillate rate u is chosen as a control variable. The total mass balance implies that $0 \leq u(t) \leq V$. Eqs. (3.1)-(3.4) provide a complete representation of the column dynamics and they preserve the total mass and the mass of the light component in the system. Note that Eqs. (3.1) and (3.3) blow up if either the reboiler or tank is empty. To avoid such a situation, the final time t_f must be short enough to prevent the reboiler emptiness. In our

computations, $t_f=0.8h$, corresponding to 88% of the time needed to empty the reboiler under the regime of zero reflux ($u=V$). One also assumes that at $t=0$ the tank contains a small amount of the distillate $U_{a,init}$ ('the first drop') of the same composition as in the condenser plate 1.

The purity requirement of the final product is commonly described by the following integral relation (Diwekar, 1992; Kim and Diwekar, 2001; Upreti, 2012):

$$x_{D,spec} \int_0^{t_f} u(t) dt = \int_0^{t_f} u(t) x_1(t) dt \quad (4)$$

According to Eqs. (3.1) and (3.4), the right-hand side of Eq. (4) is equal to $m_{x,a}(t_f) - m_{x,a}(0)$, where $m_{x,a}(t)$ is the mass of the light component in the accumulator tank. Thus, Eq. (4) assigns the purity $x_{D,spec}$ of the product accumulated during the process independently of the first drop amount and composition.

In batch distillation operation, the fixed purity specification $x_{D,spec}$ is usually smaller than the steady-state concentration of the light component in the head of the column reached at the end of the total reflux phase. Hence, the true concentration of the light component $x_a(t_f)$ is greater than $x_{D,spec}$ because Eqs. (3.1), (3.4) imply that

$$x_a(t_f) = x_{D,spec} + \frac{(x_a(0) - x_{D,spec}) U_a(0)}{U_a(t_f)} \quad (5)$$

The integral form (4) of the purity requirement creates certain technical difficulties both for the theoretical analysis and for the numerical computations. For this reason, an equivalent differential form is used, by introducing a new variable, referred below as a 'purity deviation':

$$p(t) = \int_0^t u(x_1 - x_{D,spec}) dt \quad (6)$$

By definition, it verifies the following initial value problem

$$\frac{dp}{dt} = u(x_1 - x_{D,spec}), p(0) = 0 \quad (7)$$

The purity constraint Eq. (4) prescribes the final time condition for p :

$$p(t_f) = 0 \quad (8)$$

At $t=0$ the column is supposed to be at steady state under total reflux ($u=0$). Given the initial composition in the reboiler $x_{N,init}$, the steady state concentrations $x_{i,ss}$ can be easily calculated by backward recursion:

$x_{i,ss} = y_{i+1}(x_{i+1,ss})$, $i=N-1, \dots, 1$. So, for the optimal control computations, Eqs. (3.1)–(3.4) should be coupled with the following initial conditions

$$x_a(0) = x_{1,ss}, x_N(0) = x_{N,init}, x_i(0) = x_{i,ss}, i = 1, \dots, N-1 \quad (9)$$

$$U_i(0) = U_{i,init}, i = a, 1, \dots, N$$

Summing up, one gets the following formulation of the maximum distillate problem:

$$\max_{0 \leq u(t) \leq V} U_a(t_f) \quad (10)$$

where the column dynamics verifies the initial value problem defined by Eqs. (3.1)–(3.4), (7), (9) and the final time condition (8). Such an optimal control problem is a standard optimal control problem of Mayer's type, affine with respect to a single bounded

control. Indeed, recalling that $\{U_i\}$, $i = 1, \dots, N-1$ are constant and defining the state space of the system as

$$X = \left\{ q \in \mathbb{R}^{N+4} : q = (x_a, x_1, \dots, x_N, U_a, U_N, p), x_a, x_i \in [0, 1], \right. \\ \left. i = 1, \dots, N \right\}$$

the maximal distillate problem formulated above can be written in the more general form

$$\max_{u(\cdot)} G(q(t_f)) \\ \text{subject to} \\ \frac{dq(t)}{dt} = F_0(q(t)) + uF_1(q(t), u(t)), q \in X, u \in [0, u_{max}] \quad (11)$$

$$q(0) \in X_0, q_{N+4}(t_f) = 0$$

where $u(\cdot)$ is an admissible control, $u_{max}=V$ and $G(q) = q_{N+2}$. The set X_0 describes the set of initial conditions (7) and (9), and F_0 and F_1 are the drift and the control vector fields defined by Eqs. (4.1)–(4.4), (7).

3.2. The optimal distillate policy structure: preliminary analysis

Pontryagin's maximum principle (PMP, see for instance in Trelat, 2008 or in Upreti, 2012) provides the necessary optimality conditions for the solutions of the optimal control problem (11). In particular, it describes explicitly all possible types of optimal controls in terms of the Hamiltonian function associated to (11). The detailed application of PMP goes beyond the aim of this paper. Still some preliminary conclusions concerning the optimal control structure can be useful for the qualitative analysis of the numerical results discussed in the next section.

The Hamiltonian function of the affine control problem (11) has the form $H(\psi, q, u) = H_0(\psi, q) + uH_1(\psi, q)$, where $q \in X$, $\psi \in \mathbb{R}^{N+4}$ denotes the co-state, and $H_i(\psi, q) = \psi \cdot F_i(q)$, $i = 0, 1$. The PMP states that if $u_{opt}(t)$ is associated to the optimal solution $q_{opt}(t)$ of problem (11), it must necessarily satisfy the following maximization condition:

$$H(\psi(t), q_{opt}(t), u_{opt}(t)) = \max_{0 \leq w \leq u_{max}} H(\psi(t), q_{opt}(t), w), \\ t \in [0, t_f].$$

In particular, it follows that $u(t) = 0$ if $H_1(\psi(t), q(t)) > 0$, $u(t) = u_{max} = V$ if $H_1(\psi(t), q(t)) < 0$ at some $t \in [0, t_f]$. Otherwise, i.e. if along some piece of the optimal solution $H_1(\psi(t), q(t)) \equiv 0$, the optimal control can be found from the equation $\partial H(\psi, q, u) / \partial u = 0$. The control Hamiltonian H_1 plays the role of the switching function of the problem. In the optimal control literature, the optimal controls of the first two types $u(t) = 0$ and $u(t) = u_{max} = V$ are called of 'bang' type, whereas in the third case it is referred as a singular control. More details on this computation can be found in Stojkovic et al. (2017).

The above analysis shows that in principle both types of optimal control: bang and singular, can appear in the solution of the maximum distillate problem. This conclusion follows from the rigorous application of the necessary conditions for optimality given by PMP, and is based on the particular form of the optimal control problem (11), which is affine with respect to the bounded distillate flow rate $u \in [0, V]$.

As an alternative, that most of the literature considers, one could have taken the reflux ratio $R=L/u=V/u-1$ as the control variable. Motivation of the preference for the choice of u as the control variable is as follow. Observe that $R \in [0, +\infty)$ and, since $u = V/(R+1)$,

Eqs. (3.1)–(3.4), (7) are highly non-linear with respect to R . The corresponding optimal control problem is much more complicated and difficult to treat using the methods of optimal control and calculus of variations. Indeed, starting from the work of [Converse and Gross \(1963\)](#) and repeated later in [Diwekar \(1992\)](#), [Kim and Diwekar \(2001\)](#) and [Diwekar \(2014\)](#), only the singular type control was taken into account because the boundary conditions on the reflux ratio were not correctly treated in the application of the PMP.

