

# Spreadsheet to illustrate the application of relaxation methods for multicomponent distillation separations

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## ABSTRACT

Rigorous calculation methods to simulate multicomponent distillation processes involve large number of variables and equations that are difficult to solve by hand and require the use of specific software. With this purpose, commercial process simulators have been included for years as learning tools in the syllabus of Chemical Engineering degrees. Nevertheless, there is thus a possibility of using these packages as a black box and strategies to mitigate that risk have been developed, as the use of spreadsheets where students can follow and check the calculation algorithms and the details of such calculations. One alternative to solve multicomponent distillation problems is the use of relaxation methods, that find the steady-state solution of a continuous distillation column by solving unsteady-state equations from a specified initial condition, thus providing an analogy with the column startup. In this work, a novel spreadsheet to apply a relaxation method is proposed. Calculation begins with the simulation of a distillation column at total reflux, which is a common way to start up these processes. In order to facilitate the development of unsteady-state equations and operation, a batch distillation column is also simulated. Finally, the evolution of a continuous distillation column from a specified starting condition to steady-state is simulated.

## 1. Introduction

Relaxation methods for multicomponent distillation columns are based in assuming a starting condition of a continuous distillation column, where the temperature, flowrates and composition profiles are known and specified, and the unsteady-state equations describing the evolution with time of the process variables are solved until reaching the steady-state solution, when variables do not change with time anymore. These methods can model the actual operation of the column, and could be developed for the study of transient behavior of column designs and for the analysis and design of batch distillation columns (Sinnott, 2005). This process could be said to mimic the physical startup of the column, but the actual objective is not to follow the dynamic operation of the column, but to seek the steady-state solution (Kister, 1992). Relaxation methods are described by Kister (1992), who explains that the column is brought to the steady-state conditions by successive approximations of the unsteady-state distillation equations. According to Sinnott and Towler (2012), relaxation methods are not competitive with steady-state methods in the use of time computer, because they converge slowly. Nevertheless, as they model the actual operation of a column, they

should provide a converged solution for every practical situation, and can be used in dynamic simulations, being useful to understand the control and the operation of a column. Sinnott and Towler (2012) report that relaxation methods are used in rate-based models in Aspen Plus RateFrac™ and BatchFrac™. However, usually they are not considered in many common textbooks. Then, the availability of a learning tool to illustrate their application may be interesting for separation process lecturers. The objective of the tool provided in this work is not to compete with licensed specialist simulation software, much more powerful, but sometimes being used as a black box, it is to illustrate how these methods work.

Real distillation columns are dynamic, with variable flows, compositions, temperatures and pressures that have to be controlled and/or adjusted in order to obtain the desired products within the adequate range of specifications. Then, perhaps the ideal system of MESH equations (i.e., Material balances, Equilibrium relations, Summation equation and energy -or Heat- balances) should include terms to consider the start-up, maintenance and shutdown events, among others. However, the quantitative simulation of a real dynamic distillation column is out of the scope of the conventional courses of separation processes. In fact,

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such aspects are not usually considered in most of textbooks. These questions are very well developed in H.Z. Kister's book "Distillation-Operation" (Kister, 1990) that, being realistic, by far exceeds the possibilities of our courses. Perhaps the engineering problems below the mathematical theory and modelling developed in the classroom are trivial, but maybe the most important thing is to provide students the basic skills that allow them to acquire the needed knowledge quickly and efficiently at other levels, if it were possible in a parallel way to the mathematical models explained, at pilot plant experimentation subjects, or at external internships.

The equations involved in relaxation methods are modifications of the steady-state MESH equations to include the changes of the MESH variables with respect to time, for all the components and for all the stages of the column. The difficulty of solving them "by hand" is very well known, and different rigorous equilibrium-based methods have been developed, which are described in textbooks of separation processes with different level of detail but, in all cases, stating that their application requires the use of specific simulation software (see, as an example Kister, 1992; King, 1980; Sinnott, 2005; Seader et al. 2011 or Wankat, 2012). According to Kister (1992), *bubble point* methods, *sum rates* methods and *simultaneous correction* methods can be converted to *relaxation* methods by substituting the relaxation composition calculation for the one used in the specific method. In this way, the difficulty of the calculation procedures is increased because the need of applying the method in successive time intervals, solving the Euler's equation to obtain the correction of variables, is added to the drawbacks of the method. Recently, Lane (2019) has published an excellent textbook focused on the objectives of a separation processes course for ungraduated students. Explaining multicomponent distillation, Lane (2019) proposes a "brute force" method to solve problems with ideal mixtures of only a few components and few column stages, where the process variables and equations are counted and considered, and an efficient algorithm to solve them with a spreadsheet is then proposed. This approach cannot be considered at the same level than the standard rigorous methods because cannot be applied when the number of components and/or stages increase. Nevertheless, it has useful learning purposes because it avoids the drawbacks associated with the mathematical resolution of the problem and allows students to focus on deepening in the use and the meaning of equations.

The advantages of using spreadsheets as teaching resource has been very well recognized for years (Grulke, 1986; Iglesias et al., 2004; Stammou and Rutschmann, 2011; Gómez-Siurana and Font-Escamilla, 2012, Stammitti, 2013; Park et al. 2018; Nachtigalova et al., 2020; Briones et al., 2020, Gómez-Siurana and Font-Escamilla, 2022). When the algorithms involved are difficult to apply by hand, it is very useful to provide students with spreadsheets with solved examples where they can see how the calculation is performed and what are the mathematical difficulties. Gómez-Siurana and Font-Escamilla (2022) have proposed and shared with the community a learning approach based on Excel files containing solved examples of rigorous methods for multicomponent separations, where the main approaches of resolution of the steady-state MESH equations are described with high level of detail. Nevertheless, *relaxation* methods were not included in that approach, which focused on equilibrium-based methods.

In the present work, the unsteady-state MESH equations are considered, and an example of application of a *relaxation* method is presented. In order to avoid the mathematical complexity of solving MESH equations, that it is pointed out elsewhere (Gómez-Siurana and Font-Escamilla, 2022), the "brute force" procedure (Lane, 2019) is applied, and a hypothetical ideal ternary mixture is considered to be separated in a column with a total condenser, one equilibrium stage and a partial reboiler. The proposal starts with a spreadsheet to simulate the operation at total reflux, that is a usual point to start up a column, probably already practiced by students at their pilot plant assignments. After that, the unsteady-state MESH equations for a batch distillation column are considered, and the simulation of the operation at constant

reflux and at constant reboiler duty or at constant distillate flowrate is shown. Finally, the equations are modified to include a feed stream and the extraction of a bottoms product, and the continuous distillation column is simulated. The Excel file with the solved examples can be found at <http://bit.ly/3K5z4MN>, and the description of the involved procedures and the design and use of the spreadsheets are detailed in the following sections.

## 2. Intended learning outcomes

The learning approach based on providing students solved examples as complementary material has been already applied with MSc students of Chemical Engineering at the University of Alicante (Spain) with very satisfactory results (Gómez-Siurana and Font-Escamilla, 2012 and 2022; Gómez-Siurana et al., 2019a and 2019b). Over the last years, lectures about rigorous methods for multicomponent separations have been reinforced by a complementary tool based on providing students spreadsheets with solved examples of equilibrium-based methods. That kind of methods are very difficult to apply "by hand", but in the spreadsheet is easy to follow and analyze the calculation details and the difficulties involved. Students are asked about these examples in the final exam, and they have to be able to identify the method and locate or identify the type of calculations and/or the objective searched at some block of the spreadsheet, proving that they understand it.

