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# NOVEL SPREADSHEETS TO ENHANCE LEARNING OF RIGOROUS EQUILIBRIUM-BASED METHODS FOR MULTICOMPONENT SEPARATIONS

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## INTRODUCTION

The rigorous calculations involved in the design or simulation of a multicomponent vapor-liquid cascade of equilibrium stages to separate a mixture requires solving the MESH equations, i.e., the mass balance and phase-equilibrium relations for each component (M and E equations, respectively), the mole fraction summation conditions (S equations) and the energy balances (H equations) for all the stages of the column. This results in a large number of variables and highly nonlinear equations that have to be solved by iterative techniques. There are different equilibrium-based methods to solve these equations for multicomponent separations. Details about the history of these methods can be found in the textbooks by Seader et al.<sup>[1]</sup> and Kister<sup>[2]</sup> and in an article published by Seader<sup>[3]</sup> in 1985. An example of the set of equations for each stage as well as the calculation algorithms and the details of application for the methods considered in this work are provided in the Methodology section. However, it is necessary to check different textbooks in order to find detailed examples for all of the multicomponent calculation steps. As an example, in the classical book by King,<sup>[4]</sup> the *simultaneous correction*, *bubble point*, and *sum rates* methods are described, but the required equations are not showed and examples of application are not provided; in Kister's excellent text on distillation design,<sup>[2]</sup> the *bubble point*, *sum*

*rates*, *simultaneous correction*, and *inside-out* methods are well explained, but examples are not included. Kister<sup>[2]</sup> also includes the explanation of *homotopy-continuation* methods that are not mentioned in most textbooks. Wankat<sup>[5]</sup> mentions the *sum rates* and *bubble point* methods but mainly focuses on *simultaneous correction* methods that are very



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well developed and described in detail, including examples of application as well as proposed exercises. To solve these problems is a long process, and this is clearly pointed out by Wankat:<sup>[5]</sup> “*This is a long and involved problem. The solution will be shown without all the intermediate calculations.*” In the same way, most of the proposed exercises are classified as “*problems requiring other resources*” and “*computer simulation problems.*” The *bubble point, sum rates, isothermal sum rates, simultaneous correction* and *inside-out* methods are also very well explained by Seader et al.,<sup>[1]</sup> including a detailed description of equations and algorithms involved as well as further application examples. More recently, Lane<sup>[6]</sup> has published an interesting textbook on separation process in which the application of spreadsheets for numerical calculations and data presentation is described and used extensively. The comparison of results with those provided by commercial chemical process computer-aided design software is highly recommended. Nevertheless, Lane<sup>[6]</sup> mainly focused on processes that can be graphically described by means of phase equilibrium diagrams (i.e., binary distillation, absorption of one component, and ternary liquid-liquid extraction). With respect to the rigorous methods for multicomponent distillation, a “brute force” method is proposed where the involved equations are written in the spreadsheet and solved with the Microsoft Excel<sup>®</sup> Solver tool, and the above-mentioned rigorous methods are not described.

All these methods are usually difficult to apply by hand and require the use of process simulators as ChemCAD from Chemstations<sup>™</sup>, Inc.<sup>[7]</sup> or Aspen HYSYS<sup>®</sup> and Aspen Plus<sup>™</sup> from Aspentech.<sup>[8]</sup> In fact, Henley et al.<sup>[9]</sup> group these methods in a chapter entitled “Computer-Aided Equilibrium-Based Methods.” During theoretical lectures, students can learn the algorithms corresponding to each method, but most of the time they do not have the opportunity of learning by doing or, at least, solving these calculations by hand. Only some of these methods, those that are simpler, can be applied by hand; however, the time constraints of a typical course make this activity excessively time-consuming. An intermediate possibility is to provide students with examples of applications solved and explained in an Excel sheet, in such a way that the calculation details and successive iterations of each method can be deeply followed and analyzed. This approach has been successfully applied in the Advanced Separation Processes course of the Chemical Engineering MSc of the University of Alicante. In this work, the results of this experience are presented, and the six solved examples corresponding to different rigorous methods are shared at <https://bit.ly/2SLhsNJ>.

In 1985, in an article where different methods for solving equations for multicomponent multistage separation operations were presented, Seader<sup>[3]</sup> recognized that the number of nonlinear equations involved makes it impossible to solve them directly, requiring the use of computer-aided simulation programs. Nevertheless, he<sup>[1]</sup> stated that some manual calcula-

tions on simple examples should be performed using complete tearing methods to help develop a basic understanding. Dahm et al.<sup>[10]</sup> analyzed the effectiveness of the use of process simulation in chemical engineering courses and pointed out a potential pedagogical drawback: it is possible that students do not really understand the physical phenomena within each unit operation. In the same way, the “black-box” effect of process simulators has been reported by Roman et al.,<sup>[11]</sup> describing how to create an efficient learning environment that combines the use of simulator and Mathcad<sup>®</sup>. Moreover, it is important that the e-learning tools implemented to develop computing skills among chemical engineering students are developed with learning outcomes in mind and, if possible, in accessible format.<sup>[12]</sup> In this context, the proposal raised in this work could provide support for lecturers of separation processes.