3.3. Numerical resolution of the optimal control problem

To solve the problem numerically the so-called direct method of optimal control is used (see in [Trelat, 2008](#)). The method is based on a full time discretization of the dynamics of the system using an appropriate numerical scheme. In this way, the original optimal control problem is transformed into a standard non-linear optimisation problem. This method is implemented in the recently developed optimal control solver BOCOP ([Martinon, 2016](#)) that uses the IPOPT algorithm as the non-linear solver. The possible choice of the discretisation scheme varies from order 1 (Euler's method) to order 6 (Lobatto's method). Until otherwise stated, the results discussed below were obtained with the 4-th order Gauss scheme with 1800 discretisation points.

3.4. Rigorous batch distillation simulation

The optimal solution found by BOCOP is verified later with the Batchcolumn[®] simulator. It uses a full Mass, Vapour–Liquid Equilibrium, Mole Fraction Summation, Enthalpy Balance (MESH) dynamic model of batch distillation, solved with the predictor-corrector Gear's method ([Prosim, 2015](#)).

Several differences exist between the Batchcolumn[®] and the BOCOP simulations. Firstly, the VLE model in Batchcolumn[®] thermodynamics assumes perfect gas and uses the group contribution activity coefficient model UNIFAC Modified Dortmund 1993 ([Gmehling et al., 1993](#)) combined with the DIPPR extended correlation for the vapour pressure to describe the liquid phase fugacity. Nevertheless, [Fig. 2](#) showed that UNIQUAC VLE prediction agrees with the simple VLE model given in Eq. (1) used in BOCOP and with experimental data. Second, the vapour flow rate in the MESH model varies during the batch column simulation whereas it is kept constant in BOCOP's model. Third, the rigorous simulation starts with the reboiler loading step whereas BOCOP's model starts under steady-state conditions achieved under total reflux. Considering molar units for the rigorous simulation, the reboiler initial load is adjusted in Batchcolumn[®] to obtain a steady-state solution under total reflux ([Table 4](#)) that matches BOCOP's initial steady-state values ([Table 3](#)) for carrying later a faire comparison.

The reboiler heat duty adjustment in Batchcolumn[®] is also intended to obtain the desired distillate purity in the distillate tank. The plates' molar hold-ups are constant and equal for both Batchcolumn[®] and BOCOP models once the steady state is achieved.

4. Results and discussion

4.1. Optimal control policy near the minimum number of plates

First, the structure of the optimal control policy is described for the three binary zeotropic mixtures: n-hexane–p-xylene, methanol–water, and benzene–ethylenediamine. Numerical results are shown in [Table 5](#). For a number of plates $N = N_{\min} + 2$, one follows the optimal evolutions of the control variable $u(t)$, namely the distillate flow rate, and of the liquid molar compositions for n-hexane–p-xylene ([Figs. 3 and 4](#)), methanol–water ([Fig. 5](#)) and benzene–ethylenediamine ([Fig. 6](#)) respectively.

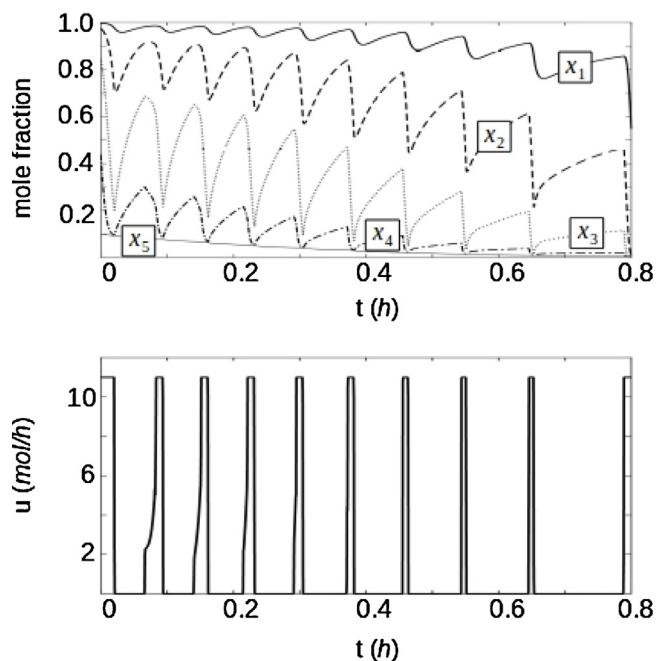


Fig. 3. n-hexane–p-xylene, $N = 5$: mole fractions evolution vs. optimal control.

In [Table 5](#), the recovery rate of the light component is computed as the ratio of the amount of the light component in the tank at the end of the process divided by its total amount in the system:

$$\text{recovery}(\%) = 100 \times \frac{x_a(t_f) U_a(t_f)}{x_a(0) U_a(0) + \sum_{i=1}^N x_{i,ss} U_{i,ss}} \quad (12)$$

As shown on [Figs. 4–6](#), a similar bang-bang type optimal control policy pattern is found for all three mixtures when the number of plates is close to its minimal value, $N_{\min} + 2$. A few short singular arcs are also found. The bang-bang type behaviour (BB in [Table 5](#)) refers to the alternation of maximal distillate rate ($u(t) = u_{\max}$)/zero distillate rate ($u(t) = 0$) cycles. The BB pattern resonates with the cyclic policy described in the literature. The number of cycle n_{cycle} is incremented from the Figures each time the control variable u reaches its maximal value $u_{\max} = V$. This is slightly different from the original definition of a cycle by [Jorgensen and Toftgard \(1987\)](#) recalled in the introduction, since our model does not use a variable hold-up reflux drum below the condenser. To our knowledge, this is the first time that the cyclic type of policy is found by solving the optimal control problem.

Because of the BB pattern, the molar liquid compositions in the column and the liquid hold-up in the reboiler and in the tank also show the cyclic behaviour ([Fig. 3](#)). During each u_{\max} period as the distillate is removed at its full rate, the diagrams show that the molar content in light key product decreases on each plate. Between each u_{\max} period, apart from a few short singular arcs, the zero control is used, hence all the condensed vapour is refluxed to the column. This provokes an enrichment of the product content on each plate.

On the other hand, the evolution of the distillate composition is not cyclic but is stepwise, because it is governed by the purity deviation function (Eq. (6)).

[Fig. 7](#) shows (for the mixture p-xylene–n-hexane with $N = 5$), that at $t = t_f$ the purity deviation meets the final condition given by Eq. (8) indicating that the purity specification $x_{D,\text{spec}} = 0.95$ is achieved by the optimal control policy. [Sorensen and Prenzler \(1999\)](#) optimized the batch distillation with four cycles and noticed a gradual decrease of the tank concentration with time to match at the end

Table 3
Steady state for BOCOP's model with mixture n-hexane–p-xylene.

N	$U_{a,init}$ [mol]	$U_{i,init}$ [mol]	$U_{N,init}$ [mol]	$x_a(0)$	$x_{1,ss}$	$x_{2,ss}$	$x_{3,ss}$	$x_{4,ss}$	$x_{5,ss}$	V [mol/h]
5	0.1	0.1	10	0.9962	0.9962	0.9744	0.8448	0.4375	0.1	11

Table 4
Process data for n-hexane–p-xylene batch distillation simulation with Batchcolumn® simulator.

