

# Treball Final de Grau

**Obtaining distillation and residue curves for nonideal ternary systems.**

**Obtención de curvas de destilación y residuo para sistemas ternarios no ideales.**

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*January 2015*



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*No podemos resolver problemas pensando de la misma manera que cuando los creamos.*

Albert Einstein

Agradecimientos a las personas que me han acompañado en este viaje que ha sido la universidad: mis padres, compañeros, amigos, tutores y profesores. Sin duda alguna ese apoyo recibido me ha influenciado y ayudado a alcanzar mis metas.

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La universidad ha sido para mí una experiencia placentera y me ha hecho progresar de muchas maneras, el camino puede ser difícil a veces pero con dedicación podemos resolver cualquier problema y al hacerlo sabemos que hemos aprendido algo nuevo. Aún queda un largo camino, y aún más por aprender.



**REPORT**





# CONTENTS

<b>1. SUMMARY</b>	<b>3</b>
<b>2. RESUM</b>	<b>5</b>
<b>3. INTRODUCTION</b>	<b>7</b>
3.1. 1 <sup>st</sup> Residue curve map	8
3.1.1. 2 <sup>nd</sup> Residue curves	9
3.1.2. 2 <sup>nd</sup> Thermodynamic model and considerations	10
3.1.2.1. 3 <sup>rd</sup> UNIFAC model	10
3.1.2.2. 3 <sup>rd</sup> Ideal vapour phase	11
3.1.2.3. 3 <sup>rd</sup> Liquid-Vapour equilibrium	11
3.1.2.4. 3 <sup>rd</sup> Vapour pressure	12
3.1.3. 2 <sup>nd</sup> Features of RCM	12
3.2. 1 <sup>st</sup> Distillation curve map	13
3.2.1. 2 <sup>nd</sup> Distillation curves	15
3.2.2. 2 <sup>nd</sup> Thermodynamic model and considerations	16
3.2.3. 2 <sup>nd</sup> Distillation borders	16
<b>4. OBJECTIVES</b>	<b>16</b>
<b>5. DEVELOPMENT: RCM DESIGNER</b>	<b>17</b>
5.1. 1 <sup>st</sup> Bibliography review	17
5.2. 1 <sup>st</sup> Election of the algorithm	17
5.3. 1 <sup>st</sup> Codification	18
5.4. 1 <sup>st</sup> Validation of the results	19
<b>6. RESULTS AND DISCUSSION</b>	<b>20</b>
6.1. 1 <sup>st</sup> Sections of the program	20
6.1.1. 2 <sup>nd</sup> Section 1: New RCM	21

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6.1.2. 2 <sup>nd</sup> Section 2: Customization	23
6.2. 1 <sup>st</sup> Analysis of E-acetate/M-acetate/Methanol mixture	24
6.3. 1 <sup>st</sup> Ternary mixture: Acetone/Methanol/Hexane	33
<b>7. CONCLUSIONS</b>	<b>35</b>
<b>8. REFERENCES AND NOTES</b>	<b>37</b>
<b>APPENDICES</b>	<b>39</b>
<b>APPENDIX 1: RAYLEIGH EQUATION</b>	<b>41</b>
<b>APPENDIX 2: NEWTON-RAPHSON METHOD</b>	<b>43</b>
<b>APPENDIX 3: RCM DESIGNER AND DISTILLATION CURVES</b>	<b>45</b>

# 1. SUMMARY

The aim of this work is the creation of an EXCEL program that draws distillation and residue curves of homogeneous ternary mixtures, where the user can select the components to study and work pressure.

The industry is based on the best utility and use of raw materials and resources, which means finding an optimal design, often this takes a lot of complexity to find the most efficient use. The separation of the different compounds in a multicomponent blend can be complicated when the boiling point difference is very small, which does not allow a simple distillation or also by the presence of azeotropes in the mixture. In fact the first thing that has to be known for designing a separation process, is to know if the mixture forms an azeotrope or not. This work may be useful in such cases and detect the possible formation of azeotropes and its composition in a ternary system (residue curves), as well as to define the distillation curves and distillation regions which will conditionate the strategy of the separation process. There are several commercial simulation softwares that allow to build residue curve maps (Aspen), however, these programs are expensive, and for some purposes, e.g. educational ones, it might be an interesting option to possess a home-made program. This work also pretends to give the user more options for the design of residue curve maps.

This program called RCM Designer (residue curve map) will be tested for several mixtures and some of the results will be compared to the ones obtained with ASPEN simulator in order to assert the validity of the results.

During the development of the program we encountered a problem, finding an algorithm to build distillate lines was unsuccessful and RCM Designer cannot calculate the necessary points to build distillate lines, except for a few mixtures (an example will be discussed).

**Keywords:** Residue, distillation, curve, map, nonideal, ternary, unific.



## 2. RESUMEN

El tema de este trabajo es la creación de un programa EXCEL que dibuje curvas de destilación y de residuo de mezclas ternarias homogéneas, de manera que el usuario seleccione los componentes a estudiar, así como la presión de trabajo.

La industria se basa en la mejor utilidad y aprovechamiento de las materias primas y recursos, es decir en la búsqueda de un diseño óptimo, esto muchas veces suele llevar una gran complejidad para encontrar el uso más eficiente. La separación de un sistema multicomponente en componentes puros puede ser complicada cuando la diferencia de puntos de ebullición es muy pequeña, lo cual no permite una destilación simple o también por la presencia de azeótropos en la mezcla. De hecho, lo primero que debe conocerse en el diseño de un proceso de separación, es saber si la mezcla forma un azeótropo o no. Este trabajo puede ser útil en dichos casos ya que detecta la posible formación de un azeótropo y su composición en el sistema ternario (curvas de residuo), también define las líneas de destilación y regiones de destilación que condicionaran la estrategia del proceso de separación. Existen diversos software comerciales de simulación que permiten construir mapas de curvas de residuo (Aspen), sin embargo, estos programas son caros, por ejemplo para uso didáctico puede ser interesante optar por poseer un programa casero. Este trabajo además pretende darle al usuario más opciones para diseñar mapas de curvas de residuo.

El programa llamado RCM Designer (diseñador de mapa de curvas de residuo) será puesto a prueba con diferentes mezclas y algunos de los resultados serán comparados con los obtenidos mediante el simulador ASPEN para así afirmar la validez de los resultados.

Durante el desarrollo del programa surgió un problema al encontrar un algoritmo que construyera líneas de destilado por lo cual RCM Designer no puede construir las exceptuando algunas mezclas (un ejemplo de esto será discutido).

**Palabras clave:** Residuo, destilación, curva, mapa, no ideal, ternario, unifac.



### 3. INTRODUCTION

The distillation and residue curves are mainly used as a step in the sequencing of separation trains because they establish a kind of frontier in which a feed can be separated. Being this method of study in the mixtures when azeotropes are formed and therefore it's required an azeotropic distillation.

As expected, the calculation complexity is conditioned by the number of components present in the mixture, being able to consider three different cases: binary mixtures, ternary mixtures or multicomponent mixtures. For binary mixtures, calculation is relatively simple, widely studied and explained, this can be resolved graphically by McCabe-Thiele or Ponchon-Savarit methods or analytically by Sorel- Lewis.

For the ternary mixtures, solving equilibrium equations for non-ideal blends is more complicated. Even when graphical methods can be applied these are not as obvious as it cannot be represented on a plane of two directions as in binary mixtures, instead it is necessary working with three-dimensional representations.

Since the case of ternary mixtures will be our topic of study, the subject will be addressed using projections in a ternary diagram and not three-dimensional representations (set of multiple projections), this projections work at a given pressure by the user. In the industry, azeotropic mixtures with more than three compounds are rather unusual.