In 1986 Grulke<sup>[13]</sup> wrote about using spreadsheets for teaching design, stating one of the advantages of this tool: the student is responsible for all the spreadsheet inputs and knows which thermodynamic equations, reactor models, and heat transfer correlations have been used. The advantages of using spreadsheets for solving engineering problems have also been pointed out by Kanyarusoke and Uziak,<sup>[14]</sup> who recognized that the main disadvantages are the low solution speed in cases of very large problems and the difficulty in handling large scale branching simulations. Another risk is that one may easily make an error in embedded formulas or cell references. Nevertheless, according to Waxman,<sup>[15]</sup> risks can be mitigated if the purpose of spreadsheets is identified and those including complex formulae and code are isolated as “high risk” user tools. A review of the Excel use in chemical engineering has been done by Nachtigalova et al.,<sup>[16]</sup> in a paper where a spreadsheet-based tool for solving a case study of simulation and control of an electrically heated water heater was reported. Other authors, such as Stamou and Rustchmann,<sup>[17]</sup> presented a procedure for teaching simple water quality models based on Excel to solve, simulate, and examine the problem. These authors<sup>[17]</sup> report the use of Excel by other lecturers and state that this solution approach is preferred by students because Excel is a tool very well known by them. Gómez-Siurana and Font-Escamilla<sup>[18]</sup> developed an Excel spreadsheet with an example of application of homotopy methods in order to help students who understand such methods. Stammitti<sup>[19]</sup> described the use of spreadsheets prepared by the instructor and delivered to students in a transport phenomena laboratory in order to reduce the time involved in data processing and focus on the analysis, critical thinking, and report writing skills. Park et al.<sup>[20]</sup> presented a spreadsheet-based class project using an Excel worksheet to simulate a flash drum. According with Briones et al.,<sup>[21]</sup> the solution of optimization problems of distillation sequences requires the use of specific software that requires long-term training for students to adequately harness. Nevertheless, it can be done by means of Excel’s Solver tool, already known by students since the first years of their degree. Natchigalova et al.<sup>[16]</sup> described an application based

on Excel for studying process dynamics and designing control systems. Finally, Iglesias et al.<sup>[22]</sup> used Excel to develop an elemental simulator for chemical process and recognized that, despite the existence of powerful calculation tools, learning tools based on spreadsheets imply an environment and techniques well-known by students. All these examples support the learning methodology proposed in this work.

## METHODOLOGY

In this work examples of solved exercises corresponding to the following cases are shared:

- Complete simulation of a multicomponent distillation column by a bubble point (BP) method
- Complete simulation of a multicomponent absorption column by a sum rates (SR) method
- Three iterations of the simulation of a multicomponent liquid-liquid extraction column by an isothermal sum rates (ISR) method
- Calculation of one single multicomponent equilibrium stage by a simultaneous correction (SC) method
- First iteration of the simulation of a multicomponent distillation column by an inside-out method
- Complete calculation of liquid-vapor equilibrium of an azeotropic binary system by a homotopy method

BP, SR, ISR, SC, and inside-out methods are explained in detail by Seader et al.,<sup>[1]</sup> whereas the procedure for applying homotopy methods is perfectly described by Kister.<sup>[2]</sup> The main characteristic of BP, SR, and ISR methods is the use of the Thomas algorithm for solving the tridiagonal matrix resulting from a modified form of mass balances ( $M$  equations), whereas SC methods are based on the simultaneous solution of MESH equations, usually by the Newton-Raphson method. BP methods differ from SR and ISR methods in the way the temperature in each column stage is calculated: bubble point calculations in BP methods and energy balances in SR methods. ISR methods are a simplified isothermal version of SR methods, applicable when isothermal operation can be assumed or when all the stage temperatures are known. Inside-out methods were developed to decrease the time spent in computing thermodynamic properties and use two set of thermodynamic models. One of them is very simple and approximated, and it is used to solve the MESH equations in an inner loop. The other is complex and rigorous, and it is used in an outer loop to calculate the parameters of the approximate models. Homotopy methods are based on the use of the homotopy function, constructed as a continuous blending of two functions representing the case of a complex column whose solution has to be obtained, and a simpler problem whose solution is known or is easy to obtain. Then, the homotopy parameter, which travels between 0 and 1, allows

us to pass, step by step, from the initial known solution to the final solution, which corresponds to the desired rigorous solution of the complex or difficult distillation column. More details about the features of MESH equations, the tridiagonal matrix, and calculation algorithms are provided in the Results and Discussion section. It is worth mentioning that all these methods are also applicable to continuous contact operations if the concept of height equivalent to a theoretical tray (HEPT) concept is applied.

The application of BP and SR methods by hand can be relatively easy if the thermodynamic models for the equilibrium ratios ( $K$ -values defined for each component as the ratio between the mole fraction in the light phase and in the heavy one) and enthalpies are not very complicated; for example, if there are temperature-dependent polynomial equations available to describe the behavior of the system. Usually, ISR methods are used to calculate liquid-liquid extraction columns, and they need the application of models such as NRTL or UNIQUAC, that describe the behavior of highly non-ideal mixtures. Then, ISR methods are difficult to apply by hand. The algorithms for SC, inside-out, and homotopy methods are slightly more complicated and also difficult to be applied by hand. In fact, SC and inside-out methods are implemented in ChemCAD,<sup>[7]</sup> in SCDS and Tower units, respectively. The best description of all these methods can be found in the referred bibliography,<sup>[1-6]</sup> and some basic details where the students' attention should be focused on are provided in the next section, together with the description of the proposed examples. In order to allow students to know the details of each application method, the above-mentioned examples, solved in Excel worksheets, have been provided to the students.

