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Thermodynamic topological analysis at infinite and finite conditions for reactive mixtures of acetates

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Abstract

When designing conventional and non-conventional distillation processes shortcut methods for predicting feasible separations are widely used. The thermodynamic topological analysis based on phase equilibrium and distillation maps study is a good approach allowing the knowledge of basic tower configuration at extreme conditions (infinite efficiency: total reflux and infinite number of stages). At these conditions usually the prediction is qualitatively approximate to that at total reflux. However some times the prediction strong differs from that, found during rigorous simulation. Additionally because of the infinite efficiency these regimes are not the optimal from the point of view of energy consumption. Making the thermodynamic topological analysis at finite reflux gives a closed region into the concentration simplex where feasible separations take place with a limit of minimal reflux number (minimal energy consumption).

Three component nonideal mixtures from acetates with different arranges of distillation maps are studied and the distillation configuration as well as parameters for rigorous simulation are presented. The mathematical method for solving the differential equations systems involved in phase equilibrium models is innovative and characterized by accuracy and low time calculations. All this information is used and explained as a way for the analysis of reactive distillation processes at finite reflux.

Keywords: conceptual design and simulation, thermodynamic topological analysis, reactive distillation

1. Introduction

The reactive mass-exchange process is a process where, the chemical reaction and separation of the reaction mixture occur *simultaneously and combined* (in one apparatus) *with predominant removing of target reaction products.* As was shown by Pisarenko and coworkers today the design of reactive distillation processes consists of several stages. These stages could be resumed in three basic blocks: shortcut methods, rigorous methods and experiments. However this design strategy as many more showed in the literature does not consider the technological optimization looking for

improvements in the final synthesized process. Shortcut methods based on thermodynamic-topological analysis are very helpful to minimize simulation and laboratory experiments and also allow understanding further possibilities in higher conversion and selectivity achievement. In this work this kind of modification to these shortcut strategies are explained and complemented with new developments in analysis of finite and infinite efficiency RD columns. For the reactive distillation relatively few systematic methods or approaches exists (Pisarenko, et al, 2001), however no all methods maximizes the synergy effect between reaction and the separation. The short-cut methods, based on the study of the topology of the system (topological thermodynamic), are very used to obtain a first approach, allowing the reduction of simulation and experimentation time. In addition, the prediction of the limiting steady states (Static analysis at infinite reflux), characterized by the maximum conversion and selectivity is included in this stage. This work developed a methodology for better understanding of interactions between phase and chemical equilibrium at finite conditions of operation, determining the real separation possibilities for the reactive distillation process. Then one could have a range of ideas in the conceptual design of the process, minimum demanded energy and catalyst requirements. From this information the rigorous simulation can be made on the basis of theoretical validated parameters.

1. Thermodynamic Topological Analysis (T.T.A):

1.1 Residue Curve Map

The open evaporation, also known like simple distillation or Rayleigh distillation, is a batch distillation process with an equilibrium stage where the formed steam is continuously removed, thus, at any time the removed steam is in equilibrium with the residual liquid. The trajectory of liquid composition of a simple distillation is known in literature like residue curve. Therefore, when we make a mass balance in a process of open distillation, the following equation describes the residue curves in the concentracional simplex, thus:

$$\frac{dx}{d\tau} = x_i - y_i \tag{1.1}$$

$$\frac{dx}{d\tau} = x_i\left(1 - K_i\right) \qquad \text{For } i = 1,2,...C-1 \tag{1.1.1}$$

Where x_i, y_i are the molar fractions of "i" compound in the liquid an vapor phase respectively, C is the number of compounds that the feed represent ; τ can understand like a coordinate function of the time, on the level of liquid in the container of open evaporation from a initial time $t = t_o$, when start the evaporation, to some "t" time . The mixture will contain C species with n_k number of mol $(k = 1,...,c)$, so the mixture composition will be defined by a $c-1$ molar fraction vector $X = [x_1, x_2, ...x_{C-1}]$. The trajectories described by the solution of equation (1)

are denominated residue curves, and are defined by the initial condition that to a given composition of liquid, the vector that lies the equilibrium composition is tangent to residue curve, and its named "lead line" $(X' = AX)$, (V.N Kiva, E.K Hilmen et al., 2003) , consequently in order to solve the system of differentials equations is required a relation between y_i and x_i , thus in isobaric conditions, we considered that : $Y = F(P,T,X)$, then $Y = E(X)$, where $E(X)$ represent the function that describes the thermodynamic model depending on the degree of regularity or irregularity of the mixture, then:

$$E(X) = \frac{P_i^{sat}(T)x_i\gamma_i(T,P,X)}{\phi_i^v(T,P,Y)P} \quad \acute{o} \quad E(X) = \frac{\phi_i^{lL}(T,P,X)}{\phi_i^V(T,P,Y)}x_i \qquad (1.1.2)$$