N	$U_i = 1, 4$ [mol]	$U_{N,init}$ [mol]	Q_b [kcal/h]	$x_{p-xylene}^{load}$	$x_{n-hexane}^{load}$
5	0.1	10	96.5	0.87	0.13
$x_a(0)$	$x_{1,ss}$	$x_{2,ss}$	$x_{3,ss}$	$x_{4,ss}$	$x_{5,ss}$
1	0.997	0.984	0.897	0.495	0.100
					V [mol/h]
					0.23

Table 5
Influence of the number of plates on the optimal control policy for the three mixtures for achieving $x_a = 0.95$.

Mixture	N	Optimal control policy pattern	n_{cycle}	Distillate $U_a(t_f)$ [mol]	Recovery rate, (%)	$(\sigma_{sep,diff})$ Degree of separation difficulty, (%)
1	5	Near BB	10	1.39534	93.35%	0.690
	9	Mixed BS	4	1.88885	98.58%	0.050
	12	Mixed BS	3	2.20997	99.02%	0.007
	14	BB	3	2.42212	99.21%	0.002
2	6	BB	9	1.35570	86.21%	7.30
	9	Mixed BS	4	1.84238	97.64%	3.35
	12	Mixed BS	4	2.17336	98.67%	1.68
	14	Mixed BS	4	2.28831	98.97%	1.09
3	8	BB	7	1.41719	80.51%	24.76
	9	Mixed BS	7	1.71289	92.24%	21.23
	12	Mixed BS	6	2.12791	97.79%	14.28
	14	Mixed BS	4	2.35108	98.536%	11.36

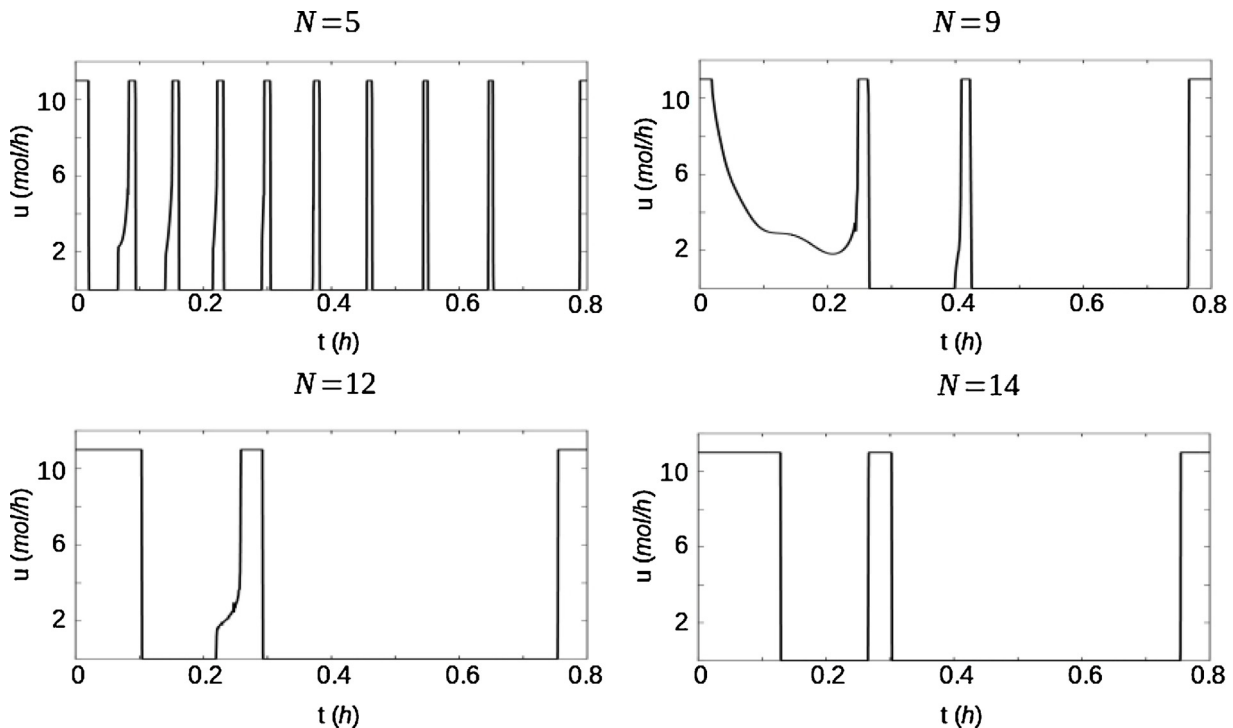


Fig. 4. n-hexane–p-xylene: optimal control structure for $N = 5, 9, 12$ and 14 plates.

the desired purity. This also happens for a batch distillation task operated with an increasing reflux policy. Unlike all of Sorensen's works, our model does not have a variable hold-up reflux drum and Fig. 7 shows a different trend: there is a gradual increase of the positive deviation (and of the distillate composition), until a final abrupt decrease. A similar trend was obtained for all cases

discussed in this paper. It tells more about the initial and final features of the presumed optimal solution to match the purity constraint. At $t = 0$ the process begins with the steady state conditions given in Table 3, and the initial product purity is 0.9962, which is well over the desired purity 0.95. Hence, the solver can start the optimal control strategy with a maximum distillate rate plateau

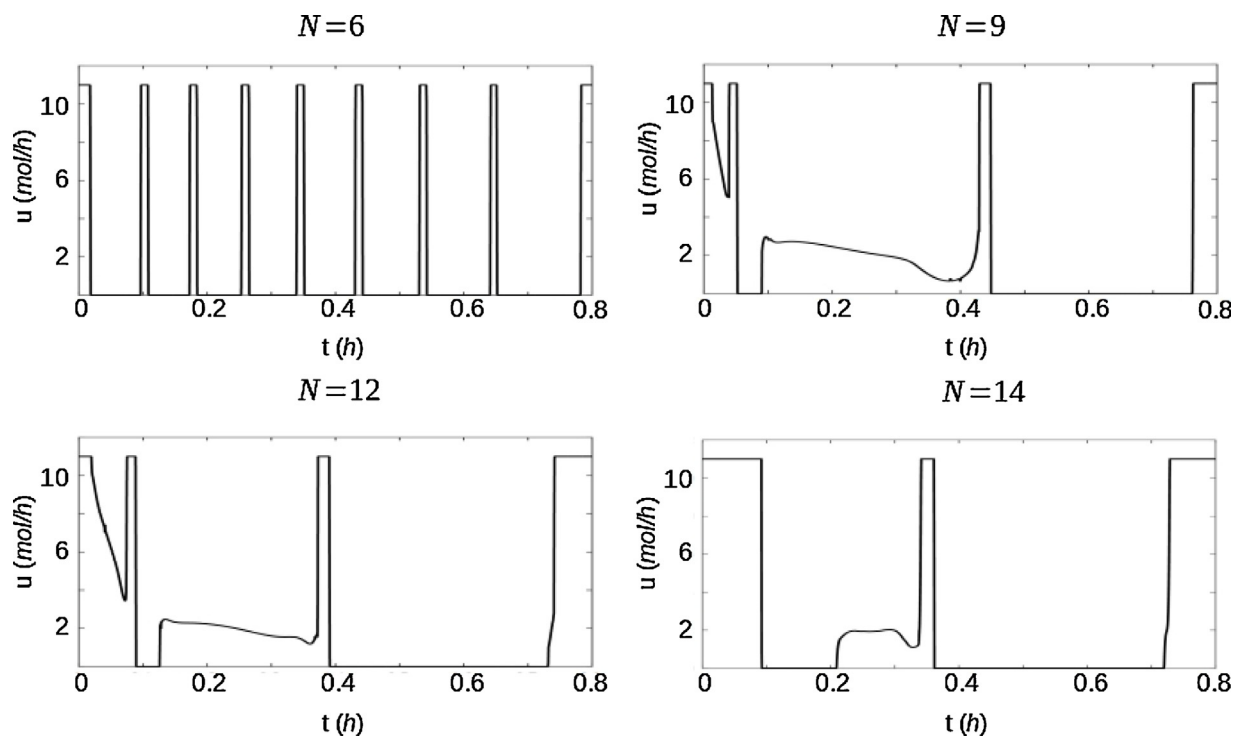


Fig. 5. Methanol-water: optimal control structure for $N=6, 9, 12$ and 14 plates.