## LEARNING OUTCOMES

For more than 20 years, after explaining rigorous equilibrium-based methods for multicomponent distillation, students asked us how they should study and what they were expected to learn about them. In fact, the mere knowledge of the involved algorithms seemed to be too superficial, but the calculations involved were too difficult to allow us to plan practical sessions, as in other parts of the course (for example, solving problems of approximated methods or phase equilibrium calculations) and the use of simulation packages did not help because they work as a black box and do not reflect how rigorous methods work. Then, this alternative, based on providing students examples solved in Excel spreadsheets as complementary material, has been used in order to help students to learn how to solve a complicated problem in a more obvious, visual way. The principles and the calculation algorithms corresponding to rigorous methods are explained in the theory classes, and their application is illustrated by means of the description of these solved examples. After that, students can access the corresponding Excel files where they

can follow and analyze the calculations details and the difficulties involved. The intended learning outcomes focus on the objective skills that students should be able to demonstrate after working with these spreadsheets, students acquire the following skills:

- Describe how the MESH equations can be applied to a multicomponent distillation using rigorous equilibrium-based methods
- Explain, at a high level, the mathematical calculation tools involved
- Describe the main difficulties of programming these methods
- Explain the importance of the initial estimations to start iterative methods

In order to encourage all the students to check these materials, they are warned that they will be asked about these examples in the final exam. Thus, as a part of the final exam, one of these examples is provided without the titles, comments and explanations, and students are asked to identify the method as well as some details such as “what type of calculations are performed in a zone of the sheet?” or asking them where some block of the algorithm is calculated. Once the course is finished and students have been evaluated, an anonymous survey is administered to check what students think about the usefulness of these exercises and the time spent in their study. Always, diversity, equity, and inclusion principles are considered in the theory lectures and in the practical sessions, and the anonymous survey ensures that all the students are free to express their opinion. In general, these spreadsheet examples are well received by students.

## RESULTS AND DISCUSSION

In this section an application guideline of each method and how it is implemented in the corresponding spreadsheet is provided. More information can be found in the shared Excel files. The main objective of these exercises is to allow students to be aware of the details and difficulties involved in the development of these algorithms. This can be easily followed in the corresponding flowsheets.

Figure 1 shows the scheme of an equilibrium stage with the nomenclature used in this work. Capital letters represent the flowrate of each stream;  $x$ ,  $y$ , and  $z$  are, respectively, mole or mass fractions of a component in a liquid, vapor, or any thermal condition stream. Subscript  $i$  refers to each component and  $j$  to each stage of the column.  $L_j$  is the liquid flow rate entering at stage  $j+1$  from stage  $j$ , and  $V_j$  is the vapor flow rate entering at stage  $j-1$  from stage  $j$ .  $U_j$  and  $W_j$  are, respectively, liquid and vapor side stream flowrates from stage  $j$ . Every separation column can be defined as a cascade of that type of stages. Cascades are numbered from the top (stage 1) to the bottom (stage  $N$ ).  $Q_j$  is the heat rate transferred at this stage, considered positive if it comes from the stage and negative if it leaves the stage.  $H$ ,  $h$ , and  $\mathcal{H}$  are used to represent, respectively, the enthalpies of a vapor, a liquid, or a stream in any thermal condition. For a refluxed column, stage 1 is the condenser, whereas for a reboiled column, stage  $N$  is the reboiler.

In order to obtain the MESH equations of the system, the mass and energy balances around each stage are developed, and the conditions of phase equilibrium and mole fractions summation equal to 1 are applied. In this way, the following equations are obtained, for a  $C$  component mixture:

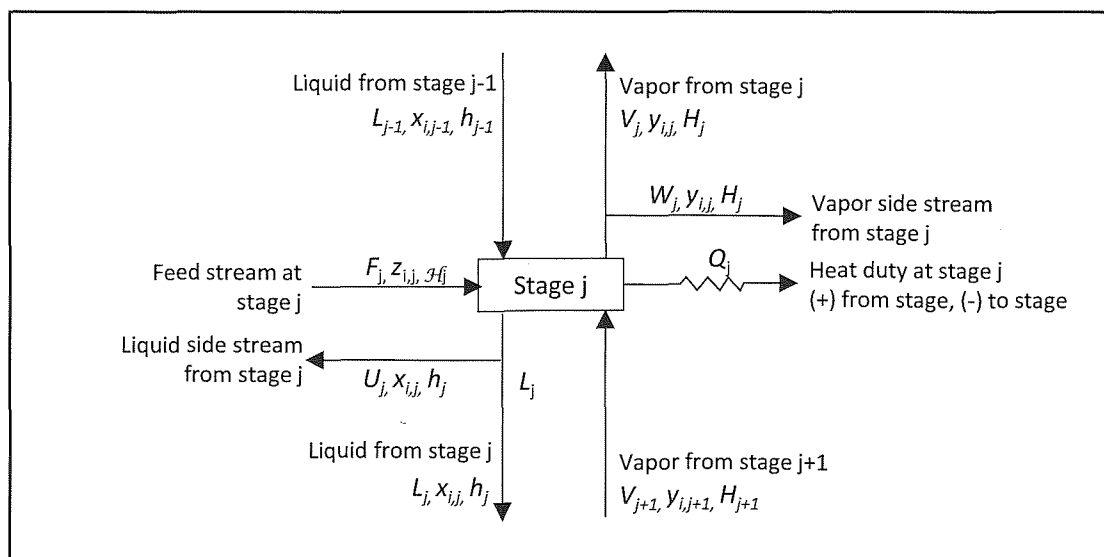


Figure 1. Scheme and nomenclature for an equilibrium stage  $j$ .