The calculation methods for ternary mixtures are the same as in the binary mixtures but its application is not so widely explained for this case and not found in elementary textbooks. Moreover, since the algebraic resolution of multicomponent systems is the same as for the ternary mixture calculation can be approached in the same way however It is not possible to obtain the graphic resolution in multicomponent systems and will not be discussed in this work.

### 3.1. 1<sup>ST</sup> RESIDUE CURVE MAP

The study of residue curve maps allow us to detect the azeotropes formed in the mixture and to know the possible areas of separation and compare the potential separator agents during the azeotropic or extractive distillation. Although this last use is specific to distillation curve maps we will use it this way because **the trajectories described by the distillation curves and residue curves of a ternary system are similar in form but not coincident**. For this the use of triangular diagrams allowing us represent residue curves that correspond to these mixtures at a specified pressure.

A residue curve is the representation of change of composition in the liquid in the boiler in a simple discontinuous distillation. A set of residue curves (obtained changing the initial concentration in the bailer), at a given pressure, form a residue curve map.

Figure 1 is an example of ternary diagram for a system with two binary azeotropes (T1 and T3). The direction of the arrows is to increasing boiling points, so the curves start from pure components or azeotropes lower's boiling points and end in pure components or a higher azeotrope boiling point. In this case all curves start from the minimum azeotrope boiling point, and one of them ends in the other azeotrope. This type of residue curve receives the name of **border distillation line** (close approximation for a real border in distillation curve map), and divides the region of the ternary mixtures in two separate distillation regions so that curves of each region end up in the same component, and curves of different Regions end up in different components.

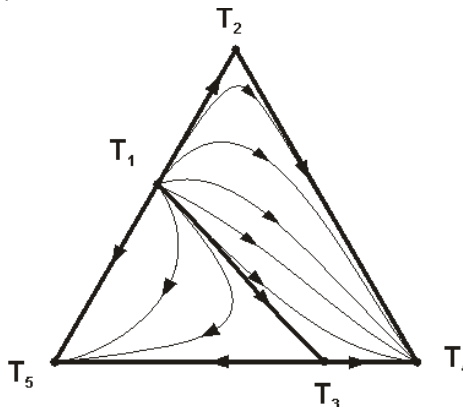


Figure 1 Example of a residue curve map with two binary azeotropes  
(Extracted from university of Alicante, Ref. 1)



The interest of these maps lies in the analogy between the composition profiles during rectification and the curves of simple distillation, providing information on the evolution of the balance of the system. Moreover, the map's features determines the validity of a separating agent for a given separation, being directly related to the sequence of columns and how they operate.

### 3.1.1. 2<sup>nd</sup> Residue Curves

A residue curve is the representation of the evolution of the composition of the residue over time in a simple distillation.

Its calculation is relatively simple since the curves are only a function of the liquid-vapour equilibrium and this balance is used to represent the ternary mixtures.

Modified Rayleigh equation:

$$\frac{dx_i}{d\varepsilon} = x_i - y_i$$

*Equation 1 Rayleigh equation*

*Note: For equation 1 deduction see **appendix 1**, ref. 2*

$$y_i = K_i \cdot x_i$$

*Equation 2 Relation between the compositions in the liquid and vapour phases of a component*

$$\sum_{i=1}^3 K_i \cdot x_i = 1$$

*Equation 3*

Where  $x_i$  and  $y_i$  are the molar compositions of the component  $i$  in the liquid and vapour phases, respectively,  $\varepsilon$  is the dimensionless time and  $K_i$  is an equilibrium parameter which depends of the pressure, temperature and compositions of the mixtures: liquid and vapour.

Starting from an initial composition if we integrate equation 1 we get a residue curve, each curve requires a large number of points to be drawn and for each of these calculations should be performed to find the compositions in the vapour phase in equilibrium with the phase liquid in the bubble point. So that the composition in the vapour phase is calculated using equation 2 and the validity of the result is checked when equation 3 converges. As we

can see then an iterative calculation is necessary where if equation 3 is not satisfied it will be repeat the process until it converges.

To a mixture of 3 components have the following variables: T, P,  $\epsilon$ ,  $x_1$ ,  $x_2$ ,  $x_3$ ,  $y_1$ ,  $y_2$ ,  $y_3$ . So we have eight unknown variables and 9 equations (3 from equation 1, 3 from equation 2, 1 from equation 3 and a condition that the sum of  $x_1$ ,  $x_2$  and  $x_3$  is equal to 1). The equations are solved by fixing P and introducing an initial concentration in the liquid, and to find the next point Rayleigh equation is integrated with increasing and decreasing intervals of time.

When the integration is done forward in time the curve will eventually end in the less volatile compound or in a maximum-boiling azeotrope, on the other hand if the integration is done backwards in time the curve will end in a minimum-boiling azeotrope or in one of the less volatile compounds.

### 3.1.2. 2<sup>nd</sup> Thermodynamic model and considerations

In equation 2, parameter K is function of total pressure, vapour pressures and the activity coefficients. There are different methods to calculate activity coefficients such as WILSON, NTRL, UNIQUAC and UNIFAC, being this last method the one used by the program.

#### 3.1.2.1. 3<sup>rd</sup> UNIFAC model

The UNIFAC model is a semi-empirical method for the prediction of activity coefficients in non-ideal mixtures. It is based on the group contribution method, using the functional groups that form each molecule to calculate the activity coefficients, each molecule is characterized by two structural parameters, a volume parameter r surface parameter q.

So that the activity coefficient is the sum of a combinatorial contribution caused by the size differences between the molecules and other residual contribution due to intermolecular forces.

$$\ln(\gamma_i) = \ln(y_i^C) + \ln(y_i^R)$$

Equation 4

Where  $\ln(y_i^C)$  is the combinatorial contribution to the activity coefficient of component i and  $\ln(y_i^R)$  is the residual contribution.

The combinatorial contribution is calculated according to the equation 5:

$$\ln(y_i^C) = \ln\left(\frac{\phi_i}{x_i}\right) + 0.5 \cdot Z \cdot q_i \cdot \ln\left(\frac{\theta_i}{\phi_i}\right) + L_i + \left(\frac{\phi_i}{x_i}\right) \sum_{j=1}^n (L_j \cdot x_j)$$

Equation 5 combinatorial contribution

The residual contribution is calculated according to the equation 6:

$$\ln(y_i^R) = q_i \left[ 1 - \ln \sum_{j=1}^n (\theta_j \cdot \tau_{ji}) - \ln \sum_{j=1}^n \left( \frac{\theta_j \cdot \tau_{ji}}{\sum_{k=1}^n (\theta_k \cdot \tau_{kj})} \right) \right]$$

Equation 6 Residual contribution

Where  $L_i$ ,  $\theta_j$ ,  $\phi_j$  y  $\tau_{ji}$  can be calculated with the next equations:

$$L_i = 0.5 \cdot Z \cdot (r_i - q_i) - r_i + 1$$

Equation 7

$$\theta_j = \frac{q_i \cdot x_i}{\sum_{j=1}^n q_j \cdot x_j}$$

Equation 8

$$\tau_{ji} = \frac{a_{ij}}{RT}$$

Equation 9

Where  $q_i$  and  $r_i$  are the area and volume parameters respectively,  $x_i$  is the mole fraction of component  $i$ ,  $T$  is the temperature and  $Z$  is the coordination number equal to 10.

Considering the following restrictions:  $\tau_{ij} \neq \tau_{ji}$ ,  $\tau_{ij} = \tau_{ji}$ ,  $a_{ij} = a_{ji}$ ,  $a_{ii} = a_{jj}$

### 3.1.2.2. 3rd Ideal vapour phase

It is considered that the vapour phase behaves ideally taking the fugacity coefficients equal to 1 ( $\phi_i = 1$ ).