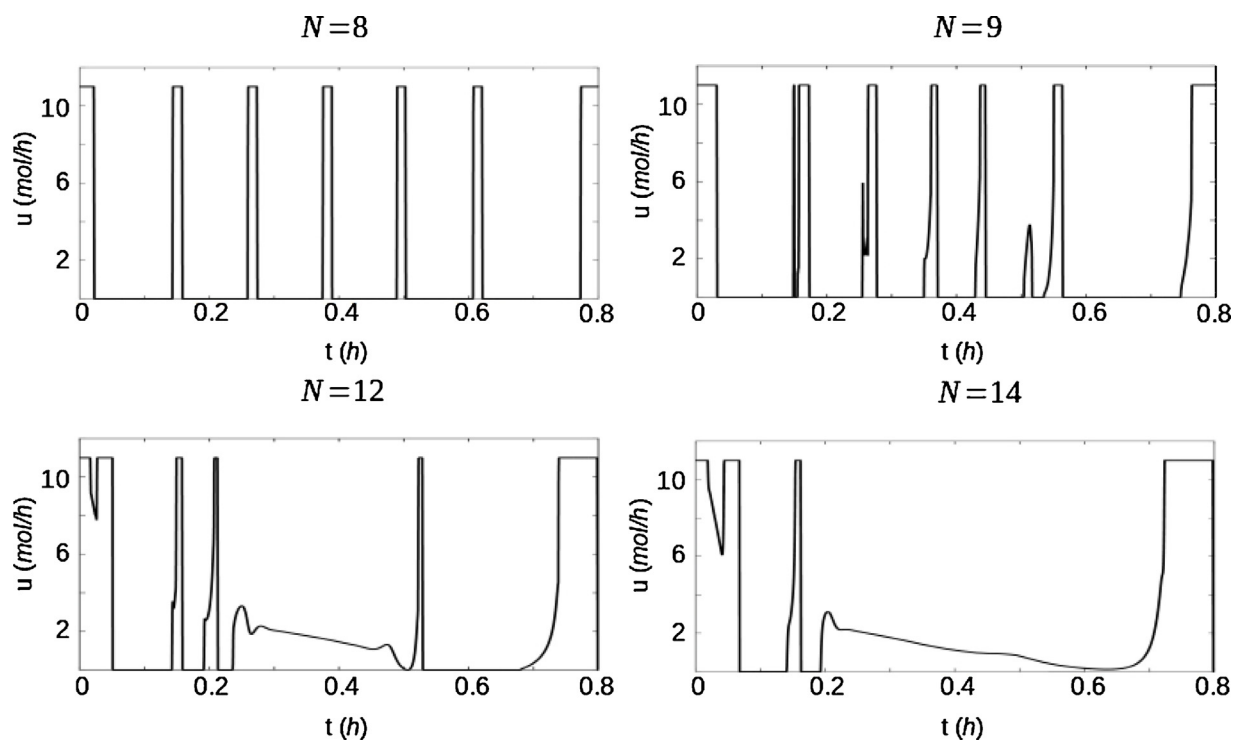


Fig. 6. Benzene-ethylenediamine: optimal control structure for $N=8, 9, 12$ and 14 plates.

that steadily reduces the product quality. When the final time is neared, Fig. 6 shows that the purity deviation is still positive. Consequently, the solver finds again a maximum distillate rate plateau (see Fig. 3) to reduce safely the product purity until the deviation becomes null to match Eq. (8).

4.2. Influence of the total number of plates on the optimal control policy

This section exposes the influence of the total number of plates on the optimal control structure. For the mixture

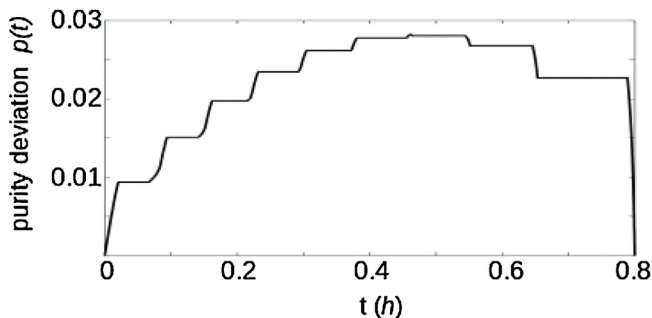


Fig. 7. The purity deviation evolution for the optimal control policy for p-xylene-n-hexane at $N=5$.

n-hexane–p-xylene Table 3 and Fig. 4 show the results for a total number of plates $N=5, 9, 12$ and 14 . Figs. 5 and 6 show the results for the second and third mixtures.

For small and large total number of plates a distinctive BB control pattern is observed for mixture 1. In between “singular” arcs appear along with the BB cycles. It is named Mixed BS behaviour in Table 3. For the two other mixtures, with a higher degree of separation difficulty, the BB pattern is not found at the maximum plate number studied $N=14$. But, one might infer that it shall appear because the mixed BS pattern is observed with a very long singular arc when $N=9$ or $N=12$ for mixture 2 and when $N=12$ for mixture 3 and it is alike the one observed for $N=9$ for mixture 1. Namely, a first singular arc appears between the first and second maximum distillate flow rate plateaus. Then, later during the distillation, a long lasting singular arc appears between the two plateaus.

From Figs. 4–6, it can also be perceived that the duration of the last maximum distillate plateau period lasts longer when the total number of plates increases, likely because of the way the solver nullifies the purity deviation shown in Fig. 7, as discussed earlier. Regarding the total number of cycles, it decreases when the total number of plates increases for all mixtures.

In summary, one has noticed that: 1) for a small number of plates, a bang-bang type optimal control pattern is found with multiple cycles; 2) for an intermediate total number of plates, the optimal control is a combination of bang-bang type and singular type optimal control that can be repeated several times 3) for a high total number of plates a bang-bang type optimal control with a very a small number of cycles is obtained.

4.3. Influence of the relative volatility and degree of separation difficulty

In this section, the influence of the degree of separation difficulty is discussed. First, Table 3 shows a straightforward trend, namely that for the same desired product purity, the product recovery yield decreases when the difficulty increases, either for the same mixture when the number of plates increases or between the three mixtures with the same number of plates ($N=9$ or 12).

The impact on the optimal control structure is less evident. From Figs. 4–6, one can notice that for $N=N_{\min} + 2$, a BB pattern is found but the number of cycles decreases with the degree of separation difficulty increase. With more plates, the separation is easier and mixed-BS pattern are found, then for more plates, a BB pattern arises again. Looking at the same total number of plates $N=9$ one finds two features: shifting from the easiest mixture n-hexane–p-xylene to methanol–water, the mixed-BS pattern exhibits again 4 cycles but a longer singular arc. Then, for the most difficult mixture (benzene–ethylenediamine), the BB pattern occurs once again with more (7) cycles. Hence, one cannot find a correlation between the number of cycles and the degree of separation difficulty for separating the same mixture. On the other hand, from one mixture to

the other, the cyclic pattern is recommended, as one gets closer to N_{\min} and the degree of separation difficulty increases.