M equations (mass balance of each component in each stage):

$$M_{i,j} = L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_jz_{i,j} - (L_j + U_j)x_{i,j} - (V_j + W_j)y_{i,j} = 0 \quad (1)$$

E equations (phase equilibrium relation for each component in each stage):

$$E_{i,j} = y_{i,j} - K_{i,j}x_{i,j} = 0 \quad (2)$$

S equations (mole fraction summations of streams leaving each stage):

$$(S_y)_j = \sum_{i=1}^C y_{i,j} - 1 = 0 \quad (3)$$

$$(S_x)_j = \sum_{i=1}^C x_{i,j} - 1 = 0 \quad (4)$$

H equations (energy balance at each stage, neglecting kinetic and potential energy changes):

$$H_j = L_{j-1}h_{j-1} + V_{j+1}H_{j+1} + F_j\mathcal{H}_j - (L_j + U_j)h_j - (V_j + W_j)H_j - Q_j = 0 \quad (5)$$

In order to obtain the tridiagonal matrix, a total mass balance with the top of a countercurrent cascade is considered:

$$L_j = V_{j+1} + \sum_{m=1}^j (F_m - U_m - W_m) - V_1 \quad (6)$$

and the following set of modified M equations are obtained by using equation (6) to replace the liquid flowrates with the vapor flowrates, and the  $K$ -ratios to substitute the vapor mole fractions for the liquid mole fractions:

$$A_j x_{i,j-1} + B_{i,j} x_{i,j} + C_{i,j} x_{i,j+1} = D_j \quad (7)$$

where

$$A_j = V_j + \sum_{m=1}^{j-1} (F_m - U_m - W_m) - V_1 \quad 2 \leq j \leq N \quad (8)$$

$$B_{i,j} = -[V_{j+1} + \sum_{m=1}^j (F_m - U_m - W_m) - V_1 + U_j + (V_j + W_j)K_{i,j}] \quad 1 \leq j \leq N \quad (9)$$

$$C_{j,i} = V_{i,j+1}K_{i,j+1} \quad 1 \leq j \leq N - 1 \quad (10)$$

$$D_{i,j} = -F_j z_{i,j} \quad 1 \leq j \leq N \quad (11)$$

Then, to apply methods based on the tridiagonal matrix, the set of equations (7) must be grouped for each component to give  $C$  systems of equations, one for each component, that can be solved to obtain the  $x_{i,j}$  values along the  $N$  stages of the cascade, as shown in equation (12). As it can be seen, the coefficients matrix has a tridiagonal structure. The system of equations (12) can be solved very efficiently using the Thomas algorithm, which is widely described in the bibliography.<sup>[1-6]</sup> Since the  $C$  systems of equations are

$$\begin{bmatrix} B_{i,1} & C_{i,1} & 0 & 0 & 0 & \dots & \dots & \dots & 0 & x_{i,1} & D_{i,1} \\ A_2 & B_{i,2} & C_{i,2} & 0 & 0 & \dots & \dots & \dots & 0 & x_{i,2} & D_{i,2} \\ 0 & A_3 & B_{i,3} & C_{i,3} & 0 & \dots & \dots & \dots & 0 & x_{i,3} & D_{i,3} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & 0 & A_{N-2} & B_{i,N-2} & C_{i,N-2} & 0 & x_{i,N-2} & D_{i,N-2} \\ 0 & \dots & \dots & \dots & \dots & 0 & A_{N-1} & B_{i,N-1} & C_{i,N-1} & 0 & x_{i,N-1} & D_{i,N-1} \\ 0 & \dots & \dots & \dots & \dots & 0 & 0 & A_N & B_{i,N} & 0 & x_{i,N} & D_{i,N} \end{bmatrix} = \begin{bmatrix} D_{i,1} \\ D_{i,2} \\ D_{i,3} \\ \dots \\ \dots \\ \dots \\ \dots \\ \dots \\ D_{i,N-2} \\ D_{i,N-1} \\ D_{i,N} \end{bmatrix} \quad (12)$$

solved independently, the sum of mole fractions calculated for each stage does not sum 1, and must be normalized by dividing each  $x_{i,j}$  by  $\sum_{i=1}^C x_{i,j}$ .

On the other hand, methods not based on the tridiagonal matrix simultaneously solve all the MESH equations, or combination thereof, by simultaneous correction techniques, such as the Newton-Raphson method. In this case one may write the MESH equations in terms of component flowrate instead of component mole fraction. The resulting expressions are provided in the Excel files corresponding to each resolved example.

In the following sections, the calculation algorithm for each method is shown, and the corresponding iteration (tear) variables (independent variables that need a set of assumed values to initiate an iteration) are indicated. Despite methods to improve the convergence of these iterative methods, in all the examples presented, tear variables have been adjusted by using the values calculated in each iteration as the assumed values to start a new iteration.

### Example of Application of a BP Method

Figure 2 shows the algorithm for a BP method application ( $P_j$  represents the pressure at stage  $j$ ). The Excel file "BP application example.xlsm", available at <https://bit.ly/2SLhsNJ>, shows how to apply this method to simulate a distillation column to separate a six-hydrocarbons mixture according to the set of specifications that provides the easiest way to solve the problem: the reflux rate and the distillate rate, that allow us to initialize the  $V_j$  profiles based on the assumption of constant-molar interstage flows. This hypothesis is the basis of the McCabe-Thiele graphical technique for designing binary distillation columns. It considers that the mole flowrates of vapor and liquid streams circulating through the column are constant within each sector of the column, and the only changes appear when a feed stream is introduced or a side product stream is extracted from the column. This condition will be fulfilled if all the components have similar latent heat of vaporization and if their heat of mixing is negligible.