### 3.1.2.3. 3rd Liquid-Vapour equilibrium

The composition of the vapour phase in equilibrium with the liquid mixture is calculated according to the following equation:

$$y_i = \frac{x_i \cdot \gamma_i \cdot P_i^{sat}}{P}$$

Equation 10

### 3.1.2.4. 3rd Vapour pressure

The vapour pressure can be calculated with the extended Antoine equation:

$$\ln(P^{sat}) = A * \text{Log}(T) + B / T + C + D * T^2$$

Equation 11 Extended Antoine equation

Where T is the temperature, and the values of A, B, C and D are specific of each component, giving the result in mmHg.

### 3.1.3. 2<sup>nd</sup> Features of residue curve maps

In a triangular diagram, all vertices (pure components) and the points where the azeotropes are represented are singular points or fixed points of the residue curves because in these points  $dx/d\varepsilon=0$ .

Three different cases can be presented in a residue curve map.

Case 1: The singular point is a stable node. This is the pure component or the higher boiling point azeotrope and it is the point where all residue curves end that belong to the same region.

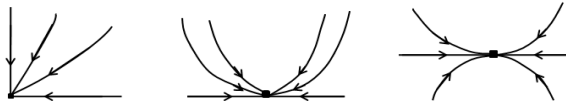


Figure 2 Stable node

(Reproduced from university of Alicante, Ref. 1)

Case 2: The singular point is the point of origin of all curves in a region. Therefore it is the lowest point of local boiling point. In this case it is an unstable node



Figure 3 Unstable node

(Reproduced from university of Alicante, Ref. 1)

Case 3: The singular point is such that the residue curve approach and then moves away of these point, receiving the designation of saddle. Within a region distillation saddles are pure components or azeotropes with intermediate boiling points between a stable and an unstable node.

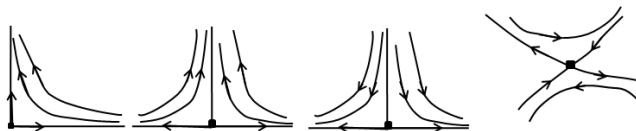


Figure 4 Saddle  
(Reproduced from university of Alicante, Ref. 1)

### 3.2.1<sup>ST</sup> DISTILLATION CURVE MAP

The presence of azeotropes as mentioned above prevents the separation of a mixture into its pure components, this can be explained similarly to a binary mixture, in which an azeotrope of minimum boiling point is presented (Figure 5).

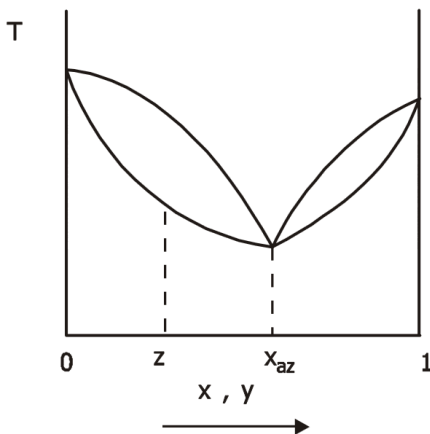


Figure 5 Temperature-composition diagram  
of a binary mixture of A and B with an azeotrope of minimum boiling point  
(Adapted from university of Alicante, Ref. 1)

As shown in figure 5, a mixture of composition  $z$  can be split into a distillate with a composition between  $z$  and  $x_{AZ}$  and a residual composition between  $0$  and  $z$ . In this case, in order to know the separation limit it is only required the boiling points of the azeotrope and

pure components and the azeotrope's concentration. However for a ternary mixture is not so simple, though the same information is required and the composition obtained depends on the initial concentration in the ternary diagram too, when there is an azeotrope the composition profiles in a rectifying column cannot go any zone but it is limited by internal borders (distillation border) that divide the diagram into different zones (distillation regions).

It is necessary to know these boundaries, otherwise when there are actual azeotropes, a distillation problem for ternary mixtures can't be solved correctly. Recently, an application for binary mixtures with azeotropes has been reported, known as assisted distillation in which a separator agent allows separate the initial components in concentrations that could not be achieved by ordinary distillation. [Note: information obtained from ref. 1]

This section is intended to address the study and identification of regions of possible products for separation by distillation of ternary mixtures. This information will allow us:

- For the separation of a ternary mixture by standard rectification, a distillation curve map will provide enough information to estimate the separation expected, strategies to improve the separation of the bend (multiple rectification towers and their working pressures). Also for binary mixtures with close volatilities, the selection of entrainer that forms an azeotrope with the mixture (allowing the separation) can be studied. Additionally, the possibility of separation by change of phase in the distillate can be of interest (although RCM Designer does not take in account the separation of phases in mixtures).

- For assisted distillation a distillation curve map will provide the basis for the selection of working parameters, and for detecting non-viable configurations of the column.

### 3.2.1 2<sup>nd</sup> Distillation curves

A distillation curve represents the composition profile in a rectification column, operating at total reflux, a group of curves at the same pressure establish a curve distillation map.

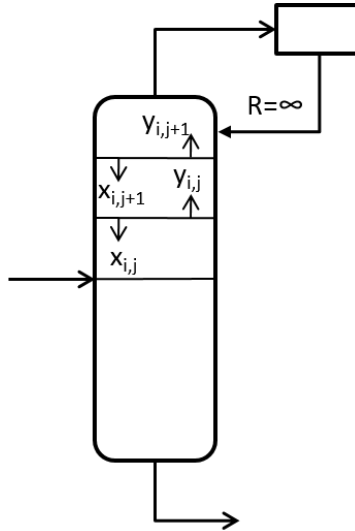


Figure 6 Rectification column representation with total reflux

Its Calculation starts with the first line of a known composition, designated as plate 1, the next plates are numbered toward the head of the column. Therefore, the direction of the distillation curves, unlike the curves residue, are to decreasing boiling points.

If the column is working at total reflux, a condition is imposed for any interstage position as it is demonstrated in equation 12.

$$x_{i,j+1} = y_{i,j}$$

Equation 12

Note: For equation 12 deduction and use in the program see **appendix 3**.

Equation 2 will be used as before, the value of K calculated with UNIFAC and working at bubble point.

$$y_i = K_i \cdot x_i$$

Equation 13 Relation between the compositions in the liquid and vapour phases of a component *f*

### 3.2.2 2<sup>nd</sup> Thermodynamic model and considerations

The equations used will be same as in the previous section (residue curves). So the UNIFAC method will be used to estimate the activity, considering the behaviour of the vapour phase as ideal. Also the liquid-vapour equilibrium and bubble pressure will be calculated as before (equations 10 and 11, respectively).

### 3.2.3 2<sup>nd</sup> Distillation borders

Distillation borders appear as a result of the changes in the relative volatility in ternary mixtures due to the presence of azeotrope's boiling points.

A study of these borders show that they must meet the following condition:

- The relative volatilities of the two components along the border tend to be equal to 1, because when passing through the border, a reversal of the volatility will occur.

Of great interest is the effect of distillation boundaries on the operation of distillation towers. To summarize a growing body of literature, it is well established that the composition of a distillation tower operating at total reflux cannot cross the distillation-line boundaries, except under unusual circumstances, where these boundaries exhibit a high degree of curvature. This provides the total-reflux bound on the possible (feasible) compositions for the distillate and bottoms products. [*Product & Process Design Principles* p. 269, ref. 2]

## 4. OBJECTIVES

- The objective of this work is to build a computer program using Excel that draws distillation and residue curve maps of components selected by the user.
- The program will show possible azeotropes in the mixture and its nature (maximum or minimum boiling point, or saddle).
- Validate the results using a commercial simulator and data found experimentally.



## 5. DEVELOPMENT: RCM DESIGNER

In order to create the program, this project will follow four basic steps: bibliography review, election of the algorithm, codification, and validation of the results.