The number of spreadsheets delivered to the students has been increasing over time, and the 2021–2022 course was the first time that the overall set of equilibrium-based methods explained in the theory classes (i.e., those included in the Kister (1992) and Seader et al. (2011) textbooks) was available. Thus, once students had been evaluated, an anonymous survey was conducted to check their opinion about the usefulness of these exercises and the time spent in their study, with very satisfactory results; and the experience was published and the spreadsheets shared with the community (Gómez-Siurana and Font Escamilla, 2022). Relaxation methods, that are not equilibrium-based methods, were not included in the above-mentioned set, and the convenience of developing the corresponding spreadsheet was considered, especially considering that unsteady-state MESH equations are usually not described at the same level than the steady-state case (even, frequently they are not described in literature). Then, the tool presented (and shared) in this work will be delivered to students for the 2023–2024 course, increasing the number of complementary materials used in previous courses. Its usefulness is endorsed by the previous experience with other materials based on the same methodology: as an example, the comparison between the results obtained by students in the final exam performed in 2018, when the complete set of solved exercises of equilibrium-based methods was not provided yet, and in 2022, when this strategy was already used, has been performed. Years have been selected looking for courses with similar number of students (12 and 11, respectively). In both cases, a true-false test with around 40 questions was posed. The results obtained have shown that 48% of the questions on the final exam related with rigorous methods were correctly answered in 2018 whereas in 2022, this percentage increased to around 65%. It is worth to mention the case of three questions that were equal in both exams: the results corresponding to two of them improved significantly when students were provided of solved examples (from 8% to 64% and from 58% to 91% of correct answers in each case) but a worsening has been observed in the third one (from 67% to 36% of correct answers). Therefore, despite these results are very dependent of the number and characteristics of each student's cohort but, globally, seems to reflect that learning this kind of methods that involve difficult calculations improves when students are provided with tools as that proposed in present work.

The learning outcomes of this approach intend that students improve their knowledge and understanding of concepts and theories involved in multicomponent distillation processes as well as the needed intellectual abilities to apply unsteady-state equations for modelling problems. It is

expected that working with the provided spreadsheets contributes to develop the practical and professional skills because their position when use simulation software should change from black box-users to conscious-users. Therefore, once the principles of these methods have been explained in the classroom and students have worked with the file shared in this work, they will acquire the following skills:

- Improve their knowledge of the operation at total reflux.
- Go beyond the design of binary batch distillation based on McCabe-Thiele diagrams.
- Describe the unsteady-state MESH equations for a batch and a continuous distillation column.
- Be able to develop efficient algorithms based on Excel spreadsheets to solve complex problems applied to simple cases.
- Understand the characteristics of relaxation methods for continuous distillation and its usefulness to reproduce the startup of a column.

On the other hand, this material can be used as supplementary material in experimental courses. For example, in Chemical Engineering education, it is quite common that students complete experimental assignments with laboratory or pilot-plant scale distillation columns. This work and, specifically the spreadsheet, can be easily modified to compare calculated results with their experimental counterparts. It could be used as a powerful teaching resource in advanced separation processes because students can have a deeper knowledge about a distillation column startup, noticing the experimental difficulties as well as the calculating ones.

In the next sections, the equations to be solved, the calculation procedure applied and, finally, the structure and use of the spreadsheets shared with the community are presented. The results of the solved examples have been checked by comparison with those yielded by a process simulator.

### 3. Equations to be solved

In this section the unsteady-state MESH equations are developed. First of all, the batch distillation case is considered, followed by the continuous distillation column description. The procedure used to solve the equations for each case is presented in the “results and discussion” section.

#### 3.1. Multicomponent batch distillation

Regarding batch distillation, textbooks are usually focused on the separation of binary mixtures, and it is explained based on McCabe-Thiele diagrams (King, 1980; Wankat, 2012). Kister (1992) presents examples of multicomponent mixtures with small number of theoretical stages and small number of components, that are considered as binary mixtures on the basis of the light key component and using also McCabe-Thiele diagrams. The book of Seader et al. (2011) includes a complete section for multicomponent batch distillation and introduces a shortcut method, where the column is treated as a sequence of continuous steady-state rectification steps solved by the Fenske-Underwood-Gilliland method, as well as stage-by-stage rigorous computer-based methods. An alternative also proposed by Seader et al. (2011) consists in a “rapid-solution” method based on treating the problem as a succession of a finite number of continuous steady-states of short duration, where the changes between one state and the next one are simulated by feed streams and/or liquid sidestreams. Then, the successive systems of steady-state equations can be solved by conventional methods as *simultaneous correction* or *inside-out*.

In this work, the objective to facilitate the learning of the unsteady-state behavior of multicomponent distillation columns, both batch and continuous, and to show how *relaxation* methods for continuous columns work. It is worth to point up that these topics are not usually treated deeply and sometimes are not included in the separation processes

programs. Therefore, the unsteady-state MESH equations are presented and, to facilitate the development of spreadsheets, applied to a ternary mixture fed to a column with a total condenser, one ideal equilibrium stage and a partial reboiler. To simplify, ideal gas and ideal solution behavior are considered, and an algorithm to solve the set of differential MESH equations by calculating the corrections of variables by Euler’s equation is applied. These equations are also valid for columns having more than one intermediate equilibrium stage, nevertheless, in that case, solving by hand the set of MESH is more cumbersome, because the increase in the number of equations and variables involved.

As usual in operations based on countercurrent cascades of stages, a column can be described as a sequence of general equilibrium stages, as those shown in Figs. 1 and 2, connected to each other. For a conventional batch column, the feed is charged at the reboiler, where heat is supplied, and the only products extracted are the successive liquid distillate cuts, from a total condenser. The stages between the reboiler and the condenser are considered as adiabatic and the only heat exchanges are the condenser and reboiler duties.  $x_{i,j}$  and  $y_{i,j}$  are, respectively, mole fractions of a component in a liquid and a vapor. Subindex  $i$  refers to each component and  $j$  to each column stage. Cascades are numbered from the top (stage 1) to the bottom (stage  $N$ ).  $L_j$  and  $V_j$  represent, respectively, the liquid and vapor flowrate of internal streams leaving stage  $j$ , that are equal to those entering the adjacent stages because no sidestreams are drawn, and  $D$  is the distillate flowrate.  $Q_j$  is the heating rate transferred at stage  $j$ , considered positive if supplied and negative if removed.  $H_j$  and  $h_j$  represent, respectively, the enthalpies of a vapor and a liquid stream leaving stage  $j$ . Reflux ratio,  $R$ , is defined as the  $L_1/D$  ratio. These are the usual variables for a steady-state operation but, for unsteady-state operations, two additional variables are needed to introduce the quantity of liquid retained on a plate by an outlet weir:  $G_j$  and  $M_j$  are, respectively, the volumetric and the molar holdup at stage  $j$ . Typically,  $G_j$  is assumed not to change with time, being constant for all  $j < N$ . Note that this is a simplified description of stages and variables that does not consider the extraction of sidestreams from intermediate stages.

The behavior of the system is described by MESH equations obtained for each column stage. According to Fig. 1, equations are different for stages 1,  $j$  ( $1 < j < N$ ) and  $N$ . The resulting equations, also shown by Seader et al. (2011) -with other stages numbering-, are introduced in Table 1, where  $K_{ij} = y_{ij}/x_{ij}$  represents the equilibrium ratio of component  $i$  at stage  $j$ . To obtain equation (6), the enthalpy balance at the total condenser is combined with equation (4) to give  $V_2$ , whereas to obtain equation (7),  $L_j$  in the enthalpy balance around stage  $j$  (Fig. 1b) is substituted by the value given by equation (5). Equations (11) and (12) are used to calculate the molar holdup: at stages 1 to  $N-1$  from the corresponding constant-volume holdups,  $G_j$ , and liquid molar densities,  $\rho_j$ , and at the reboiler from a total material balance, considering the initial charge at reboiler,  $M_N^{t=0}$ . Furthermore, temperature-dependent correlations for calculating equilibrium ratios,  $K_{ij}$ , specific enthalpies of vapor,  $H_j$ , and liquid,  $h_j$ , and liquid molar densities will be needed. In this case, that ideal behavior is assumed,  $K_{ij}$  are calculated from the Raoult Law, by means the Antoine equation for vapor pressure (i.e.,  $K_{i,j} = P_{i,j}^0/P$ , being  $P_{i,j}^0$  and  $P$  the vapor pressure at the temperature of stage  $j$ ,  $T_j$ , and total pressure, respectively).

Table 2 lists the number of variables (58) and equations (49) involved in the three stages and three components batch column, showing that there are 9 degrees of freedom, that are used to specify the time ( $t$ ),  $P$ ,  $G_1$ ,  $G_2$ ,  $x_{i,3}^{t=0}$  ( $i = 1, 2$ ),  $M_N^{t=0}$  (calculated from the initial volume, composition and temperature of the mixture loaded at the reboiler) and 2 additional operational variables (i.e.  $R$  and  $Q_3$  or  $R$  and  $D$ ).