The solved example is exercise number 10.20 proposed by Seader et al.,<sup>[1]</sup> which is suggested to be solved using the Soave-Redlich-Kwong equation for liquid-vapor equilibrium calculations. Nevertheless, in order to simplify calculations and focus on the BP application method, we use the same simplest polynomial correlations with temperature for  $K$ -values and enthalpies that were proposed for the same exercise in an older version of the book.<sup>[23]</sup> The Excel file contains three sheets: the first shows a detailed explanation of the first iteration, the second prepares to complete the iterative calculation, and, finally, the last sheet contains the comparison results obtained in that Excel file and those obtained by ChemCAD v7.1.4 for the same separation using the same polynomial correlations for  $K$ -values and enthalpies as well

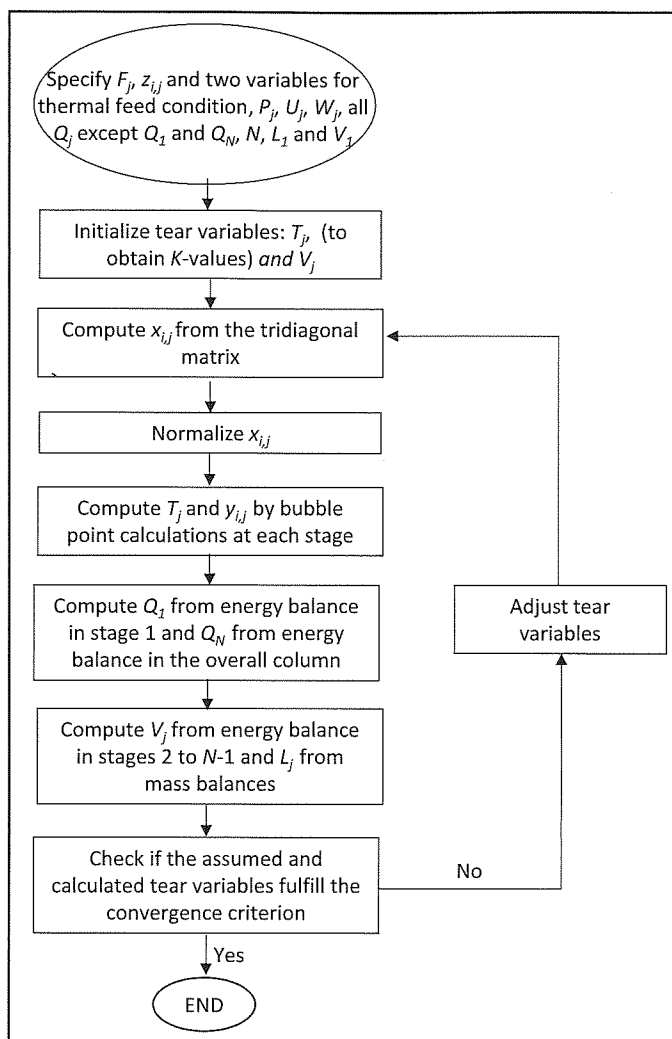


Figure 2. Algorithm for an BP method.

as using the Soave-Redlich-Kwong thermodynamic model. These comparisons can be used to check that the calculations are performed correctly. Since students are very familiar with bubble point calculations, this exercise is especially useful for instructing them how to work with the tridiagonal matrix. It is worth mentioning that Seader et al.<sup>[1]</sup> provide a solved example showing the first iteration for a column with three stages plus condenser and reboiler to separate a ternary mixture. Another example, completely solved with a computer program, corresponds to the simulation of a 12-stages column plus condenser and reboiler to separate a five-component mixture, where the results are presented and discussed.

### Example of Application of an SR Method

Figure 3 shows the algorithm for a SR application method. Input specifications are typical for an absorber or, in general, for an equilibrium stages cascade without condenser and reboiler. The application of a SR method requires the input

of all the heat duties in the column in order to compute the stage temperatures from energy balances; therefore, this is not the best option for simulating distillation columns where the condenser and reboiler duties depend on the separation being carried out. In the Excel file “SR application example. xlsx”, available at <https://bit.ly/2SLhsNJ>, this method has been applied to the simulation of an absorber where a five light hydrocarbon mixture is absorbed with n-decane in a 15-stage column. This example has been obtained from exercise number 9.22 proposed by Seader et al.<sup>[1]</sup> to be solved with an approximated method. As in the BP method example, the Excel file contains three sheets: one of them showing and explaining with detail the first iteration, another prepared to complete the iterative calculation and, finally, one sheet with the comparison between results obtained with those obtained with ChemCAD v7.1.4 for the same separation and using the same polynomial correlations for  $K$ -values and enthalpies. This comparison shows the accuracy of the calculations carried out. Considering that students have previously studied the BP example and know the tridiagonal matrix behavior, in this example, attention should be focused on the application of the sum rates equation. To solve the energy balance set of equations is a laborious task, but it is not difficult to understand, especially taking into account that we use a polynomial model. In the SR method example shown by Seader et al.<sup>[1]</sup> only the problem statement and the converged results are presented.

### Example of Application of an ISR method

The ISR methods are a variant of SR methods to be applied for isothermal conditions or in cases where the temperature of all the stages is set and known. Therefore, it is especially useful for simulation of liquid-liquid extractors because it allows the student to obtain the results of the problem without solving the liquid-liquid equilibrium, which is complicated due to the high nonideality degree involved in the existence of two immiscible liquid phases. Figure 4 shows the algorithm used for an ISR method, and in the Excel file “ISR application example.xlsx”, available at <https://bit.ly/2SLhsNJ>, this method has been applied to the same case as in example 10.5 by Seader et al.<sup>[1]</sup>  $\gamma_{Lij}$  and  $\gamma_{Vij}$  represent, respectively, the activity coefficients of component  $i$  in the liquid and vapor phases at stage  $j$ . This file contains the three first iterations, each iteration in a different sheet, and another sheet with the comparison with the results obtained with ChemCAD, using the same thermodynamic model and binary interaction parameters. In this case some small deviations appear, most likely related to the low number of iterations completed. The existence of the inner loop shown in the algorithm of Figure 4, which is exactly the point where the liquid-liquid equilibrium calculation is bypassed, has been especially laborious to develop in Excel because it requires that some results have to be “stored” to allow the successive  $K$ -values calculation. In this case, the students should focus on the inner loop because they