### 5.1 1<sup>ST</sup> BIBLIOGRAPHY REVIEW

Selection of the thermodynamic model, in this case UNIFAC model (equations 4 to 9).

Also it is selected the equations that will be used in the calculation of pure components and ternary mixtures, these are presented in the introduction (equations 1, 2, 3, 10 and 11).

Selection of different compounds to study, using the data base from ChERIC (Chemical Engineering Research Information Center).

### 5.2 1<sup>ST</sup> ELECTION OF THE ALGORITHM

This section it's focus in the development of a simple algorithm for the construction of residue curve maps, using the proper equations for plotting residue curves and for the thermodynamic model. The process's mathematical model used in the program involves the equations for vapour-liquid equilibrium, the extended Antoine equation (Equation 11) for the calculation of the vapour pressures and the equations present in the thermodynamic model UNIFAC (Equations 4 to 9). The database ChERIC will be used to obtain the parameters for the Antoine equation.

Each point of the curve is calculated with the algorithm sketched in Figure 7. Once a point has been calculated Excel will proceed to calculate another using Rayleigh equation (equation 1) to find the next points. The increments in time can be configured (0.1 by default), and after obtaining several points, the process is repeated for negative time increments and finally allowing us obtain a residue curve when the points (liquid concentrations) are plotted in a ternary map.

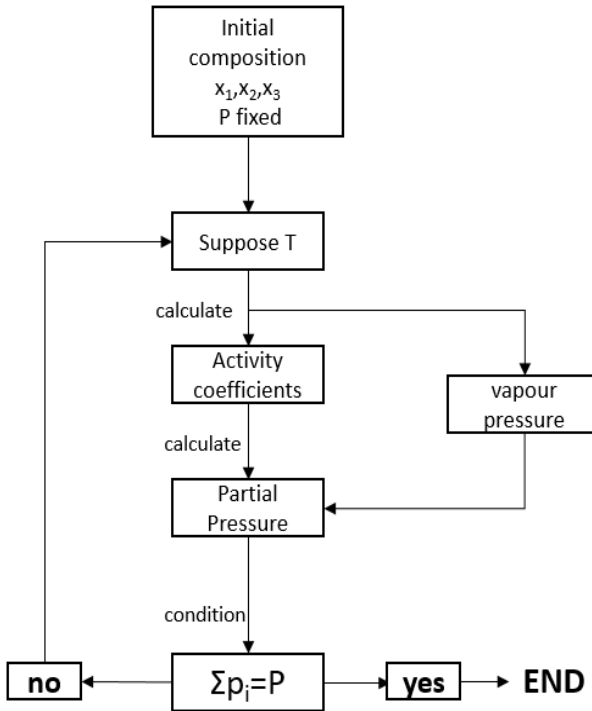


Figure 7 Algorithm to find boiling points for homogenous ternary mixtures

Note: The new values of  $T$  are obtained through a quasi Newton-Raphson algorithm. See appendix 2

### 5.3 1<sup>ST</sup> CODIFICATION

The algorithm in figure 7 has been coded using the thermodynamic model UNIFAC and the proper equations to draw residue curves. The codification has been done using **VISUAL BASIC FOR APPLICATIONS** a programming language and integrated development environment in Excel. Visual Basic has the same basic commands as many other visual programs like Visual C++ or VISUAL BASIC.

In order to carry out realistic calculations, the program's database has been built, we can separate them in two parts, the first one with all the data that UNIFAC model requires for calculating activity coefficients ( $r$  and  $q$  parameters for pure components and the binary

interaction parameters). The second data base contains Antoine's equation constants required for calculating vapour pressure.

**Note:** UNIFAC model has been coded by Dr. David Curcó Cantarell (Department of Chemistry Engineering, University of Barcelona).

## 5.4 1<sup>ST</sup> VALIDATION OF THE RESULTS

In order to check if the residue curve maps plotted represent correctly the reality with its stable and unstable nodes and saddles, we compare with maps created with Aspen Plus, an AspenTech simulator. Aspen Plus is a recognized software created to simulate and design distillation columns and it has an application for drawing residue curve maps.

For this we need to vary the work conditions for both programs and evaluate the response for this changes. It is known that the mixture's behaviour varies depending on the system pressure, because it affects the molecule interaction of the components, and hence their relative volatility. With the intention of observing the software's accuracy in the calculation and plotting of residue curve maps at different pressures, different maps were built, the results being compared with those calculated by Aspen.

The comparison criteria will be the trends and location of the different nodes (stable, unstable or saddle) at different pressures keeping the same initial compositions for both programs.

## 6. RESULTS AND DISCUSSION

### 6.1 1<sup>ST</sup> SECTIONS OF THE PROGRAM

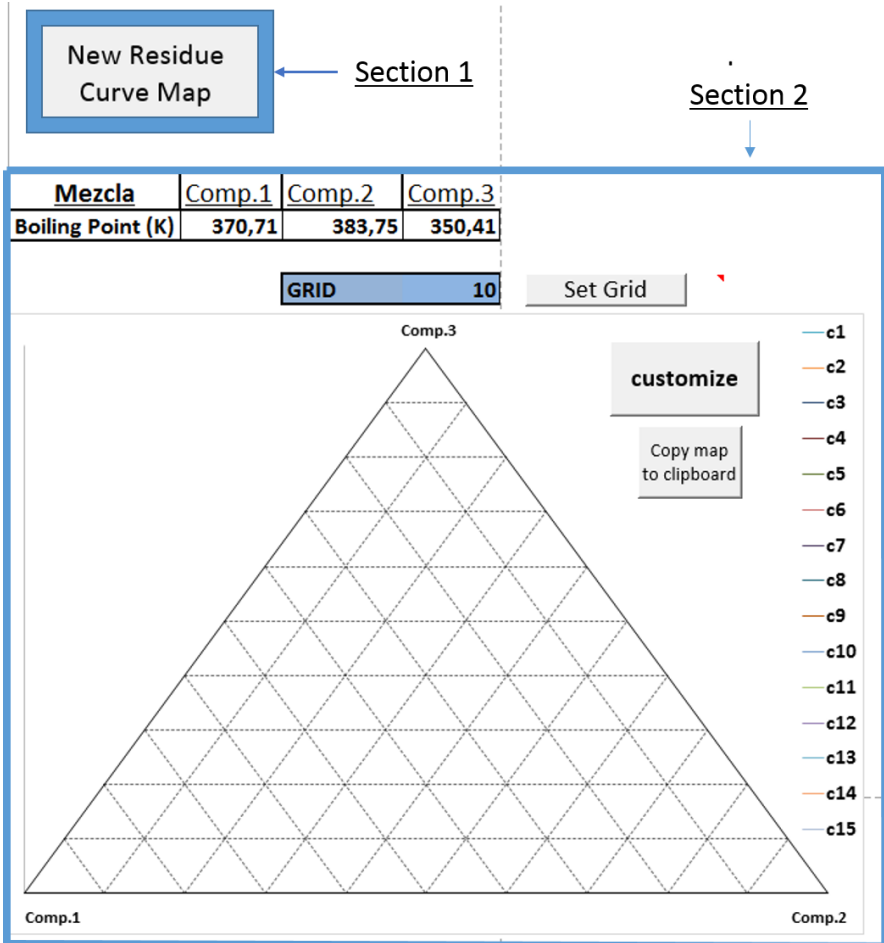


Figure 8 RCM Designer graphic interface

The program's graphic interface (GUI) is divided in 2 sections. Section 1 is where the user introduce the data required for the calculation and graphing the residue curve map. Section II is where is located the triangular diagram, where the calculated curves are plotted.

### 6.1.1. 2<sup>nd</sup> Section 1: New RCM

By pressing the "New Residue Curve Map" button the program displays a form as shown in figure 9.