#### 3.2. Unsteady-state equations for multicomponent continuous distillation

Equations for an unsteady-state continuous column can be drawn

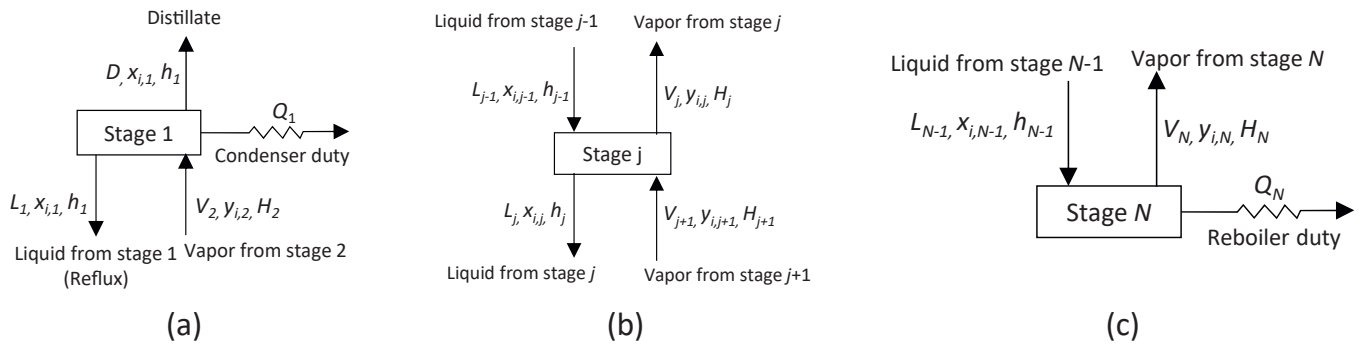


Fig. 1. Stages to be considered for a batch column. (a) Total condenser, (b) intermediate equilibrium stage, (c) reboiler.

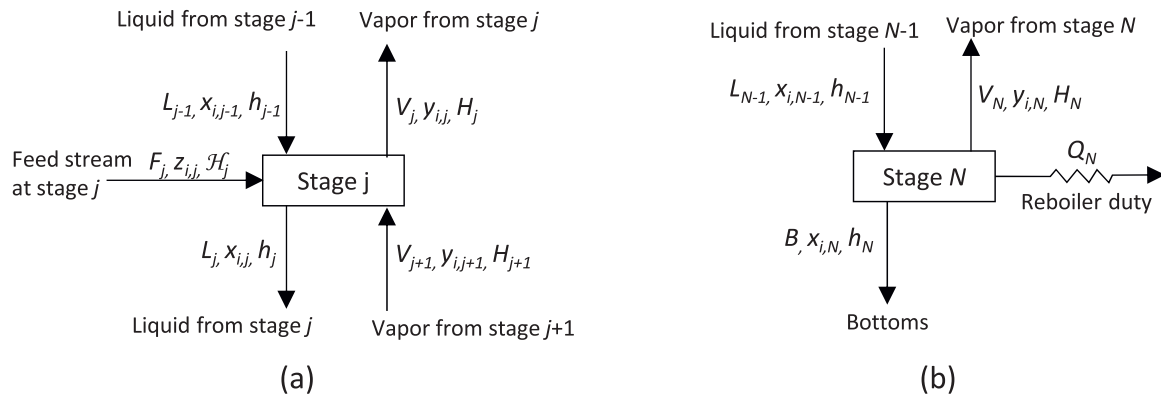


Fig. 2. Stages to be considered for a continuous column. (a) intermediate equilibrium stage, (b) reboiler.

Table 1

Set of equations for a batch distillation column.

Type of equation	Equation to be solved	NUM
Component material balance at stage 1	$\frac{dx_{i,1}}{dt} = - \left[ \frac{L_1 + D}{M_1} + \frac{dM_1}{dt} \right] x_{i,1} + \left[ \frac{V_2 K_{i,2}}{M_1} \right] x_{i,2}$	1
Component material balance at stage $j$	$\frac{dx_{i,j}}{dt} = \left[ \frac{L_{j-1}}{M_j} \right] x_{i,j-1} - \left[ \frac{L_j + K_{i,j} V_j}{M_j} + \frac{dM_j}{dt} \right] x_{i,j} + \left[ \frac{V_{j+1} K_{i,j+1}}{M_j} \right] x_{i,j+1} \quad 1 < j < N$	2
Component material balance at stage $N$	$\frac{dx_{i,N}}{dt} = \left[ \frac{L_{N-1}}{M_N} \right] x_{i,N-1} - \left[ \frac{K_{i,N} V_N}{M_N} + \frac{dM_N}{dt} \right] x_{i,N}$	3
Total material balance at stage 1	$V_2 = D(R+1) + \frac{dM_1}{dt}$	4
Total material balance at stage $j$	$L_j = V_{j+1} + L_{j-1} - V_j - \frac{dM_j}{dt} \quad 1 < j < N$	5
Energy balance at stage 1	$Q_1 = V_2(H_2 - h_1) - M_1 \frac{dh_1}{dt}$	6
Energy balance at stage $j$	$V_{j+1} = \frac{1}{(H_{j+1} - h_j)} \left[ V_j(H_j - h_j) - L_{j-1}(h_{j-1} - h_j) + M_j \frac{dh_j}{dt} \right] \quad 1 < j < N$	7
Energy balance at stage $N$	$Q_N = V_N(H_N - h_N) - L_{N-1}(h_{N-1} - h_N) + M_N \frac{dh_N}{dt}$	8
Phase equilibrium relation	$y_{ij} = K_{ij} x_{ij}$	9
Mole fraction summation	$\sum_{i=1}^C y_{ij} = \sum_{i=1}^C K_{ij} x_{ij} = 1$	10
Molar holdup at stage $j$	$M_j = G_j \rho_j \quad j = 1, \dots, N-1$	11
Molar holdup at stage $N$	$M_N = M_N^{t=0} - \sum_{j=1}^{N-1} M_j - \int_0^t D dt$	12

from those exposed in the previous section: the total condenser can be described by the same scheme than Fig. 1a, and then, equations (1), (4) and (6) will be still applicable. A general intermediate stage is shown in Fig. 2a and considers the eventual introduction of a feed stream; to simplify, the extraction of sidestreams is not considered. Fig. 2b shows

the scheme for the partial reboiler, from which the liquid bottoms product is obtained.  $B$  represents the bottoms flowrate, and  $F_j$  and  $z_{i,j}$  the flowrate and mole fractions of the feed stream at stage  $j$ .  $z_{i,j}$  and  $H_j$  are used to identify the composition and enthalpy, respectively, of a stream at any thermal condition. In this case, it is assumed that the feed enters

**Table 2**

List of variables and equations involved in the problem of a three-stages batch column for the separation of a ternary mixture. The only product is a liquid distillate.

Variables	Equations
$x_{i,j}$ (9, for all $i$ and $j$ )	Eqn (1) (3, for all $i$ )
$y_{i,j}$ (9, for all $i$ and $j$ )	Eqn (2) (3, for all $i$ )
$L_j$ (2, $j = 1, 2$ )	Eqn (3) (3, for all $i$ )
$V_j$ (2, $j = 2, 3$ )	Eqn (4) (1)
$D$ (1)	Eqn (5) (1, for $j = 2$ )
$Q_j$ (2, for $j = 1$ and 3)	Eqn (6) (1)
$R$ (1)	Eqn (7) (1, for $j = 2$ )
$G_j$ (2, for $j = 1$ and 2)	Eqn (8) (1)
$M_j$ (3, for all $j$ )	Eqn (9) (9, for all $i$ and $j$ )
$H_j$ (3, for all $j$ )	Eqn (10) (3, for all $i$ )
$h_j$ (3, for all $j$ )	Eqn (11) (2, for $j = 1$ and 2)
$\rho_j$ (3, for all $j$ )	Eqn (12) (1)
$K_{i,j}$ (9, for all $i$ and $j$ )	$R = L_1/D$ (1)
$M_n^{t=0}$ (1)	$K_{i,j} = P_{i,j}^0/P$ (9, for all $i$ and $j$ )
$x_{i,3}^{t=0}$ (3, for all $i$ )	$\sum_{i=1}^3 x_{i,3}^{t=0} = 1$ (1)
$T_j$ (3, for all $i$ and $j$ )	$H_i$ as a function of component enthalpies (3, for all $j$ )
$P$ (1)	$h_i$ as a function of component enthalpies (3, for all $j$ )
$t$ (1)	$\rho_i$ as a function of component densities (3, for all $j$ )
Total variables = 58	Total equations = 49

at the column pressure.