4.4. Sensitivity analyses

The sensitivity analyses are carried out for the mixture 1 example of p-xylene-n-hexane with a total number of plates $N=5$.

4.4.1. Vapour flow rate influence

The influence of the vapour flowrate variation is investigated within the range from 11 to 30 mol/h. As it was specified in Section 3, for $V=11$ mol/h the total operation time t_f was set in order to prevent the reboiler emptying, the chosen value 0.8 h corresponding to 88% of the initial reboiler load $U_{N,init}$ divided by V . When V varies, the final time is adjusted similarly, since the initial load in the reboiler is kept constant. The results are shown in Table 6.

Table 6 shows that the influence of V is marginal and leads to optimal control values $U_N(t_f)$, $x_a(t_f)$, and BB pattern with 10 cycles similar to the one displayed in Fig. 3 for $V=11$ mol/h. The recovery rate is the same to the first digit, meaning that by increasing V the same product quantity and quality can be obtained in a shorter time.

4.4.2. Constant plate hold-up influence

The influence of the hold-up is analysed by varying the hold-up on the internal plates (reboiler and tank keep their nominal values in Table 7), on the internal plates plus tank after steady state (reboiler at nominal value in Table 8) and on the tank only (Table 9). The nominal hold-up value is 0.1 mol for internal plates and the tank initial hold-up (Table 1). Recall that internal plate hold-ups $U_{i,i=1,4}$ remain constant but that in our model the tank hold-up will increase up to $U_a(t_f)$ as distillate pours in.

For all cases, the final tank purity $x_a(t_f)$ overcomes the desired value $x_{D,spec} = 0.95$, as it is predicted by Eq. (5). When only the internal plate hold-up increases (Table 7), $x_a(t_f)$ also decreases but differences are attributed to the optimal control policy changes in the number and duration of each cycle (see below).

Regarding the optimal control pattern, it remains of bang-bang type for all cases (Fig. 8). But the total number of cycles decreases drastically from 20 to 3 over the internal plates hold-up variation range (Tables 7 and 8).

The total duration of the maximum flow rate period $u_{\max} = V = 11$ mol/h varies in the opposite way: over the three cycles for a plate hold-up of 0.5 mol, it is longer than in the other cases, approx. 1.5 times more than 0.3 mol, 2 times more than 0.1 mol and 4 times more than 0.05 mol. That indicates that more distillate is produced, in agreement with the values of $U_a(t_f)$ in Tables 7 and 8. Nevertheless, the light component recovery decreases. The reason is that in our model, increasing the internal plate hold-ups from 0.05 mol to 0.5 mol add 1.8 mol on the internal plates, of which 1.4561 mol of light component (the steady state composition is the same; see Table 3). But with the same vapour flow rate and as the distillate purity is nearly constant, the light component recovery decreases, despite more distillate $U_a(t_f)$ is recovered.

When only the tank hold-up is varied (Table 9), the amount and the purity related to the first drop slightly increase the final distillate purity $x_a(t_f)$ and consequently the product recovery.

on the optimal distillate rate evolution for p-xylene-n-hexane, $N=5$.

4.4.3. Desired purity influence

The influence of the light component desired purity in the tank is shown in Table 10 for $x_{D,spec}$ varying from 0.95 to 0.99. Compared to the nominal case ($x_{D,spec} = 0.95$), increasing the desired purity reduces significantly the distillate amount and the product

Table 6
Influence of the vapour flow rate.

V [mol/h]	11	15	21	25	30
t_f [h]	0.8	0.59	0.42	0.35	0.29
$U_N(t_f)$	8.70466	8.70410	8.70449	8.70537	8.70601
n_{cycle}	10	10	10	10	10
$x_a(t_f)$	0.9533	0.9533	0.9533	0.9533	0.9533
Recovery rate %	93.35	93.40	93.36	93.30	93.26

Table 7
Influence of internal plate hold-up variation.

$U_{i,i=1,4}$ [mol]	0.05	0.1	0.3	0.5
$U_{a,init}$ [mol]	0.1	0.1	0.1	0.1
$U_a(t_f)$ [mol]	1.26060	1.39534	1.92751	2.45822
$U_N(t_f)$ [mol]	8.83940	8.70466	8.17248	7.64178
n_{cycle}	20	10	4	3
$x_a(t_f)$	0.9537	0.9533	0.9524	0.9519
recovery rate%	95.24	93.35	88.45	85.83

Table 8
Influence of internal plate and tank hold-up variation.

$U_{i,i=1,4}$ [mol]	0.05	0.1	0.3	0.5
$U_{a,init}$ [mol]	0.05	0.1	0.3	0.5
$U_a(t_f)$ [mol]	1.21060	1.39534	2.12752	2.85822
$U_N(t_f)$ [mol]	8.8394	8.70466	8.17248	7.64178
n_{cycle}	20	10	4	3
$x_a(t_f)$	0.9519	0.9533	0.9565	0.9581
recovery rate%	95.05	93.35	89.46	87.64

Table 9
Influence of tank hold-up variation.

$U_{i,i=1,4}$ [mol]	0.1	0.1	0.1	0.1
$U_{a,init}$ [mol]	0.1	0.2	0.3	0.4
$U_a(t_f)$ [mol]	1.39534	1.49573	1.59573	1.69573
$U_N(t_f)$ [mol]	8.70466	8.70427	8.70427	8.70427
n_{cycle}	10	10	10	10
$x_a(t_f)$	0.9533	0.9562	0.9587	0.9609
recovery rate%	93.35	93.81	94.19	94.53

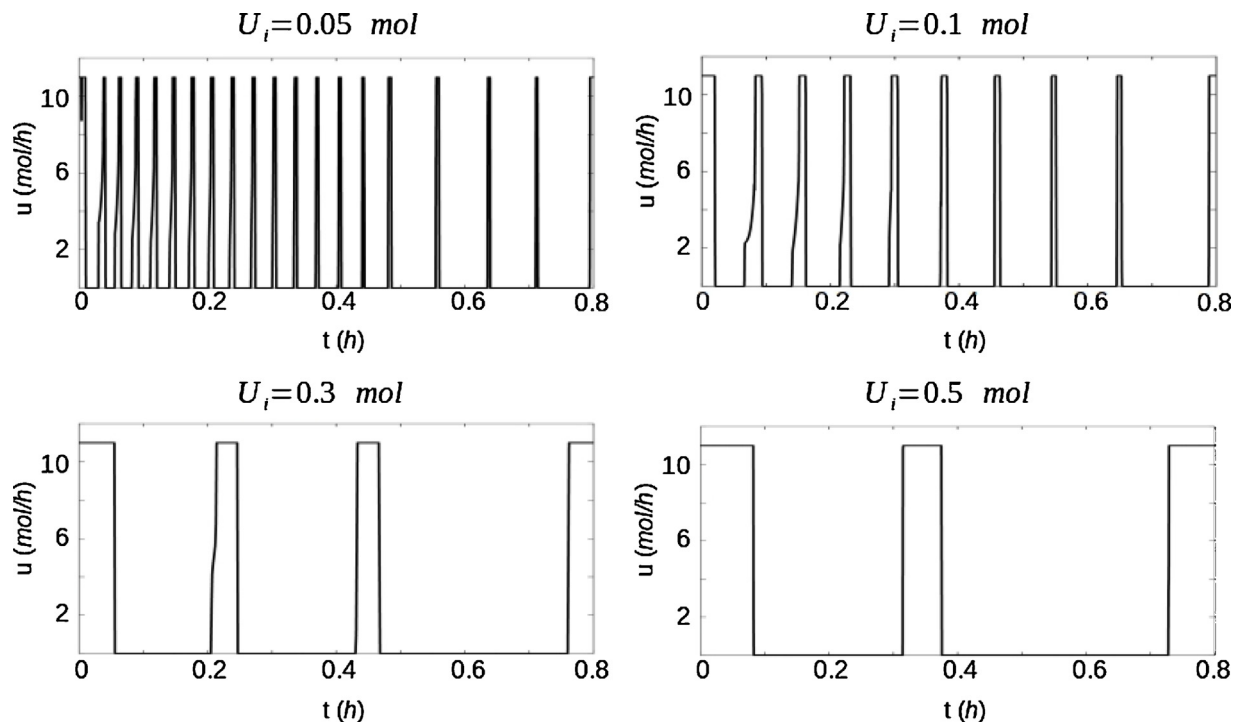


Fig. 8. Influence of the internal plate hold-up on the optimal distillate rate evolution for p-xylene-n-hexane, $N=5$.