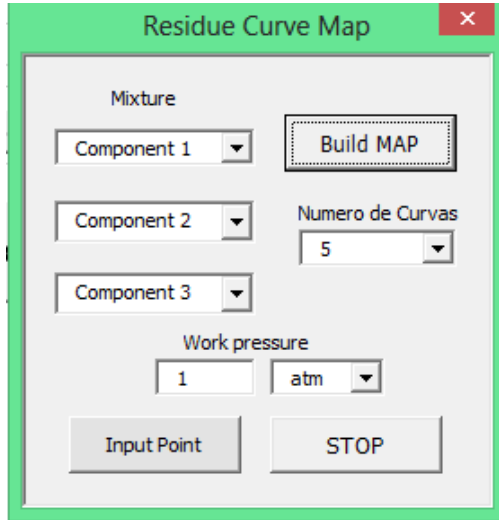


Figure 9

#### 1) Selection of the components

Here you choose between different components in drop-down list that have been added to the data base (as an open source program, the user has the possibility to add the substances that he wishes).

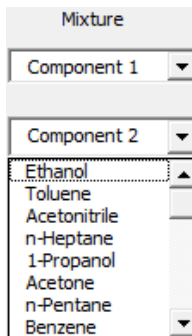


Figure 10

## 2) Number of curves

Deploys a drop-down list to choose between 5, 10 or 15 which are the number of curves that will be calculated, the initial points are the same by default. 5 curves will be calculated by default.

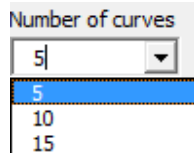


Figure 11

## 3) Work pressure

Deploys a drop-down list with different pressure units. The user then will introduce the work pressure in the textbox (1 atm by default).

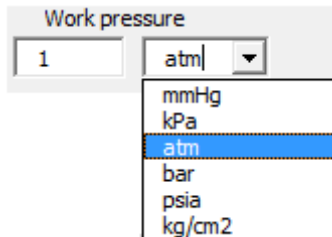


Figure 12

## 4) Button "Input point"

In the case the user prefers to use different starting points for each curve, this button opens a form where different compositions can be selected to be calculated and plotted. The user can introduce 10 points using the textboxes.

Figure 13

5) Button "Build MAP"

This button starts calculating the curves with the values selected by the user.

6) Button "STOP"

This button stops the calculation.

**6.1.2. 2<sup>nd</sup> Section 2: Customization**

Once a new residue curve map has been built the results can be observed in the triangular diagram in this section, 3 buttons are in this zone.

1) Grid lines

A button called "Set grid" allow us to manipulate the grid lines by changing the number of a cell in the sheet.

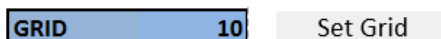


Figure 14

## 2) Button “Customize”

This button opens a form where the user can add a new curve to the map or replace one of them by introducing a starting concentration point. This should be used after a new map has been built, this let us more control for on the map’s design.

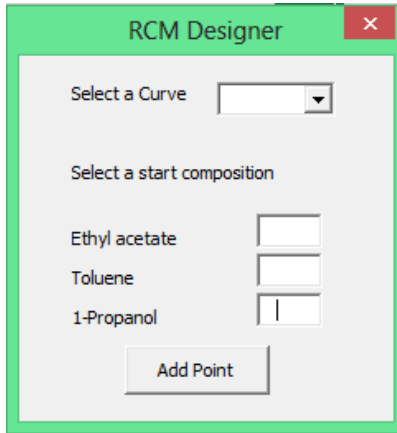


Figure 15

The user selects a curve from drop-down list, in case there that curve number has not been used it will create a new one, if it is already used a confirmation form will be opened asking to be sure to overwrite the data.

## 3) Button “Copy map to clipboard”

This button copies the triangular diagram. There are 2 diagrams plotted, the triangular coordinate as shown in the example and the Cartesian coordinate.

## 6.2. 1<sup>ST</sup> ANALYSIS OF E-ACETATE / M-ACETATE / METHANOL MIXTURE

This mixture has been studied to see a detailed example of how to read a residue curve map and the usefulness of the program to analyse a distillation separation. For this mixture we find 2 azeotropes that present a low variation, one formed by methyl acetate and methanol (components with low and intermediate boiling points), and another located by methanol and ethyl acetate (components with intermediate and high boiling points).

The initial analysis is done at 1 atm and the results are shown in figure 16.



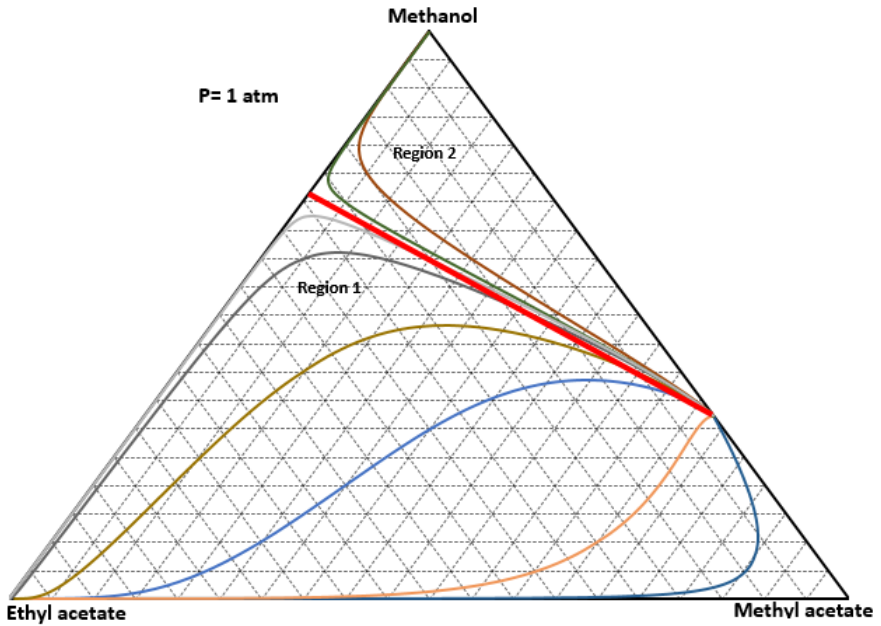


Figure 16 RCM with distillation border and distillation regions at 1 atm

1 atm	Pure components		
	Ethyl acetate	Methyl acetate	Methanol
Boiling T (K)	350,4	330,2	337,7
Node	Stable	Saddle	Stable

Table 1 Pure components data



1 atm	Azeotropes	
	Ethyl acetate-Methanol	Methyl acetate-Methanol
Boiling T (K)	335,3	327,0
Node	Unstable	Saddle
Ethyl acetate	0,281	0
Methyl acetate	0	0,677
Methanol	0,719	0,323

Table 2 Azeotrope data for E-Ac/M-Ac/Methanol mixture at 1 atm

Figure 15 shows a residue curve map for Methanol, Methyl acetate and Ethyl acetate mixture at 1 atm, it has been obtained with Unifac model and considering vapour's behaviour as ideal. This shows the trend toward increasing boiling temperatures and also a boundary between both azeotropes. **The boundary has been found by trial over a straight residue curve.**

The first of the azeotropes formed between Methyl acetate and Methanol and characterized for having a lower boiling point than the components that form it, it is an unstable node where residue curves first originate. The second azeotrope formed between Methanol and Ethyl acetate is also a lower boiling point azeotrope, it forms a saddle because its temperature is intermediate respect the other azeotrope, to Methanol and Ethyl acetate, so the curves get close to this point and then end in stable nodes (Methanol or Ethyl acetate). This can be observer in the data in tables 1 and 2.

The line formed by this 2 azeotropes is a distillation border and causes a very difficult separation to pure components because there are different regions and usually distillation borders cannot be crossed.

Region 1 is formed between the azeotropes, Methyl acetate and Ethyl acetate, and the region 2 by the azeotropes and methanol.