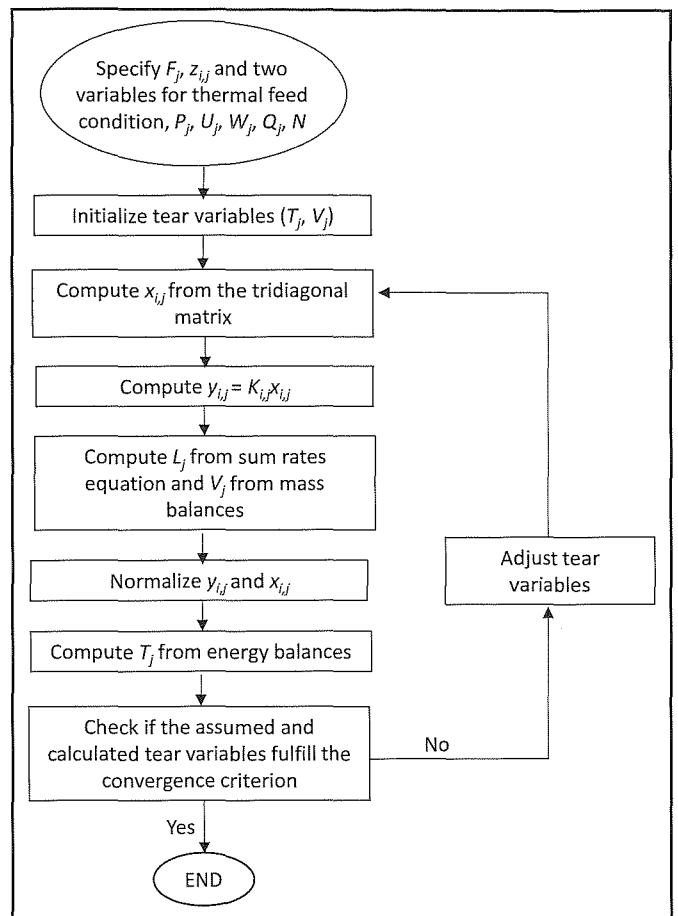


Figure 3. Algorithm for an SR method.

have already learned the tridiagonal matrix and the sum rates equation in the previous examples. In the example presented by Seader et al.<sup>[1]</sup> the initial assumptions for the distribution of components through the column and the final converged solution are shown.

### Example of Application of an SC Method

Perhaps the SC methods are the easiest to understand. They can be simply explained by saying, “Write the set of MESH equations for all the stages and all the components and solve with the Newton-Raphson method”. Nevertheless, it is obvious that things are not so simple. The Jacobian, or matrix of partial derivatives of MESH equations, is very difficult to obtain due to the high nonlinearity of equilibrium relations and enthalpy equations as well as because of the large number of equations, even for small columns to separate few component mixtures. In order to focus on how this method works, the SC method has been applied to solve a single equilibrium stage fed with a binary mixture, considering the same polynomial correlations as in the example of the BP method (“SC application example” at <https://bit.ly/2SLhsNJ>). The solved example focuses on how to build and arrange the Jacobian