Table 10
Influence of the final distillate desired purity.

Desired purity $x_{D,spec}$	0.95	0.96	0.97	0.98	0.99
$U_a(t_f)$ [mol]	1.39514	1.3606	1.31331	1.23387	1.01476
$U_N(t_f)$ [mol]	8.70486	8.74021	8.78669	8.86613	9.08524
n_{cycle}	10	10	10	10	10
$x_a(t_f)$	0.9533	0.9626	0.9719	0.9813	0.9906
recovery rate%	93.35	91.92	89.59	84.97	70.55

Table 11
Influence of the initial charge composition.

$x_{N,init}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7
$\sigma_{sep,diff}$	0.69	0.61	0.53	0.45	0.36	0.28	0.20
$U_N(t_f)$ [mol]	8.7049	7.6454	6.6304	5.6212	4.5249	3.6203	2.6068
$U_0(t_f)$ [mol]	1.3951	2.4546	3.4696	4.4788	5.4851	6.4897	7.4932
n_{cycle}	10	7	4	3	2	–	–
$x_a(t_f)$	0.9533	0.9519	0.9514	0.9511	0.9509	0.9508	0.9507
Recovery rate %	93.35	96.31	97.07	97.20	97.00	96.58	96.13

Table 12
Comparison of different reflux policies on the recovery rate under fixed purity constraint.

	BOCOP	BatchColumn (R = optimal policy approximation)	BatchColumn (R = variable)
Thermodynamics	Eq. (1)	UNIFAC	UNIFAC
Column model	MESH	MESH	MESH
$x_a(t_f)$	0.9533	0.9542	0.9540
Recovery rate %	93.35	94.50	80.27

recovery. That is in full agreement with a simple McCabe Thiele graphical construction, because the vapour flow rate is kept constant, which fixes the maximum reflux in the column and the total number of plates.

4.4.4. Initial composition influence

The effect of the light component composition in the initial load is studied by increasing it from the base case 0.1–0.7, for the separation of mixture 1. In each case, the steady-state initial conditions are recomputed. Table 11 shows that the desired purity is achieved in each BOCOP simulation.

The recovery increases first by 3% and then remains nearly constant, and high. Combined with the desired purity, the final tank content increases steadily as the initial light component composition is increased. The main influence is seen on the optimal control pattern structure in Fig. 9. First, while the base case (Fig. 3) shows a bang-bang pattern with approximately 10 cycles, increasing $x_{N,init}$ gradually reduces the number of cycles to two maximum distillate rate $u = u_{max}$ periods for $x_{N,init} = 0.5$. For $x_{N,init} = 0.6$ and 0.7, the control u never null, and strictly speaking there is no bang-bang pattern. The disappearance of the bang-bang pattern is substituted by a singular arc, of increasing duration up to $x_{N,init} = 0.5$. Second, near $t = 0$ and near $t = t_f$, two periods of maximum distillate flow rate removal (no reflux) are seen for each case. Besides, they constantly increases along with $x_{N,init}$ increasing.

The degree of separation difficulty $\sigma_{sep,diff}$ is reduced if the initial composition in the reboiler is greater in the light component of each mixture (Table 11). One may then propose an explanation to the optimal control pattern change by noticing that the appearance of singular arcs has also been evidenced when $\sigma_{sep,diff}$ decreased. It happened for mixture 1 with $N = 9$ (Fig. 4), for mixture 2 with $N = 9$ and 12 (Fig. 5), for mixture 3 with $N = 9$ and 12 (Fig. 6), compared respectively to mixture 1 $N = 5$ (Fig. 3), mixture 2 $N = 6$ (Fig. 5), and mixture 3 $N = 8$ (Fig. 6). Fig. 9 shows that as the separation gets easier, the first and the last bang periods $u = u_{max}$ are longer. That happens because the desired purity can be maintained longer at the beginning. Then the optimal control reduces the distillate flow rate

(u decreases) with a singular arc. Before $x_{N,init} = 0.5$ bang-bang type cycles are seen. After, only the last plateau of maximum distillate rate occurs, being the expression of how BOCOP's algorithm solves the purity deviation constraint by maintaining a positive deviation until near t_f where it nullify the deviation by maximizing the distillate flow rate (see Fig. 7).

Finally, one recalls that Sorensen and Skogestad (1994) noticed with their sensitivity analysis approach that the “cyclic operating policy [...] and found it to be more favourable for difficult separations with a low amount of light component”. Our optimal control results confirm that.

4.5. Validation of the optimal control policy in a rigorous batch simulator

Using the protocol described in Section 3.4 BOCOP's results were verified with the BatchColumn® Simulator (Prosim, 2015), coded with a MESH mathematical model. The UNIFAC thermodynamics model agreed with the simple model of Eq. (1) (see Section 2.2). Considering the case of p-xylene-n-hexane in a batch column with $N = 5$ plates, the “bang-bang” optimal control policy is compared with variable and increasing reflux policies in terms of purity of the tank final product and of the recovery rate. BOCOP's quasi bang-bang type optimal control policy for the distillate flow rate (Fig. 10) is approximated as a succession of zero reflux total reflux cycles with the same duration. Figs. 10 and 11 compare both software in terms of control variable for BOCOP and distillate flow rate for BatchColumn (Fig. 10) and reflux (Fig. 11). For the sake of figure readability, BOCOP's results are displayed in arbitrary units, but one recalls that BOCOP's maximum value is 0.183 mol/min. Fig. 10 shows that the distillate flow rate obtained with the rigorous simulator remains nearly constant with the bang-bang approximated policy despite the enthalpy balance. This allows a fair comparison with BOCOP's results.

Table 12 compares BOCOP and the two rigorous simulations, with optimal reflux policy and variable reflux policy.