The set of unsteady-state equations for a continuous distillation column is shown in Table 3. As it has been stated, for the considered continuous column, equations (1), (4), (6) are valid, as well as equations for mole fractions summation (equation 10), liquid-vapor equilibrium ratios (equation 9) and molar liquid holdup at the stages (equation 11). Equation (17) is obtained by substituting  $L_j$  given by equation (15) in the enthalpy balance around stage  $j$  (Fig. 2a). Furthermore, when  $dM_N/dt$  from equation (16) is substituted in the enthalpy balance around the reboiler shown in Fig. 2b, the resulting equation is the same as equation (8). The overall mole balance (equation 18) has also been introduced.

Table 4 lists the number of variables (60) and equations (50) involved in the three stages and three components batch column,

**Table 3**

Set of unsteady-state equations for a continuous distillation column.

Type of equation	Equation to be solved	NUM
Component material balance at stage 1	$\frac{dx_{i,1}}{dt} = - \left[ \frac{L_1 + D + \frac{dM_1}{dt}}{M_1} \right] x_{i,1} + \left[ \frac{V_2 K_{i,2}}{M_1} \right] x_{i,2}$	1
Component material balance at stage $j$	$\frac{dx_{i,j}}{dt} = \left[ \frac{F_j}{M_j} \right] z_{i,j} + \left[ \frac{L_{j-1}}{M_j} \right] x_{i,j-1} - \left[ \frac{L_j + K_{ij} V_j + \frac{dM_j}{dt}}{M_j} \right] x_{i,j} + \left[ \frac{V_{j+1} K_{i,j+1}}{M_j} \right] x_{i,j+1} \quad 1 < j < N$	13
Component material balance at stage $N$	$\frac{dx_{i,N}}{dt} = \left[ \frac{L_{N-1}}{M_N} \right] x_{i,N-1} - \left[ \frac{K_{iN} V_N + B + \frac{dM_N}{dt}}{M_N} \right] x_{iN}$	14
Total material balance at stage 1	$V_2 = D(R+1) + \frac{dM_1}{dt}$	4
Total material balance at stage $j$	$L_j = F_j + V_{j+1} + L_{j-1} - V_j - \frac{dM_j}{dt} \quad 1 < j < N$	15
Total material balance at stage $N$	$L_{N-1} = B + V_N + \frac{dM_N}{dt}$	16
Energy balance at stage 1	$Q_1 = V_2(H_2 - h_1) - M_1 \frac{dh_1}{dt}$	6
Energy balance at stage $j$	$V_{j+1} = \frac{1}{(H_{j+1} - h_j)} \left[ F_j(h_j - \bar{h}_j) + V_j(H_j - h_j) - L_{j-1}(h_{j-1} - h_j) + M_j \frac{dh_j}{dt} \right] \quad 1 < j < N$	17
Energy balance at stage $N$	$Q_N = V_N(H_N - h_N) - L_{N-1}(h_{N-1} - h_N) + M_N \frac{dh_N}{dt}$	8
Phase equilibrium relation	$y_{i,j} = K_{i,j} x_{i,j}$	9
Mole fraction summation	$\sum_{i=1}^C y_{i,j} = \sum_{i=1}^C K_{i,j} x_{i,j} = 1$	10
Molar holdup at stage $j$	$M_j = G_j \rho_j \quad j = 1, \dots, N - 1$	11
Overall material balance	$F = D + B + \sum_{j=1}^3 \frac{dM_j}{dt}$	18

showing that there are 10 degrees of freedom, that are used to specify  $t$ ,  $P$ ,  $G_1$ ,  $G_2$ ,  $F_j$ ,  $z_{i,j}$  ( $i = 1, 2$ ) and  $H_j$  (or the feed thermal condition at column pressure) and 2 additional operational variables (i.e,  $R$  and  $D$ ).

#### 4. Calculation procedure

Equations presented in the previous section have been solved for a batch column at total reflux, for a batch column operating at constant reflux ratio and two different conditions (i.e., constant reboiler duty and constant distillate flowrate), and for a continuous column. As it has been stated, this may require the application of computer-based methods (Seader et al., 2011), as those implemented at chemical process simulators, arising the risk of being used as a black box, and focusing the objective on the results more than on the calculation algorithms or equations involved. Then, the approach proposed in the present work, providing students the Excel file with solved examples, allows them to see the details of how calculations evolve, specifically how the unsteady-state equations are solved and how the system variables change with time. The Excel file containing the solved examples is described in this work and is available at <http://bit.ly/3K5z4MN>.

As it has been commented above, to simplify, a column having a total condenser, one intermediate equilibrium stage and a partial reboiler is considered for the separation of a hypothetical ternary mixture showing ideal gas and ideal solution behavior, thus allowing the liquid-vapor equilibrium calculation by the Raoult's law. Furthermore, very simple linear temperature-dependent relationships for enthalpies are proposed. Vapor pressures are calculated with Antoine's equation and a temperature-dependent correlation for liquid molar density is also used. The assumed simplifications allow us to apply a "brute force" method (Lane, 2019) to solve the examples in simple spreadsheets, by using the Excel's "Goal seek" tool when iterative calculations are needed. The proposed spreadsheets include comments and explanations to follow calculations in order to facilitate students the autonomous work. The algorithms developed for each case are described in the following sub-sections, and the structure, characteristics and use of each spreadsheet is shown in the "Results and discussion" section.

**Table 4**

List of variables and equations involved in the problem of a conventional three-stages continuous column with a total condenser.

Variables	Equations
$x_{i,j}$ (9, for all $i$ and $j$ )	Eqn (1) (3, for all $i$ )
$y_{i,j}$ (9, for all $i$ and $j$ )	Eqn (13) (3, for all $i$ )
$L_j$ (2, $j = 1, 2$ )	Eqn (14) (3, for all $i$ )
$V_j$ (2, $j = 2, 3$ )	Eqn (4) (1)
$D$ (1)	Eqn (15) (1, for $j = 2$ )
$Q_j$ (2, for $j = 1$ and 3)	Eqn (16) (1)
$H_j$ (3, for all $j$ )	Eqn (6) (1)
$h_j$ (3, for all $j$ )	Eqn (17) (1, for $j = 2$ )
$R$ (1)	Eqn (8) (1)
$G_j$ (2, $j = 1, 2$ )	Eqn (9) (9, for all $i$ and $j$ )
$M_j$ (3, for all $j$ )	Eqn (10) (3, for all $j$ )
$\rho_j$ (3, for all $j$ )	Eqn (11) (2, for all $j$ )
$K_{i,j}$ (9, for all $i$ and $j$ )	Eqn (18) (1)
$T_j$ (3, for all $i$ and $j$ )	$K_{i,j} = P_{ij}^0/P$ (9, for all $i$ and $j$ )
$F_j, z_{i,j}, P_j$ and $T_j$ (5, for $j = 2$ and all $i$ )	$R = L_1/D$ (1)
$P$ (1)	$H_i$ as a function of component enthalpies (3, for all $j$ )
$t$ (1)	$h_i$ as a function of component enthalpies (3, for all $j$ )
$B$ (1)	$\rho_i$ as a function of component densities (3, for all $j$ )
Total variables = 60	$\sum_{i=1}^3 z_{i,j} = 1$ (1, $j = 2$ )
	Total equations = 50

#### 4.1. Column operating at a total reflux

Total reflux is a usual way to start up a batch column. At such operation conditions, no stream is fed to and no product is extracted from the column. Then, a specified amount of a mixture with known composition, temperature and pressure is initially fed at the reboiler, and a constant heat duty is supplied to the reboiler. As it is well known, and can be easily demonstrated by material balances around stages, when the steady-state is reached, liquid and vapor streams crossing each other between consecutive stages have the same flowrates and compositions. Then, the simulation of the column at total reflux can be done according to the following procedure, developed in the spreadsheet “Batch-Total reflux” of the file available at <http://bit.ly/3K5z4MN>.