Residue curve for METHY-01/METHA-01/ETHYL-01

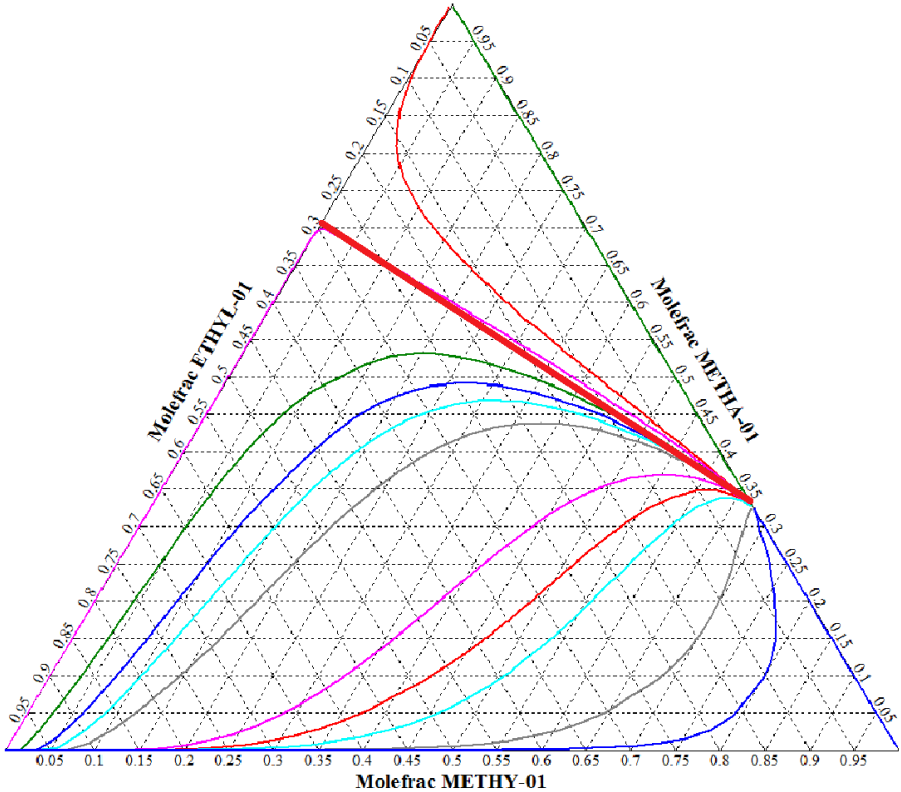


Figure 17 RCM built by ASPEN with distillation border at 1 atm

1 atm	Azeotropes	
	Ethyl acetate-Methanol	Methyl acetate-Methanol
Node	Unstable	Saddle
Ethyl acetate	0,29	0
Methyl acetate	0	0,67
Methanol	0,71	0,33

Table 3 Azeotrope data for E-Ac/M-Ac/Methanol obtained from RCM using ASPEN

Comparing figures 16 and 17 we observe the RCM's are very similar. Residue curves follow the same trends, and the azeotropes concentrations differ by little.

Finally a distillation curve map built with RCM Designer is shown in figure 18, as commented before residue curves and distillation curves are very similar. RCM Designer can be easily adapted to calculate distillation curves (**see appendix 3**), but very few mixtures can be represented correctly.

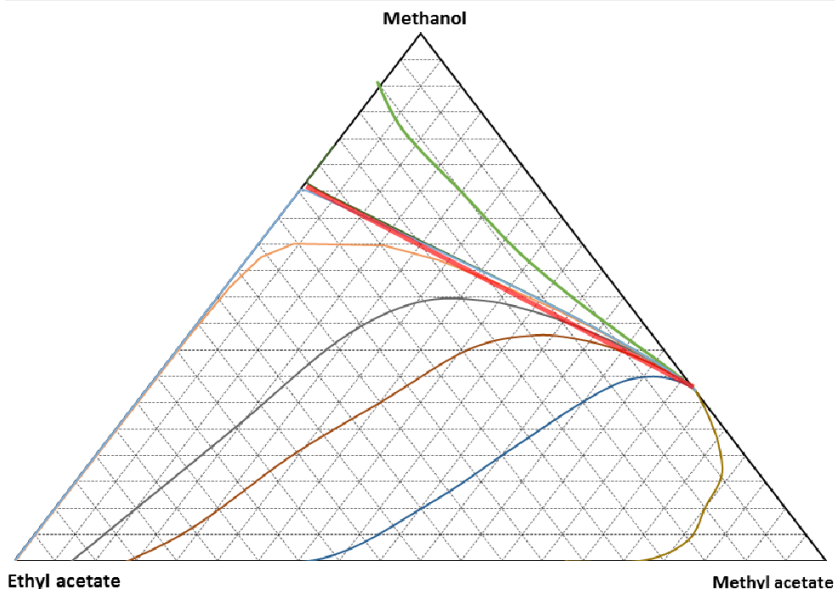


Figure 18 Distillation curve map with distillation border at 1 atm.

1 atm	Azeotropes	
	Ethyl acetate-Methanol	Methyl acetate-Methanol
<b>Boiling T (K)</b>	335,3	327,0
<b>Node</b>	Unstable	Saddle
<b>Ethyl acetate</b>	0,29	0
<b>Methyl acetate</b>	0	0,678
<b>Methanol</b>	0,71	0,322

Table 4 Distillation curve map data for E-Ac/M-Ac/Methanol

The next figures show how pressure affects residue curves.

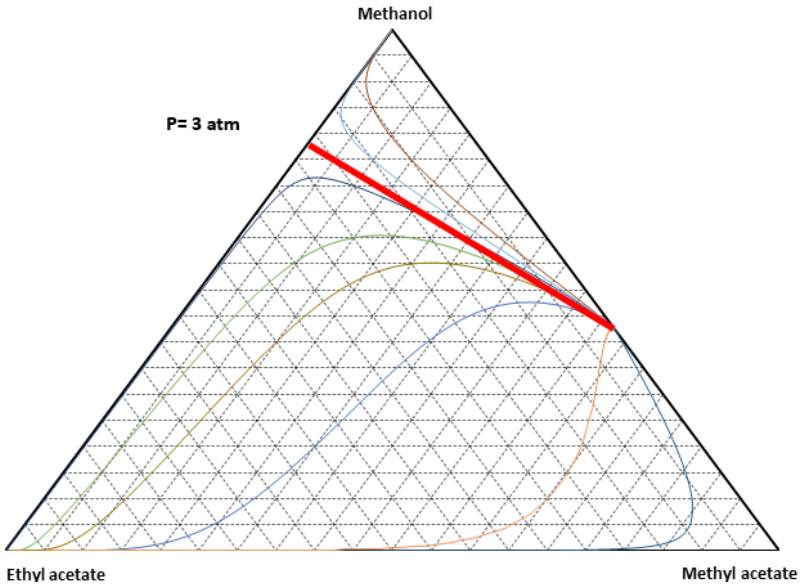


Figure 19 RCM with distillation border and distillation regions at 3 atm

3 atm		Pure components		
	Ethyl acetate	Methyl acetate	Methanol	
Boiling T (K)	388,0	365,8	368,6	

Table 5 Pure components data at 3 atm

3 atm		Azeotropes	
	Ethyl acetate-Methanol	Methyl acetate-Methanol	
Boiling T (K)	366,9	359,7	
Ethyl acetate	0,217	0	
Methyl acetate	0	0,575	
Methanol	0,783	0,425	