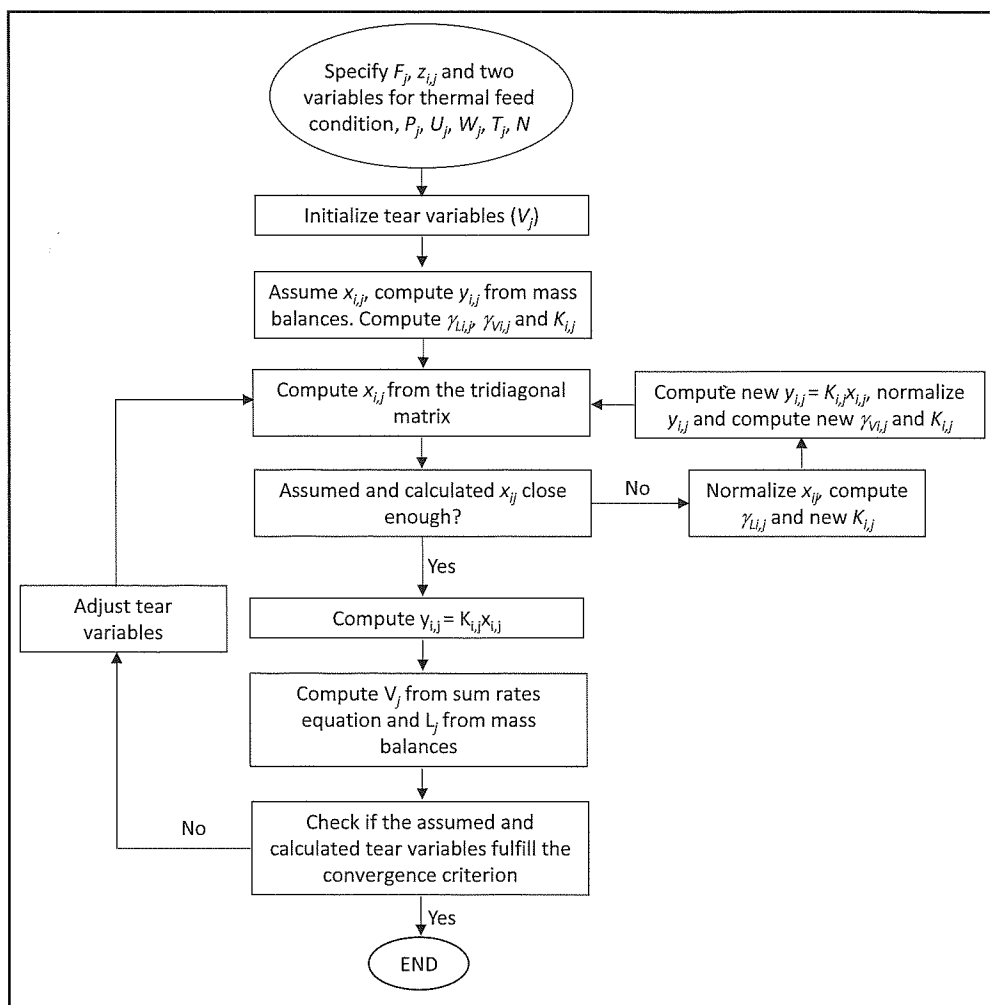


Figure 4. Algorithm for an ISR method.

and the vectors of functions and output variables. The Excel file also contains the comparison with the results obtained with ChemCAD and the same thermodynamic polynomic correlations.

Figure 5 shows the algorithm for a SC method, which provides more details than usual about how to apply the Newton-Raphson method.  $v_{ij}$  and  $l_{ij}$  represent, respectively, the flowrates of component  $i$  in streams  $V_j$  and  $L_j$  (i.e.,  $v_{ij} = V_j(y_{i,j})$  and  $l_{ij} = L_j(x_{i,j})$ ). In order to simplify the method, the scalar attenuation factor used to accelerate the convergence has not been included. SC methods are the most versatile and can be applied to every type of equilibrium stage cascade and for highly non-ideal mixtures, even in cases having three phases in equilibrium or for systems with chemical reactions. It is the method applied in ChemCAD at the SCDS module for distillation columns. The algorithm shown by Seader et al.<sup>[1]</sup> includes a more detailed set of input specifications to start calculations than for other methods, such as using the Murphree tray efficiencies or other possibilities to select specifications for side products and for top and bottom stages.

Nevertheless, in order to simplify the example, Figure 5 uses the same specifications given in Figure 2 for the BP method. Seader et al.<sup>[1]</sup> illustrate the application of this method with an example where a computer program is used to solve the case of a 12-stage reboiled stripping column for the separation of a five-component mixture. This problem has 169 output variables; despite the authors' consideration that the  $K$ -values and enthalpies are independent of composition, this problem is obviously not suitable to be solved by hand.

### Example of Application of an Inside-Out Method

Perhaps the inside-out methods are the least intuitive for students. Figure 6 shows a scheme of this type of method. In the inner loop, the problem is solved by applying a rigorous method, as in any of those above-mentioned methods, but using very simple approximated thermodynamic models to

calculate  $K$ -values and enthalpies. In this way, the most difficult part associated with those methods is avoided, but the results obtained are not correct because these approximated models are not accurate. The results of the output variables are sent to the outer loop, where they are used to calculate  $K$ -values and enthalpies by means of rigorous thermodynamic models. These rigorous values are used to compute the parameters of the approximated models used in the inner loop. This procedure is repeated until the output variables and the parameters obtained in two consecutive loops are "close enough." The TOWER module of ChemCAD for distillation columns applies an inside-out method. In the file "InsideOut application example", available at <https://bit.ly/2SLhsNJ>, this method has been applied to a three-stage column, with total condenser and reboiler, where a three-hydrocarbon mixture is separated. The polynomic correlations for enthalpies used in previous examples and the Raoult's law for  $K$ -values have been used as rigorous thermodynamic models. The approximated models are those suggested in the bibliography.<sup>[1]</sup> In this case, the example focused on how the approximated models