The operation of the column at total reflux can be derived from the equations for a batch or a continuous column, considering that the flowrates of feeds and products are zero and that the terms  $dx_{ij}/dt$ ,  $dM_j/dt$  and  $dh_j/dt$  are also zero because it is a steady-state situation. Thus, the three variables  $D$ ,  $R$  and  $t$  must be removed from the list on Table 2, giving 55 variables. In a parallel way, the 9 equations (1), (2) and (3) as well as the relation  $R = L_1/D$  have to be removed from the list of equations, giving 39 equations. On the other hand, 9 new equations are needed, corresponding to:

- the 6 equalities  $x_{i,j} = y_{i,j+1}$  for  $j = 1, 2$ , coherent with the mass balance at total reflux
- the 2 equalities  $L_j = V_{j+1}$  for  $j = 1, 2$ , coherent with the mass balance at total reflux
- the component molar balance with the amount of component initially loaded at the reboiler, given by:

$$x_{i,3}M_3 = x_{i,3}^{t=0}M_3^{t=0} - (x_{i,1}M_1 + x_{i,2}M_2) \quad (19)$$

Then, the 55 variables and 48 equations allow us to conclude that there are 7 degrees of freedom, that are used to specify the following variables:

- Pressure at the condenser. The column pressure drop is taken as zero, then all the stages of the column are at the same pressure.
- Initial load at the reboiler: total volume, temperature and composition. These variables allow us to calculate  $M_n^{t=0}$ , and provide the needed information to obtain the composition at the reboiler at total reflux (3 variables,  $M_n^{t=0}$  and  $x_{i,3}^{t=0}$  for  $i = 1, 2$ ).

- Liquid holdups  $G_1$  and  $G_2$  (i.e., at the total condenser and the intermediate stage).
- Heat supplied at the reboiler,  $Q_3$ .

Note that the composition profiles at total reflux only depend on the liquid-vapor equilibrium and then on the initial composition at the reboiler,  $x_{i,3}^{t=0}$ , and are not affected by the specified initial amount of mixture,  $M_3^0$ , or the reboiler duty,  $Q_3$ . Nevertheless, these variables are needed to calculate the flowrates of internal streams and the holdup at stages, that are going to be used as the starting point for continuous and batch columns calculations. In fact, if the only objective was to obtain the composition profiles, the problem will be reduced to a distillation line calculation, as it is described in the bibliography (Seader et al., 2011).

The proposed calculation algorithm applies an iterative calculation based on the comparison, at each step, between the assumed and calculated composition at the reboiler, and implies the following calculation sequence. The corresponding flowchart is shown in Fig. 3a:

1. Guess a steady-state composition at the reboiler ( $x_{i,3}$ ).
2. Calculate the liquid-vapor equilibrium at the reboiler to obtain temperature and equilibrium vapor composition ( $T_3$  and  $y_{i,3}$ ). This step requires to find the value of  $T_3$  that makes  $\sum y_{i,3} = \sum K_{i,3} \cdot x_{i,3} = 1$ .
3. Apply the conditions of total reflux: from the reboiler, go to the top of the column giving each liquid the composition of the crossing vapor from the stage below ( $x_{i,j} = y_{i,j+1}$ ), and calculate each vapor considering that it is in equilibrium with the liquid from the same stage ( $y_{ij} = K_{i,j} \cdot x_{i,j}$ ). These equilibrium calculations also give the stage temperatures. Here, additional liquid-vapor equilibrium calculations at each stage are performed, and, only knowing the assumed composition at the reboiler, all the values of  $T_j$ ,  $x_{i,j}$  and  $y_{i,j}$  are obtained.
4. Once the temperature and the compositions of each phase at each stage are known, calculate the corresponding specific enthalpies of vapor and liquid and the liquid molar densities with the corresponding temperature-dependent correlations.
5. Calculate flowrates  $V_3$  and  $V_2$  by enthalpy balances at the reboiler (equation 8) and at stage 2 (equation 7), respectively, considering that, at total reflux,  $V_3 = L_2$  and  $V_2 = L_1$  at the steady-state the terms  $dh_j/dt$  are zero.
6. Calculate the molar liquid holdup at each stage: for condenser and intermediate stages from their volumetric holdup and the liquid



Fig. 3. Algorithm proposed for a) Total reflux calculation b) batch distillation, case i, c) batch distillation, case ii, d) continuous distillation.

molar densities (equation 11) and, at the reboiler, by the material balance with the amount of liquid initially loaded at the reboiler,  $M_N^{t=0}$  (equation 12).

7. Calculate the composition at the reboiler by the component molar balance with the amount of component initially loaded at the reboiler given by Eq. (19).
8. Compare the calculated composition for the reboiler at step 7 with the one guessed at step 1. If they are close enough, the calculation is finished; if not, repeat from step 2 with the new values of  $x_{i,3}$ . In order to avoid negative compositions through the iterative calculation, the following expression has been applied, as it is recommended in the book of Seader et al. (2011) for the application of simultaneous correction method:

$$x_{i,3}^{(k+1)} = x_{i,3}^{(k)} \exp \left[ \frac{\lambda \Delta x_{i,3}^{(k)}}{x_{i,3}^{(k)}} \right] \quad (20)$$

where  $k$  is the iteration index of and  $\lambda$  is a scalar step factor that can be modified to diminish the possibility of obtaining oscillating values at successive iterations.

As it has been stated, each liquid-vapor calculation performed at steps 2 and 3 requires the iterative calculation needed to carry out a bubble point calculation, widely described in many textbooks (see, as an example Kister, 1992; King, 1980; Seader et al. 2011, Whankat, 2012 or Lane, 2019). Also, it is worthwhile to remember that the density of a mixture cannot be calculated as the average of components densities, and the following expression, dimensionally homogeneous, must be applied:

$$\rho_{mixture} = \frac{\sum_{i=1}^C n_i x_i}{\sum_{i=1}^C \frac{n_i x_i}{\rho_i}} = \frac{1}{\sum_{i=1}^C \frac{x_i}{\rho_i}} \quad (21)$$

#### 4.2. Batch column

The simulation of the behavior of the above-described batch column,

at constant reflux ratio and i) constant reboiler duty or ii) constant distillate flowrate, is performed in the spreadsheets “Batch-QB” and “Batch-D” of the file available at <http://bit.ly/3K5z4MN>. It is considered that the operation begins with the column at total reflux, that is a usual way to start up a column, and the initial profiles of the internal streams are those obtained in the spreadsheet “Batch-total-reflux” (despite other initial profiles can be also considered). Then, the same specifications than that used for total-reflux calculation, giving the above-mentioned profiles, must be considered, and the remaining two degrees of freedom are used to specify  $t$  and  $R$  (case i) or the  $t$ ,  $R$  and  $D$  instead of  $Q_3$  (case ii). The same temperature-dependent correlations and parameters for Antoine’s equation, specific liquid and vapor enthalpies and molar density that in the previous case are needed and the time is specified by means of time interval,  $\Delta t$ , to follow the behavior of the column. Therefore, the specified variables are:

- Pressure at the condenser. The column pressure drop is taken as zero, then all the stages of the column are at the same pressure.
- Initial load at the reboiler: total volume, temperature and composition. These variables allow us to calculate  $M_N^{t=0}$ , and provide the needed information to obtain the composition at the reboiler at total reflux (3 variables,  $M_N^{t=0}$  and  $x_{i,3}^{t=0}$  for  $i = 1, 2$ ).
- Liquid holdups  $G_1$  and  $G_2$  (i.e., at the total condenser and the intermediate stage).
- Reflux ratio,  $R$ .
- Time step,  $\Delta t$ .
- Heat supplied at the reboiler (case i),  $Q_3$ , or distillate flowrate (case ii),  $D$

The following calculation scheme has been developed. The corresponding flowcharts are shown in Figs. 3b and 3c:

1. At the start-up, the column is operating at total reflux, and  $x_{i,j}$ ,  $T_j$ ,  $y_{i,j}$ ,  $M_j$ ,  $L_j$ ,  $V_j$  and  $Q_1$  are the ones corresponding such operation. Depending on the case, i) or ii),  $Q_3$  may be the specified value or that calculated at total reflux, respectively. At this point, no distillate is being extracted and the terms  $dh_i/dt$  and  $dM_j/dt$  are

equal to zero.  $T_j$  and  $x_{i,j}$  yield the corresponding  $\rho_j$ ,  $H_j$  and  $h_j$ . Other starting profiles can be considered, but it is important to ensure that the total amount of material inside the column fulfills the mass balance with the initial mixture loaded at the reboiler ( $M_n^{t=0}$  and  $x_{i,3}^{t=0}$ ).