Table 6 Azeotrope data at 3 atm

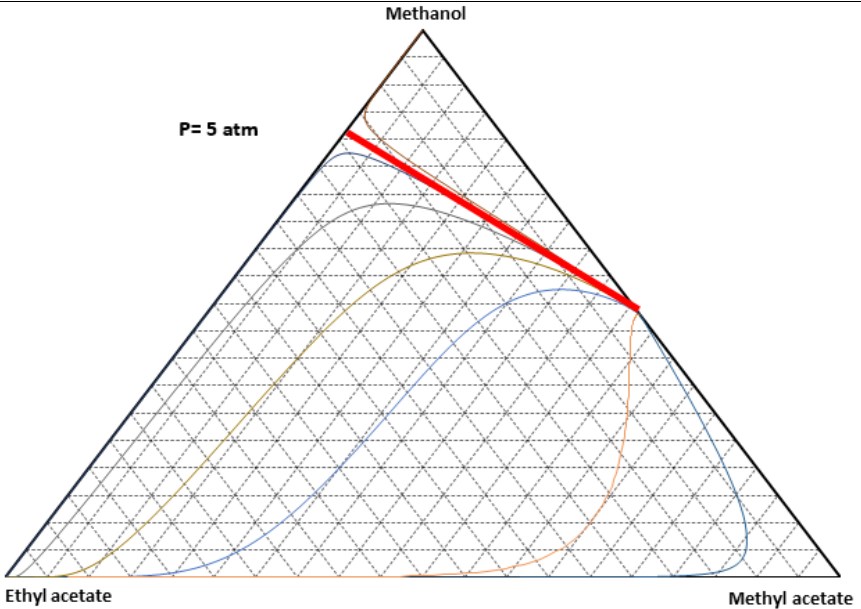


Figure 20 RCM with distillation border and distillation regions at 5 atm

5 atm	Pure components		
	Ethyl acetate	Methyl acetate	Methanol
<b>Boiling T (K)</b>	409,0	385,6	385,3

Table 7 Pure components data at 5 atm

5 atm	Azeotropes	
	Ethyl acetate-methanol	Methyl acetate-Methanol
<b>Boiling T (K)</b>	383,9	304,3
<b>Ethyl acetate</b>	0,181	0
<b>Methyl acetate</b>	0	0,520
<b>Methanol</b>	0,819	0,480

Table 8 Azeotrope data at 5 atm

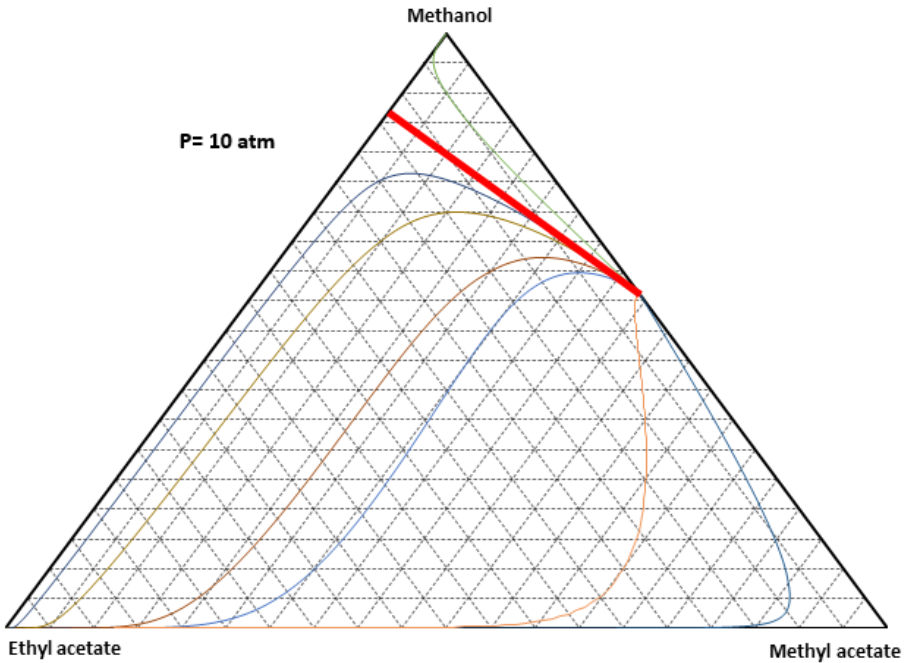


Figure 21 RCM with distillation border and distillation regions at 10 atm

10 atm	Pure components		
	Ethyl acetate	Methyl acetate	Methanol
Boiling T (K)	409,0	385,6	385,3

Table 9 Pure components data at 10

10 atm	Azeotropes	
	Ethyl acetate-Methanol	Methyl acetate-Methanol
Boiling T (K)	409,8	304,3
Ethyl acetate	0,129	0
Methyl acetate	0	0,439
Methanol	0,871	0,561

Table 10 Azeotrope data at 10 atm



As shown in figures 19, 20 and 21 changing the system's pressure modifies the residue curve map, in this case we can observe how the distillation border moves, because with increasing pressures Ethyl acetate-Methanol azeotrope change its composition approximating to the pure methanol node. Observing how pressure affects the system we can affirm that it is possible to brake this azeotrope at very high pressures. So pressure modifies residue curves, azeotrope's compositions and also distillation borders and its curvature, because of this RCM's are so important, they define the ranges where a mixture can be separated with each distillation sequence.

### 6.3. 1<sup>ST</sup> TERNARY MIXTURE: ACETONE / METHANOL / HEXANE

This mixture has been selected because it forms a ternary azeotrope, as well as 3 binary azeotropes. Figure 22 is a map built using RCM Designer.

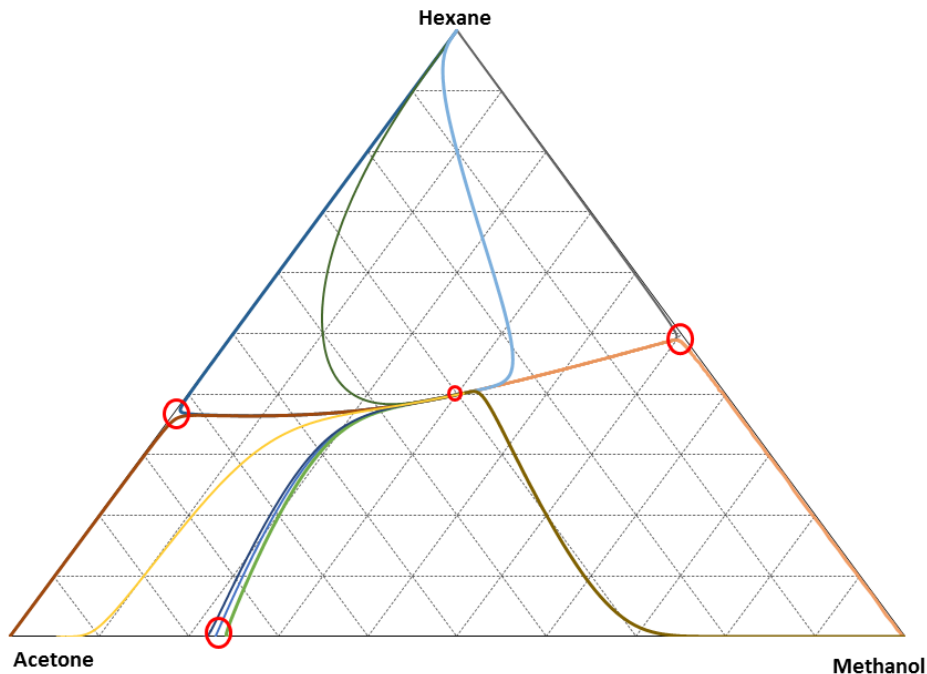


Figure 22 Acetone/Methanol/Hexane RCM at 1 atm

The results obtained results obtained are shown in tables 11 and 12.