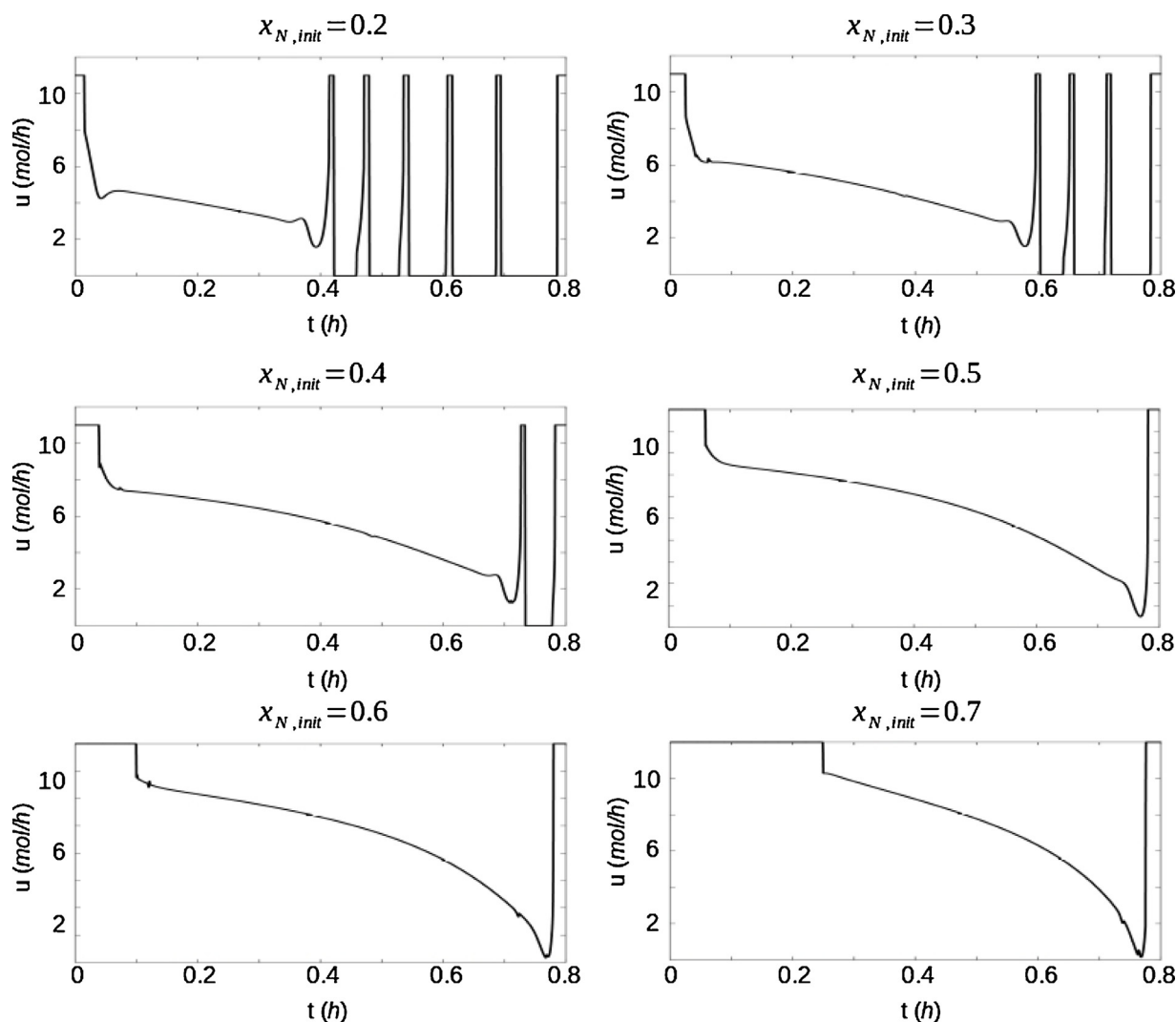


Fig. 9. Influence of the initial load content in light component on the optimal control pattern.

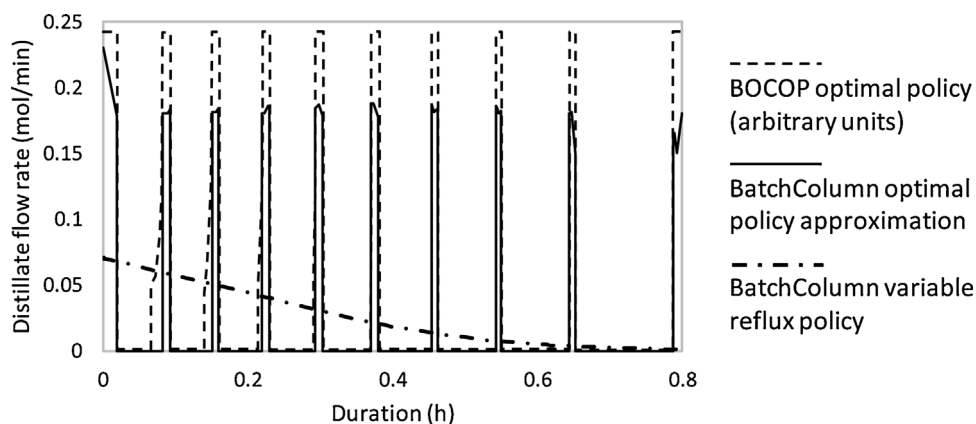


Fig. 10. Distillate flow rate BOCOP (stripped, arbitrary units) BatchColumn bang-bang approximation (bold) BatchColumn variable reflux (bold stripped) for p-xylene-n-hexane at total number of plates $N=5$.

All three simulations match the desired purity in the distillate tank at 0.953 ± 0.001 mol. Despite the enthalpy balance and thermodynamics slight differences between BOCOP's (Eq. (11)) and BatchColumn's models, the recovery rate is very similar in both BOCOP's and the rigorous simulation. The most important result is

shown in Table 12, namely that the optimal reflux policy simulation achieves 13% more product recovery while keeping the same purity. This confirms the interest of the bang-bang type policy vs the conventional variable reflux policy for recovering a high purity product from a mixture with a low product content.

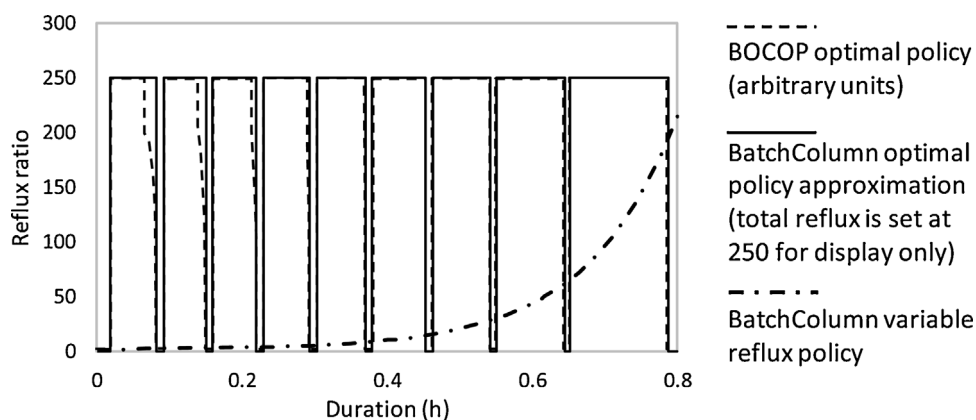


Fig. 11. BatchColumn Simulator bang-bang approximation and variable reflux policies for p-xylene-n-hexane at total number of plates $N = 5$.

5. Conclusion

Nearly thirty years ago, literature works noticed with the help of simulations that the cyclic reflux policy (bang-bang type control) is more performant than variable reflux (singular type control) or constant reflux policy when the load amount of light product is low. However, the optimal control policy reported in the relevant and numerous literature, from the 60 s to 2000 was systematically an optimized variable reflux policy. This has prompted to revisit the well-known optimal control problem of a binary non-ideal zeotropic mixture distillation in an N -stage batch column under assumptions of total condensation and constant vapour flow rate. The problem of maximizing the amount of distillate product with a desired purity in a fixed time is investigated. Results are obtained by using the direct method based on a full discretization of the optimal control problem. A novel robust problem formulation is proposed based on full column dynamics and using the distillate flow rate as control variable instead of the usual reflux and several assumptions made in literature's optimal control formulation are released. The purity constraint is also handled as a new state variable, the purity deviation. For the first time, the reflux policy is obtained as the optimal control when the separation is carried out using a plate number near its minimum for three non-ideal mixtures. The results are confirmed by rigorous simulation of the batch distillation, showing that the cyclic policy improves by 13% the product recovery over the variable reflux policy. Influence of the relative volatility, vapour flow rate, plate hold-up and initial load is discussed.