- At  $t = 0$  starts the extraction of distillate, with the liquid composition profiles through the column equal to that of total reflux.
- Perform a bubble point calculation at each stage, with the known  $x_{i,j}$ , to obtain  $T_j$  and  $y_{i,j}$  values (equations 9 and 10). Obviously, at time zero, results will be the same than those at total reflux, with only small differences related to the optimization of the goal seek function (equation 10).
- Once the compositions of each phase and the temperature at each stage are known, calculate the corresponding specific enthalpies of vapor and liquid and the liquid molar densities.
- Calculate  $M_1$  and  $M_2$  by equation (11) and  $M_3$  by equation (12). For  $M_3$  use the accumulated distillate of the previous time interval (zero at  $t = 0$ ).
- Calculate the terms  $dM_j/dt$  and  $dh_j/dt$  as  $\Delta M_j/\Delta t$  and  $\Delta h_j/\Delta t$ , respectively, considering the difference with the values of the previous time interval and the fixed time increment.
- Calculate flowrates of internal streams, quite different for cases A and B:

Case i), at constant reboiler duty: the following iterative calculation is presented:

- Guess an initial value of  $L_1$
- Calculate  $D = L_1/R$ ;  $V_2$  by equation (4),  $V_3$  by equation (7),  $L_2$  by equation (8) and  $L_1$  by equation (5)
- Compare the assumed and calculated values of  $L_1$  and repeat calculation until they are close enough
- Calculate  $Q_1$  by equation (6)

Case ii), at constant distillate flowrate: calculate  $L_1$ , (constant) as  $L_1 = R \cdot D$ ,  $V_2$  by equation (4),  $V_3$  by equation (7),  $L_2$  by equation (5),  $Q_1$  by equation (6) and  $Q_3$  by equation (8).

- Calculate  $\Delta x_{i,j}$  by equations (1), (2) and (3).
- Calculate the accumulate distillate as  $\sum_{t=0}^t D^{(t)} \Delta t$ , and check if it remains liquid at the reboiler ( $M_N > 0$ ).
- Increase time by the fixed  $\Delta t$ .
- Obtain the  $x_{i,j}$  values for the next time interval as  $x_{i,j}^{t+\Delta t} = x_{i,j}^t + \Delta x_{i,j}^t$ .  $x_{i,j}$  must be normalized because the  $\Delta x_{i,j}$  are obtained independently each other.
- Repeat from step 4, whereas it is still liquid at the reboiler (checked at step 9).

As it has been described above, besides the start-up at total reflux, this calculation scheme could be used to obtain the evolution with time from any other initial  $x_{i,j}$  profile. Nevertheless, in this case, the initial molar holdup and composition at the reboiler,  $M_n^{t=0}$  and  $x_{i,3}^{t=0}$ , have to be calculated from the initial total amount of each component through stages in order to fulfill the component mass balances.

#### 4.3. Continuous column

The multicomponent continuous column obtained when a feed stream is introduced at the intermediate stage and a bottoms product is extracted from the reboiler of the column described in previous paragraphs is considered. The simulation of such a column by a *relaxation method* (Kister, 1992) has been performed by means a “brute force” procedure (Lane, 2019), and it is shown at the spreadsheets “Continuous-total reflux” and “Continuous-uniform profile” of Excel file available at <http://bit.ly/3K5z4MN>. Once  $P$ ,  $G_1$ ,  $G_2$  and  $\Delta t$  (4 freedom degrees) are fixed, the specification of the feed stream requires involves 4 degrees of freedom, corresponding to  $F_j$ ,  $z_{i,j}$  ( $i = 1, 2$  and  $j = 2$ ) and one variable that determines its thermal condition -in this case,

saturated liquid- at column pressure (already specified). The two additional specifications required have been selected as the reflux ratio and the distillate flowrate, that are those that make easier to solve the problem. The final steady-state will be independent on the values of  $G_1$  and  $G_2$ ; nevertheless, they must be specified in order to allow calculation of the terms of matter accumulation. In this case, the liquid holdup at the reboiler is not a specification and, in the same way than  $G_1$  and  $G_2$ , the final result neither will depend on the starting  $M_3$  value. Nevertheless, the higher values of such variables the higher the time to reach the steady-state.

As Kister (1992) states, for the application of a relaxation method, the column has to be initialized considering a realistic condition such as start-up: in this case two alternatives are presented: i) the continuous column starts from the total reflux operation, that is a usual practice and ii) the temperatures and compositions at all the stages are equal to that corresponding to flash equilibrium of feed stream, that is a usual initialization of rigorous continuous distillation calculations. Other initial profiles could be also considered, and the time needed to achieve convergence will change depending on their closeness to the steady-state solution. Finally, the following scheme of calculation is applied. The corresponding flowchart is shown in Fig. 3d:

- Previously to start *relaxation method* calculations, the liquid-vapor equilibrium of the feed stream at column pressure is performed, and its specific enthalpy and density are calculated. In this case, the feed stream is a saturated liquid, i.e., at its bubble point temperature.
- At the start-up, the column is operating at total reflux (case i) or with a specified initial profile (case ii), thus yielding the initial profile of  $x_{i,j}$ ,  $T_j$ ,  $y_{i,j}$ ,  $M_j$ ,  $L_j$ ,  $V_j$ ,  $Q_j$ . At  $t = 0$  no distillate is extracted and the terms  $dh_j/dt$  and  $dM_j/dt$  are equal zero. At this point, for case i),  $M_3$  is that calculated at total reflux, whereas for case ii), a reasonable value should be assumed (see below comments about this question).
- At  $t = 0$  starts the extraction of distillate and bottoms product, having the compositions stated in the previous step.
- Perform a bubble point calculation at each stage, with the known  $x_{i,j}$ , to obtain  $T_j$  and  $y_{i,j}$  values (equations 9 and 10). Obviously, at time zero, results will be the same as those at total reflux, with only small differences related to the optimization of the objective function (equation 10).
- Once the compositions of each phase and the temperature at each stage are known, calculate the corresponding specific enthalpies of vapor and liquid and liquid molar densities.
- Calculate flowrates of internal streams:  $L_1$  (constant) =  $R \cdot D$ ,  $V_2$  by equation (4),  $V_3$  by equation (17),  $L_2$  by equation (15),  $Q_1$  by equation (6),  $Q_3$  by equation (8) and  $B$  by equation (18). When it is needed, the terms  $dM_j/dt$  and  $dh_j/dt$  corresponding to the previous time interval are used.
- Calculate  $M_1$  and  $M_2$  by equation (11) and  $M_3$  by equation (16). For  $M_3$  use the term  $dM_3/dt$  corresponding to the previous time interval (zero at  $t = 0$ ).
- Calculate the terms  $dM_j/dt$  and  $dh_j/dt$  as  $\Delta M_j/\Delta t$  and  $\Delta h_j/\Delta t$ , respectively, considering the difference with the values of the previous time interval and the fixed time increment.
- Calculate  $\Delta x_{i,j}$  by equations (1), (13) and (14).
- Increase time by the fixed  $\Delta t$ .
- Obtain the  $x_{i,j}$  values for the next time interval as  $x_{i,j}^{t+\Delta t} = x_{i,j}^t + \Delta x_{i,j}^t$ .  $x_{i,j}$  must be normalized because the  $\Delta x_{i,j}$  are obtained independently each other.
- Repeat from step 4, until steady-state is reached, i.e., when almost no changes of variables are obtained.

At step 2, the initial amounts  $M_j$  are needed. As it has been commented above, these values do not affect the final steady-state results,



but they are needed to calculate the mass accumulation terms at each step. Students must remember that the extent of separation depends on the number of stages whereas the column diameter depends on the internal flowrates, mainly of vapor streams. The knowledge of  $G_1$  and  $G_2$ , from which  $M_1$  and  $M_2$  are obtained, imply that the design characteristics of the column are known (i.e., the column diameter and the outlet weir height of the plates). On the other hand, the calculation of the reboiler liquid molar holdup,  $M_3$ , also requires to know the reboiler design. Nevertheless, the final steady state compositions and flowrates are independent of such variables, that only affect the correct fluid dynamics of the column.