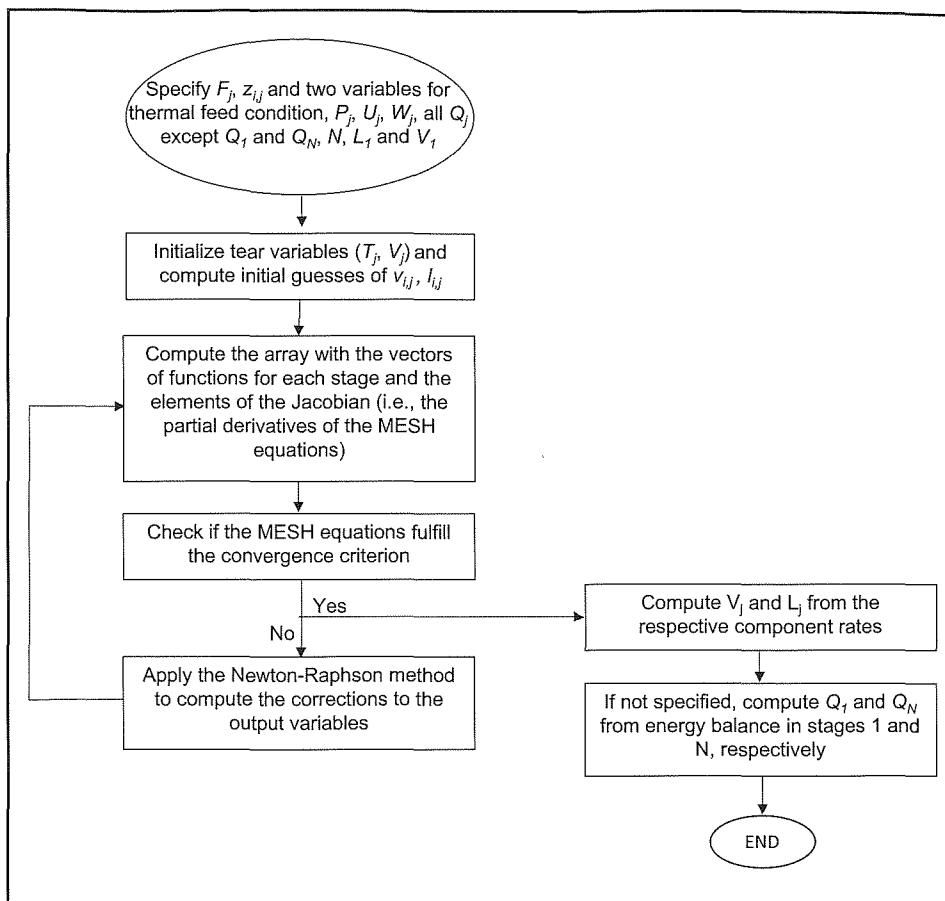


Figure 5. Algorithm for an SC method.

are used and how their parameters are obtained, and only two iterations for the outer loop are developed. It is worth mentioning that the comparison with the results obtained with ChemCAD using the same rigorous models reflects that, despite the fact that the results of two iterations of the outer loop the parameters of approximate models are not close, the results obtained for the output variables are not too bad. Moreover, the objective of illustrating how this method works is achieved. As for the SC method, the example shown by Seader et al.<sup>[4]</sup> does not present details of the application of the inside-out method and focuses on the discussion of the results obtained with the module TOWER within ChemCAD.

### Example of Application of the Homotopy or Continuation Method

The homotopy-continuation methods are described by Kister<sup>[2]</sup> and are based on the homotopy

principle that describes the homotopy function,  $\mathbf{H}(\mathbf{x}, t)$ , as the continuous blending of two functions,  $\mathbf{F}(\mathbf{x})$  and  $\mathbf{G}(\mathbf{x})$ .  $\mathbf{F}(\mathbf{x})$  represents the set of equations that describes the case of a complex column, which is a calculation difficult to solve, and  $\mathbf{G}(\mathbf{x})$  represents the set of equations of a simplified problem, where the solution is known or is easy to obtain.  $\mathbf{x}$  is the set of independent variables, and  $t$  is the homotopy parameter, which ranges between 0 and 1. The homotopy function is constructed as follows:

$$\mathbf{H}(\mathbf{x}, t) = t\mathbf{F}(\mathbf{x}) + (1-t)\mathbf{G}(\mathbf{x}) \quad (13)$$

Therefore, when  $t = 0$ , the homotopy function is that describing the simplest problem, whereas when  $t = 1$ , the homotopy function corresponds to the difficult problem. When  $\mathbf{H}(\mathbf{x}, t) = 0$  is solved for increasing  $t$  values from 0 to 1, it gives successive sets of values for the independent variables, starting from the initial known solution that is easy to obtain, to the final solution, corresponding to the complex problem where the solution was difficult to obtain.

Inspired in the work of Fidkowski et al.,<sup>[24]</sup> who applied the homotopy method for the calculation of all the azeotropes in homogeneous multicomponent mixtures, Gómez and

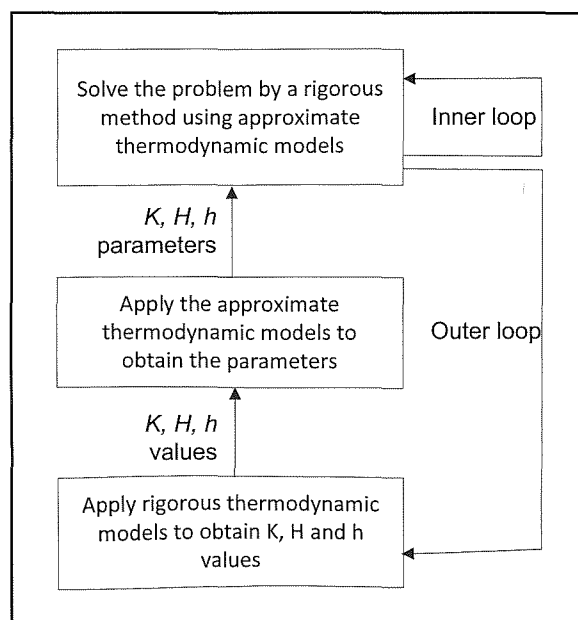


Figure 6. Scheme of application of an inside-out method.

Font<sup>[18]</sup> have shown the application of this method to calculate the liquid-vapor equilibrium of an acetone-chloroform binary mixture at atmospheric pressure. This mixture shows a maximum azeotrope. Obviously, there are more direct and efficient procedures to solve the liquid-vapor equilibrium of a binary mixture than the application of a homotopic method. However, thanks to the knowledge of the behavior of these systems that students have already acquired, it illustrates the homotopy path from the solution of  $G(x)$  to  $F(x)$ . In this case, a homotopy method has been applied to a hypothetical binary system with a minimum azeotrope; the file “Homotopy application example”, shared in <https://bit.ly/2SLhsNJ>, contains several sheets, each one showing the results for the successive values of  $t$ . The final result is checked by the comparison with the results obtained when the problem is solved by the conventional procedure bubble point calculation, i.e., calculating the temperature that leads to the summation of vapor mole fractions equal to one for each composition of the liquid phase.

## CONCLUSIONS

In this work a learning approach based on providing the students with a set of Excel files shared in <https://bit.ly/2SLhsNJ>, containing solved examples of rigorous methods for multicomponent separations is proposed. Since the application of these methods is difficult to carry out “by hand,” these examples complement the explanations of the theoretical classes and allow students to perform the direct inspection of how these methods are developed. The results of this approach have been analyzed with a survey to students, and the results are very satisfactory.

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