In perspective, other optimal control problems are under investigation, like minimum time problem, as well as the extension towards multi-component multi-product distillation.

References

- Bai, P., Song, S., Sheng, M., Li, X., 2010. A dynamic modelling for cyclic total reflux batch distillation. *Chin. J. Chem. Eng.* 18 (4), 554–561.
- Bernot, C., Doherty, M.F., Malone, M.F., 1991. Feasibility and separation sequencing in multicomponent batch distillation. *Chem. Eng. Sci.* 46 (5–6), 1311–1326.
- Betlem, B.H.L., Krijnsen, H.C., Huijnen, H., 1998. Optimal batch distillation control based on specific measures. *Chem. Eng. J.* 71, 111–126.
- Bildea, C.S., Patrut, C., Jorgensen, S.B., Abildskov, J., Kiss, A.A., 2015. Cyclic distillation technology – a mini-review. *Chem. Technol. Biotechnol.* 91 (5), 1215–1223.
- Bonnard, B., Chyba, M., 2003. Singular Trajectories and Their Role in Control Theory, vol. 40. Springer Science & Business Media, ISBN 3-540-00838-5.
- Christensen, F.M., Jorgensen, S.B., 1987. Optimal control of binary batch distillation with recycled waste cut. *Chem. Eng. J.* 34, 57–64.
- Converse, A.O., Gross, G.D., 1963. Optimal distillate-rate policy in batch distillation. *Ind. Eng. Chem. Fund.* 2, 217–221.
- Coward, I., 1967a. The time optimal control problem in binary batch distillation. *Chem. Eng. Sci.* 22, 503–516.
- Coward, I., 1967b. The time optimal problem in binary batch distillation – a further note. *Chem. Eng. Sci.* 22, 1881–1885.
- Diwekar, U.M., Malik, R.K., Madhavan, K.P., 1987. Optimal reflux rate policy determination for multicomponent batch distillation columns. *Comput. Chem. Eng.* 11, 629–637.
- Diwekar, U.M., 1992. Unified approach to solving optimal design-control problems in batch distillation. *AIChE J.* 38 (10), 1551–1563.
- Doherty, M.F., Malone, M.D., 2001. *Conceptual Design of Distillation Systems*, 1st edition. McGraw Hill chemical engineering series, ISBN 0-07-017423-7.
- Farhat, S., Pibouleau, L., Domenech, S., 1991. Optimal control of batch distillation via nonlinear programming. *Chem. Eng. Proc.* 29, 33–38.
- Gerbaud, V., Rodriguez-Donis, I., 2010. Distillation de mélanges non-ideaux: Distillation azéotropique et distillation extractive. *Choix de l'entraîneur. Technique de l'ingénieur*, J2-612.
- Gerbaud, V., Joulia, X., Rodriguez-Donis, I., Baudouin, O., Rosemain, O., Vacher, A., Castelain, P., 2006. Practical residue curve map analysis applied to solvent recovery in non-ideal binary mixtures by batch distillation processes. *Chem. Eng. Proc.* 45 (8), 672–683.
- Gmehling, J., Onken, U., 1982. Vapour-Liquid Equilibrium Data Collection. *DECHEMA Chemistry Data Series, Vol. 1*. DECHEMA: Frankfurt am Main, 12 parts.
- Gmehling, J., Li, J., Schiller, M., 1993. A modified UNIFAC model. 2. Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* 32, 178–193.
- Hansen, T.T., Jorgensen, S.B., 1986. Optimal control of binary batch distillation in stage or packed columns. *Chem. Eng. J.* 33, 151–155.
- Hasebe, S., Noda, M., Hashimoto, I., 1999. Optimal operation policy for total reflux and multi-effect batch distillation systems. *Comput. Chem. Eng.* 23, 523–532.
- Jiang, Z.K., Bai, P., 2012. Simulation of cyclic total reflux distillation without reflux drum. *Chem. Eng. (China)* 40 (5), 19–22.
- Jorgensen, S.B., Toftgard, B., 1987. Design Algorithm for periodic cycled binary distillation columns. *Ind. Eng. Chem. Res.* 26 (5), 1041–1043.
- Kim, K.J., Diwekar, U.M., 2001. New era in batch distillation: computer aided analysis, optimal design and control. *Rev. Chem. Eng.* 17 (2), 111–164.
- Logsdon, J.S., Biegler, L.T., 1993. Accurate determination of optimal reflux policies for the maximum distillate problem in batch distillation. *Ind. Eng. Chem. Res.* 32, 692–700.
- Low, K.H., Sorensen, E., 2004. Simultaneous optimal design and operation of multipurpose batch distillation columns. *Chem. Eng. Proc.* 43 (3), 273–289.
- Martinon, P., 2016. Bocop Documentation, INRIA-Saclay. Institute of Mathematics and Informatics, www.bocop.org.
- Mujtaba, I.M., 2004. *Batch Distillation Design and Operation*. Imperial college Press, ISBN-10: 186094437X.
- Noda, M., Kato, A., Chida, T., Hasebe, S., Hashimoto, I., 2001. Optimal structure and online optimal operation of batch distillation column. *Comput. Chem. Eng.* 25, 109–117.
- Prosim, 2015. Batchcolumn Manual, <http://www.prosim.net/en/software-batchcolumn-9.php>.
- Raducan, O., Woinaroschu, A., Lavric, V., 2005. Free time optimal control of a batch distillation column through genetic algorithms. *Rev. Chim. (Bucuresti)* 56 (11), 1114–1119.
- Robinson, E.R., 1970. The optimal control of an industrial batch distillation column. *Chem. Eng. Sci.* 25, 921–928.
- Rodriguez-Donis, I., Gerbaud, V., Joulia, X., 2001. Entrainer selection rules for the separation of azeotropic and close boiling point mixtures by homogeneous batch distillation. *Ind. Chem. Eng. Res.* 40 (12), 2729–2741.
- Sorensen, E., Prenzler, M., 1999. A cyclic operating policy for batch distillation – theory and practice. *Comput. Chem. Eng.* 21, S1215–1220.
- Sorensen, E., Skogestad, S., 1994. Optimal Operating policies of batch distillation with emphasis on the cyclic operating policy. *Proceedings of PSE'94*, 449–456.
- Sorensen, E., 1999. A cyclic operating policy for batch distillation – theory and practice. *Comput. Chem. Eng.* 23 (4–5), 533–542.

- Stojkovic, M., Gerbaud, V., Shcherbakova, N., 2017. [Batch distillation of binary mixtures: preliminary analysis of optimal control](#). In: [Proceedings of the 20th World Congress of the International Federation of Automatic Control](#), Toulouse, France.
- Trelat, E., 2008. [Contrôle optimal: Theorie et application](#), 2nd edition. Vuibert, ISBN 271177175X.
- Upreti, S.R., 2012. [Optimal Control for Chemical Engineers](#). CRC PRESS, ISBN 1439838941.
- Van Dongen, D.B., Doherty, M.F., 1985. [On the dynamics of distillation processes. VI. Batch distillation](#). *Chem. Eng. Sci.* 40, 2087–2093.