## 5. Results and discussion

In this section, the structure of the Excel file carrying out the calculations described in the previous section, that can be downloaded from <http://bit.ly/3K5z4MN>, is described, and step-by step instructions to use it are provided. The file contains five spreadsheets, each one showing a different solved problem:

- Batch column operating at total reflux (Sheet “Batch-Total reflux”)
- Batch column operating at R constant and QB constant (sheet “Batch-QB”)
- Batch column operating at R constant and D constant (sheet “Batch-D”)
- Continuous column operating at R constant and D constant, starting from total reflux profiles (sheet “Continuous-total reflux”)
- Continuous column operating at R constant and D constant, starting from uniform profiles taken from the feed stream (sheet “Continuous-uniform profile”)

Hypothetic components a, b and c are considered, and the corresponding temperature-dependent correlations for vapor pressure, liquid and vapor enthalpies and liquid molar densities are provided. The normal boiling point of pure components as well as their enthalpies and densities at specified temperatures have been calculated at the spreadsheets with the only purpose of illustrating some characteristics of these components, that give ideal mixtures. In fact, the vapor pressure and density correlations have been taken from that of n-hexane, n-heptane and n-octane, whereas the linear temperature-correlations for enthalpies have been obtained from their corresponding pure-component enthalpies in the range of 20–200 °C. These considerations allow us to check the obtained results by comparison with that obtained with a simulation software. The structure of the five sheets is quite similar, and it is described in this section. In all cases, the problem specifications are in red and guessed values to start iterative calculations in blue.

It is considered that the column operates at atmospheric pressure, despite it can be modified, as the other specifications. Nevertheless, the column pressure drop must be zero, i.e.,  $P_j$  is the same for all  $j$ , and cannot be changed.

### 5.1. Spreadsheet “Batch-Total reflux”

Fig. 4 shows the spreadsheet prepared for total reflux calculation. Fig. 4a shows the area with the problem statement and the calculation algorithm, on the left side of the image, and the temperature-dependent correlations and parameters, on the right side. An example of application of each temperature-dependent property for each pure component is provided in order to allow users to have an idea of the nature of hypothetical components a, b and c. At the bottom part, the area to input specifications can be seen, close to a cell with the initial molar holdup at the reboiler, calculated from the initial volume, temperature and composition loaded at time zero. Finally, the first rows of the table with calculations and the tab with the name of this specific worksheet highlighted can be observed, as well as two buttons that allow us to run macros to increase the number of iterations, whose use will be explained

afterwards. Other parts of the spreadsheet are shown in Figs. 3b and 3c. In Fig. 3b the area with a batch column flowsheet and the applied equations is presented, and at the lower-right corner, a button associated with a macro to completely run the calculation algorithm in all the rows of the table. Part of the table with the results of iterative calculations is shown in Fig. 3c: each block of calculations is shaded with different color and, at the end of the table, a text box with a description of each calculation and equations used is provided. The instructions to use this spreadsheet are:

1. State the problem specifications (in red):  $P$  (at F31),  $Q_3$  (at F33),  $G_1$  and  $G_2$  (at H32:H33), initial load at the reboiler (volume at J31, temperature at J21 and composition at K33:K34; these values allow us to calculate  $M_3^{t=0}$  at K36). Check that specifications are reasonable: the sum of  $G_1$  and  $G_2$  has to be lower enough than the volume loaded at the reboiler; the initial temperature at the reboiler should correspond to a liquid (if not, calculations do not fail, but the specification would not be coherent). The value of  $Q_3$  only affects the internal flowrates, that can be abnormally increased or decreased close to zero, also reflecting an incoherent specification. See below comments about the  $Q_3$  specification.
2. Guess initial values for  $x_{i,3}$  (at H40:J40) and for  $T_j$  at all the rows (N40:P62). A reasonable starting point could be to consider the initial composition at the reboiler and a temperature, equal at all the stages, in the range of the boiling point of pure components (that can be calculated in N5:P7).
3. Press the button to perform the bubble point calculations at each row, located in the zone AI35:AJ37. Once  $T_j$  and  $y_{ij}$  have been obtained, the rest of variables are calculated as it has been described in the previous section.
4. Check if the calculated temperatures (and compositions) are the same in successive iterations (i.e., through many of the last rows of the table N40:P62). In this case, the calculation is finished, and the results corresponding to total reflux are those of the last row. If not, repeat more iterations, as it is described in the next step. If instead of convergent values, oscillating temperatures are obtained, the scalar step factor  $\lambda$ , at P35, for Eq. (20) should be decreased ( $\lambda \leq 1$ ).
5. Press buttons “Guess new  $x_{i,3}$ ” (I38:J38) and “Guess new  $T_j$ ” (N38: P38) in order to take the last calculated values for initiating another run of iterative calculations, and repeat from step 3. The combination of high number of iterations and low value of  $\lambda$  should allow us to solve every case.

When this spreadsheet has been checked, the step scalar factor lower than 1 has been only needed for initial mixtures having  $x_{A,3}$  around 0.1 and  $x_{B,3}$  lower than 0.5. Despite it is obvious, the sum of the initial  $x_{i,3}$  guessed to initiate calculation has to be checked. If a binary mixture is considered, the initial value of the mole fraction guessed for the missing component has to be very close but not equal to zero in order to avoid numerical errors in Eq. (20). Students should be suggested to find out that for the same initial composition loaded at the reboiler, at  $t = 0$ , the total-reflux composition at the reboiler depends on the initial amount of mixture and the liquid holdup at stages. The lecturer can take advantage of this behavior in order to remember that a total-reflux composition profile provides a distillation line of the corresponding distillation-curve map of the ternary system (Seader et al., 2011), that is characteristic of liquid-vapor equilibrium of the system. Then, for the same composition at the reboiler at total reflux, the composition profiles are the same and are independent of the reboiler duty and of the internal flowrates. Thus, the effect of specifying different  $Q_3$  values can also be checked, considering that depending on the specification, the calculated internal flowrates  $V_1$  and  $V_2$  could be unrealistic, because at total reflux they have no influence on the other variables since streams crossing each other between stages have the same flowrate and composition. This fact does not mean that this tool is not useful to study the dynamics of the

(a)

(b)

(c)

Fig. 4. Different screenshots of the spreadsheet for total reflux calculation.

internal flowrates, on the contrary reflects the importance of selecting coherent specifications.

### 5.2. Spreadsheets “Batch-QB” and “Batch-D”

Spreadsheets for batch distillation are quite similar to that shown in Fig. 4. They have the same structure, and the zones with problem statement, calculation algorithm, flowsheet and equations are at the same location. The table with calculations and results is also at the same location, but now with calculations corresponding to cases i) or ii) of batch distillation. The number of rows with calculations has been increased with respect to the case of total reflux in order to provide a longer view of the evolution of the column. Overlapped with the table are graphics showing how some variables evolve. The instructions to use these spreadsheets are:

1. Run completely calculations at spreadsheet “Batch-Total reflux” for the specified  $P$ ,  $Q_3$ ,  $G_1$  and  $G_2$  and initial load at the reboiler (volume, temperature and composition) to obtain the column profiles at total reflux. Remember that other initial profiles can be considered but, in this case, the initial load at the reboiler (J33:J36) has to be calculated to be coherent with the initial column component profiles.
2. Go to the spreadsheet “Batch-QB” or “Batch-D” depending on the problem to be solved and input the desired values for the time step ( $\Delta t$ , at E33), reflux ratio ( $R$ , at E30) and reboiler duty ( $Q_3$ , at E35 in “Batch-QB” spreadsheet for case i) or distillate flowrate ( $D$ , at E35 in “Batch-D” spreadsheet) for case ii). Also input the initial guessed values of  $T_j$  (in the range N41:P80) and, for case i), of  $L_1$  (in the range AR41:AR80): the same values than that obtained at total reflux could be a good initialization of the problem. A rough approximation of the suggested value for  $\Delta t$  and a recommendation for  $Q_3$  (in case i) is intended in the range R29:S35, considering that  $\Delta t$  should allow to perform calculations in the 40 rows of the available table.  $P$ (E31),  $G_1$  and  $G_2$  (G32:G33) and initial load at the reboiler (H31:H32 and J33:J34) (in purple) must be the same than that specified for total reflux calculations.
3. Press the button to execute calculations (“Bubble point calculations and reflux calculations” or “Bubble point calculations”, close to AI35, depending on the case): if the specified variable is  $Q_3$  (case i) the associated macro firstly performs the bubble point calculations at each row, followed by the iterative calculation described in the previous section to obtain  $L_j$  and  $V_j$ ; if the specified variable is  $D$  (case ii), only the bubble point calculations are needed. After that, the rest of variables are obtained according with the scheme of calculation described in the previous section.
4. When calculations are finished, the evolution of plotted variables ( $x_{ij}$ ,  $M_3$  and  $T_j$ ) with the time can be analysed.