1 atm	Pure components		
	Acetone	Methanol	Hexane
Boiling T (K)	329,5	337,7	341,8
Node	Stable	Stable	Stable

Table 11 Acetone/Methanol/Hexane Pure components data

1 atm	Binary azeotropes			Ternary azeotrope
	Acetone Methanol	Methanol Hexane	Acetone Hexane	Acetone- Methanol- Hexane
Boiling T (K)	328,4	322,5	322,0	321,1
Node	Saddle	Saddle	Saddle	Unstable
Acetone	0,770	0	0,635	0,292
Methanol	0,230	0,505	0	0,307
Hexane	0	0,495	0,365	0,401

Table 12 Acetone/Methanol/Hexane azeotropes data

In order to compare this results with experimental data, table 13 shows azeotropes concentrations and temperatures for the same mixture.

Homogeneous system	T (K) Range	Rango $y_1$ ( $y_2$ )	Refer.	Clasif.
Acetone(1)-Methanol(2)- Hexane(3)	320.1	0.3274,0.2814	1621	3.1-2
(1)-(2)	328.25-329.1	0.75-0.816	121	
(1)-(3)	322.75-322.95	0.625-.648	500	
(2)-(3)	322.55-323.75	0.491-0.521	141	

Table 13 Acetone/Methanol/Hexane azeotropes data. References from Gmehling et al. (1994), classification according to Serafimov (1970).

Note: Table adapted from "Cálculo y Pred..." ref. 3

Comparing tables 12 and 13, the results for binary azeotrope's (temperatures and concentrations) from RCM Designer (table 12) are inside the expected ranges (table 13). For the ternary azeotrope result differ ( $\approx 0.03$ ) but are very close.

---

## 7. CONCLUSIONS

Comparing the results obtained with ASPEN we can assert that RCM Designer is consistent, because residue curves show the same trends, forms, the same nodes and also changes in the working pressure affect both programs similarly.

RCM Designer has limitations to predict some ternary azeotropes due to the thermodynamic model used, the program cannot predict azeotropes for some mixtures where alcohols are present (propanol for example).

The program, in most cases is not able to plot distillation curves since the algorithm necessary for it is complicated, nevertheless RCM can be adapted (see appendix 3) to calculate distillation curves but the necessary points to be plotted are insufficient for the majority of mixtures. As a recommendation for future works, the development of an algorithm specific for distillation curves would be necessary.



## 8. REFERENCES AND NOTES

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2. Warren D Seider, Junior D Seader, Daniel R Lewin. *Product & Process Design Principles: Synthesis, Analysis and Evaluation*, 2nd ed.; John Wiley & Sons: New York, 1999, pp 259-282.
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4. MANDAGARAN, Beatriz A y CAMPANELLA, Enrique A. Cálculo y Predicción de Azeótropos Multicomponentes con Modelos de Coeficientes de Actividad. *Inf. tecnol.* [Online]. **2008**, vol.19, n.5, pp. 73-84. ISSN 0718-0764. <http://dx.doi.org/10.4067/S0718-07642008000500009> (accessed Nov 10, 2014).



# APPENDICES

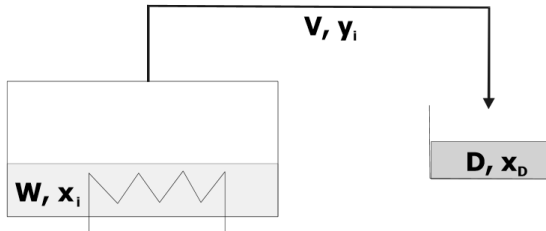




## APPENDIX 1: RAYLEIGH EQUATION

### Obtaining Rayleigh equation

Using a simple sketch for a simple distillation, Rayleigh equation will be deduced.



Where  $W$  is the number of moles in the boiler,  $x_i$  is the residue molar fraction,  $V$  is the vapour molar flow and  $y_i$  the vapour molar fraction.  $D$  is the number of moles in the distillate and  $x_D$  its composition.

$$\text{Total mass balance: } \frac{dW}{dt} = -V$$

$$\text{Mass balance for each component: } \frac{d(W \cdot x_i)}{dt} = -V \cdot y_i$$

Using balance equations and the product rule for derivative products:

$$W \frac{dx_i}{dt} + x_i \frac{dW}{dt} = y_i \frac{dW}{dt}$$

Rayleigh equation is obtained by operating previous equation:

$$\frac{dx_i}{dt} = (y_i - x_i) \frac{dW}{W dt}$$

$$\text{We define variable } \varepsilon \text{ is defined as: } \frac{d\varepsilon}{dt} = -\frac{1}{W} \frac{dW}{dt}$$

Integrating variable  $\varepsilon$  for initial conditions ( $t=0$ ):  $\varepsilon=0, W=W_0$

$$\varepsilon(t) = \ln \frac{W_0}{W(t)}$$

Since  $W(t)$  decreases monotonically with time,  $\varepsilon$  will increase monotonically, so  $\varepsilon$  can be considered a distorted dimensionless time.

Introducing variable  $\varepsilon$  in Rayleigh equation and operating, we obtain the extended Rayleigh equation used in the program.

$$\frac{dx_i}{d\varepsilon} = (y_i - x_i)$$

## APPENDIX 2: NEWTON-RAPHSON METHOD

Newton's method has been adapted to an algorithm in order to find the next supposed temperature so the program will converge faster.

$$\text{Newton-Raphson method: } x_{i+1} = x_i - \frac{f(x_i)}{df(x_i)/dx}$$

In order to apply newton's method we introduce a temperature increment and two errors, following the next sequence.

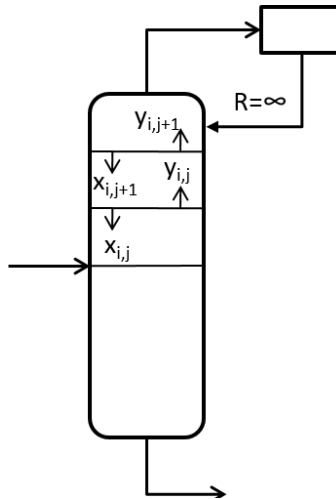
1. Suppose an initial temperature  $T_1=T_0$
2. Calculation of partial pressures
3. Define  $\text{Error1} = \sum(p_i) - P$
4. If Error1 is sufficiently low we have found the result, else we continue the sequence
5. Define  $T_2 = T_1 + \Delta T$
6. Calculation of Error2 for  $T_2$  as in steps 2 and 3
7. Calculation of error's derived:  $derror = (\text{Error2} - \text{Error1})/\Delta T$
8. Next supposed Temperature as  $T = T_1 - \text{Error1}/derror$
9. All previous steps are repeated using T (from step 8) as the new initial temperature

This algorithm is inserted in the program and repeated in a loop until an acceptable error is obtained. Also is interesting to know that the first initial temperature has been calculated the same way considering the mixture's behaviour as ideal



## APPENDIX 3: RCM DESIGNER AND DISTILLATION CURVES

Distillation curves represent the composition profile for a rectification column working at total reflux.



When it is working at total reflux, liquid and vapour mass flows along the column are equal ( $L=V$ ), and as it can be appreciate in the figure, a condition must be fulfilled in every interstage, giving as a result the equation 12.

$$x_{i,j+1} = y_{i,j}$$

In order to use this equation in the program a starting concentration and pressure must be selected. As commented before distillation and residue curves are similar and coincident in a few points. In fact, if extended Rayleigh equation (equation 1) is written for a dimensionless time equal minus 1 ( $d\varepsilon = -1$ ) we obtain the previous equation for distillation curves, where each point found is a discrete one corresponding to a stage in the column.

$$\frac{dx_i}{d\varepsilon} \approx \frac{\Delta x_i}{\Delta \varepsilon} = \frac{x_{i,j+1} - x_{i,j}}{\Delta \varepsilon} = x_{i,j} - y_{i,j} \xrightarrow{\varepsilon=-1} x_{i,j+1} = y_{i,j}$$