The effect of modifying the problem specifications can be checked. The time increment selected should not be so high to detract Euler’s method application nor so low to slow down the time evolution of variables. As it has been commented in step 2, a maximum  $\Delta t$  is suggested: in order to avoid calculation problems, the time needed to completely evaporate the initial reboiler content is calculated and it is used to estimate the maximum time that should be reached through the available 40 rows, and thus, the maximum  $\Delta t$ . This calculation and the maximum  $\Delta t$  recommended are located at R29:S35. For case i)  $Q_3$  and  $\Delta t$  should be selected accordingly: combinations of both, too high  $Q_3$  and  $\Delta t$  can lead errors related with calculated negative intern flowrates that results in absurd variables values. Errors related with high  $\Delta t$  values can be sidestepped by gradually increasing from a smaller value. The specification of  $Q_3$  determines the internal flowrates, that can reach abnormally high values when  $Q_3$  is too high, or be close to zero if it is too low (even, the tolerance of the calculation tools could yield negative flowrates!). The heat of vaporization of the mixture at the reboiler at  $t = 0$ , calculated at S33, give us an idea of the adequate order of magnitude for

$Q_3$ . Finally, it is worth to find out that the specification of very high reflux ratio (i.e.,  $R > 1000$ ) for case i) yields results very close to that of total reflux.

If calculation stops with less than 40 rows because the reboiler is empty, it will be pointed out in the first and last columns of the table (columns A and CD), and the corresponding rows and plotted points have to be rejected. This situation can occur if the liquid holdup at stages is high related to the initial volume of liquid loaded at the reboiler.

### 5.3. Spreadsheets “Continuous\_total reflux” and “Continuous\_uniform profile”

The structure of the spreadsheet for the simulation of the continuous column by a *relaxation method* is also similar to that of previous cases. Close to the zone to input problem specifications (M29:S36), there is a table with the flash equilibrium of feed calculation, with a button (close to O30) associated with a macro for a new bubble point calculation, when a new feed stream composition is specified. Two additional buttons, to start a new calculation, with the specifications of cases i) or ii), or to continue calculations if convergence is not achieved in a single run, are available in the zone U33:V36. The instructions to use the spreadsheets are:

1. Input specifications (in red) for  $P$  (31),  $R$  (E30),  $D$  (E36),  $G_1$  and  $G_2$  (G32:G33),  $F$  (J3i) and  $z_{ij}$  (J33:J34). Guess the feed temperature (N30) and press the button “New Tb calculation” to obtain the feed bubble point characteristics.
2. For case i), the column start-up is at total reflux. Then, first of all, calculations of the spreadsheet “Batch-Total reflux” must be performed, with the same values of  $G_j$  and  $P$ . It is suggested to use as initial load at the reboiler a mixture with the same temperature and composition of the feed stream. The initial amount fed at the reboiler could be of the same order de magnitude than the volumetric feed flowrate calculated at J36. Then, once total reflux has been calculated, the corresponding values (in purple) of  $P$  (E31),  $x_{ij}$  (B40:J40),  $M_j$  (K40:M40),  $T_j$  (N40:P40),  $y_{ij}$  (Z40:AH40),  $V_j$  and  $L_j$  (AP40:AS40),  $Q_1$  and  $Q_3$  (BC40:BD40) are taken and the corresponding enthalpies and liquid densities are calculated. The macro associated with the button “Start from total reflux”, close to U33, copies these values and permits to initialize a new calculation.

For case ii), the column startup considers the same temperatures and compositions than that of the feed streams in all the stages (in purple), and the constant molar overflow hypothesis (i.e, that of the McCabe-Thiele method) por the internal flowrates,  $L_j$  and  $V_j$ . Then, the macro associated with the button “Start from feed variables”, close to T33, copies the values of  $x_{ij}$  (B40:J40),  $T_j$  (N40:P40),  $y_{ij}$  (Z40:AH40) from that specified (J31:35) and/or calculated (O33:S35) for the feed stream and estimates the internal flowrates from  $D$ ,  $R$  and  $F_j$ . The rest of variables at start-up are calculated in the same way than in the rest of the rows, with the only exception of  $M_3$  that, has been arbitrarily chosen as  $10 \cdot M_2$ .

As it has been previously commented on, the steady-state results are independent of the values of  $G_1$ ,  $G_2$  and  $M_3$ , but these variables are necessary in order to calculate the terms of matter accumulation that are going to evolve to zero.

3. Specify  $\Delta t$ . If it is too high, oscillating temperatures and/or errors could appear. In this case,  $\Delta t$  must be decreased until those problems disappear. See below more information about  $\Delta t$ .
4. Input the initial guessed values of  $T_j$  (in the range N41:P78): the same values than that considered for the starting point could be a good initialization of the problem.
5. Press the button to execute calculations (“Bubble point calculations”, close to AI35): the associated macro performs the bubble point calculations at each row. After that, the rest of variables are calculated by following the procedure described in the previous section.

6. Check at the end of the table (row 78) or in the graphic profiles if the solution achieved is close to steady. If not, more time is needed: run the macro associated with the corresponding button (“More time is needed”, close to U35), that claims the last row values in order to continue calculations from that point, and return to step 3. According with Kister (1992), relaxation method application should be finished when the maximum differences between compositions and temperatures in two consecutive trials is lower than  $10^{-4}$ .

According with Kister (1992), when  $\Delta t$  is small, the changes in the independent variables are small and the method performs like a damped Newton-Raphson method, with small steps but directed to the solution without any oscillation. Nevertheless, when  $\Delta t$  is large, the method performs like a Newton-Raphson method. Therefore, the recommendation is to start with an *a priori* small  $\Delta t$  that, if calculations give oscillating temperatures and/or errors, must be decreased.

The lecturer can take advantage to remember that the separation degree depends on the number of column stages, whereas the diameter of the column depends on the internal flowrates, mainly of the vapor flowrates. Comparing the applied relaxation method with the equilibrium-methods available in simulation software, the rigorous simulation of a column does not require the specification of variables related with the column size, on the contrary, these variables are calculated from the results of the simulation. Nevertheless, if unsteady-state equations have to be solved, such variables are needed because the terms of matter accumulation. As it is expected, the time needed to reach the steady-state increases as the specified and/or assumed values for  $G_1$ ,  $G_2$  and  $M_3$  increase: the higher size of the column the harder to drive it to steady-state.

## 6. Conclusions

In this work, an Excel spreadsheet to simulate the operation of a batch distillation column and a continuous column to separate a hypothetical ideal ternary mixture is shared at <http://bit.ly/3K5z4MN>. The operation at total reflux is also simulated. The calculation of the continuous column is carried out by applying a relaxation method, that usually is not included in separation processes syllabus, and allows the analogy with the start-up of the column from an unsteady-state situation until reaching the steady-state. This file can be used as complementary material by lecturers and students of advanced separation processes.

The unsteady-state MESH equations for batch and continuous distillation have been developed and applied to an ideal ternary mixture. The determination of the degrees of freedom implies the careful analysis of each system to select the most appropriate variables to be specified and to develop the strategy to solve the system of equations. Then, not only the way to solve the problems is obtained, but also the skills needed to address this kind of problems can be improved. In the case of total reflux, the students could be focused on the need of using Eq. (20) to obtain nonnegative quantities for the unknown variable and on the flows and composition profiles characteristics of such operation, especially on its relationship with the residue curves maps. The solved examples of batch operations allow us to analyze the effect of modifying the problem specifications on the evolution of the composition profiles and, in this way, to reflect about the adequate combinations of specified variables and time step. Finally, the relaxation method applied to the continuous column gives an excellent opportunity to consider the column start-up and how variables evolve towards the steady-state. Furthermore, it can be observed that, if the initial total amount of

each component is the same, the steady-state results obtained are the same, independent of the assumed start-up conditions, and specifically, with the two alternatives studied (i.e., starting from total reflux or considering that the initial temperatures and compositions at all the stages are equal).

All the spreadsheets shared in this work have been checked by comparison with the results obtained when the same problem has been solved by means the chemical process simulator ChemCAD v8.0.2 (<https://www.chemstations.com>), and the corresponding files are available at <http://bit.ly/3K5z4MN>. The results of the comparison are shown in the sheet “Comparison” of the above-mentioned Excel file, and reflect very good alignment, especially considering that the mathematical tool used is based on a “brute force” method (Lane, 2019) instead of the rigorous equilibrium-based methods used by the simulator.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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