The integration of the differentials equations system, is made using a numerical method, like the fourth order Runge-Kutta (J.H Mathews, K.D Fink, 2000), allowing obtain the residue curve map. (Figure 1.1)
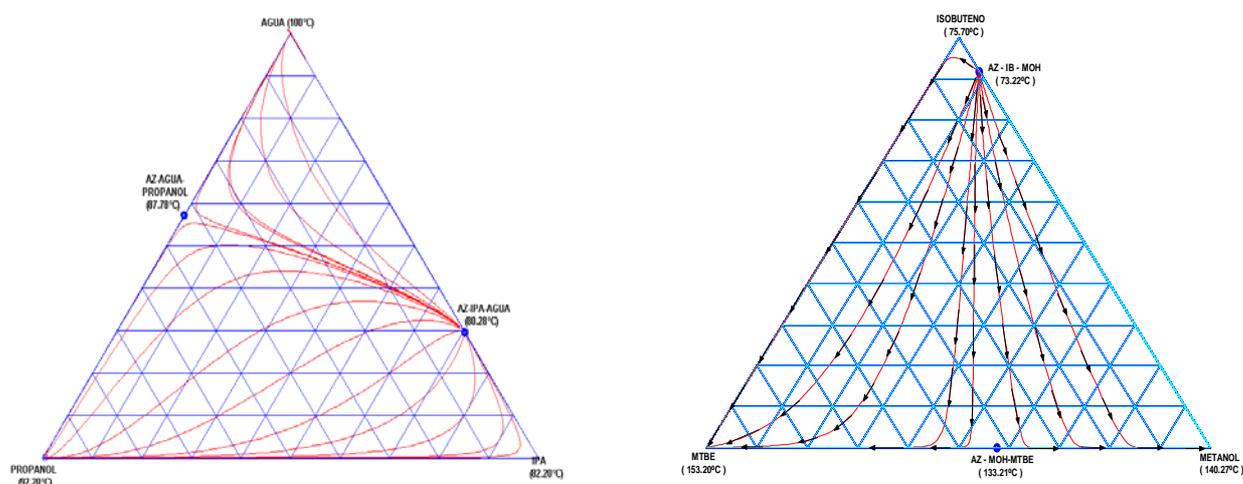
Figure 1.1) Residue curves of the **a)** Isopropanol-propanol-Water **b)** MTBE-Isobutene-Methanol systems

1.2. Computing all azeotropes in mixture and its pressure bifurcation.

The residue curve maps are an important tool in the conceptual design of distillation process, because they require little initial entrance information and provide solutions to the separation scheme; in addition they reduce the simulation and experimentation time. Predict all the azeotropes of the system (composition and temperature) and characterize their topology, are the first and more important step to generate the structure of the residue curves. If we considered a C component mixture, compute the

azeotropes can be made implemented the follow objective function (Z.T. Fidkowski, et al, 1993):

$$F(X) = Y - X \qquad (1.2.1)$$

Where X and Y are all the liquid and vapor compositions in thermodynamic equilibrium, there are $C-1$ molar fraction in each phase:

$$y_i - x_i = 0 \qquad \text{For} \qquad i = 1,2,..C-1 \qquad (1.2.2)$$

From the equilibrium relation ship:

$$y_i = \frac{\gamma_i P_i^{sat}}{\phi_i^v P} x_i \qquad \text{For} \qquad i = 1,2,...C \qquad (1.2.3)$$

Subject to the following restrictions:

$$\sum_{i=1}^{C} x_i = 1$$

$$\qquad (1.2.4)$$

$$\sum_{i=1} y_i = 1$$

Donde:

$$x_i \geq 0 \qquad \text{For} \qquad i = 1,2,...C$$

According to below exposed, a system of $2C+1$ equations with equal unknowns number is obtained. This system cannot be solved by conventional root finders methods since the thermodynamic variables that are implicit in these functions causes that the system is highly nonlinear. It is known that formulations like Newton Method $(J\Delta X = -F(X))$, will have a good performance (it makes a good linear approach) if the vector of initial guesses, is "near" to solution; outside this dominion the method can converge very slowly, or to diverge. The techniques more recently implemented and recommended for the solution of this kind of problems are the homotopy methods or continuation methods (A.Dold and B.Eckman, 1981), (D.J Vickery and R. Taylor, 1986), (E.L. Allgower, K.George, 1990), (K.S.Gritton, et al, 2001). The computing of system azeotropes, we implemented a process of "deformation" of equilibrium surface beginning from a point described by Raoult's law o using a homotopy thermodynamic (D.J Vickery and R. Taylor, 1986), which operates from the thermodynamic properties of the system.

We implemented an algorithm based in deforming the functions which represent the phases equilibrium by implementation of linear homotopy, where the variables were rewritten in terms of them arc length; in addition we applied a predictor-corrector method, implementing the Euler's Method to approximate, and the Haselgrove's method like a step corrector and return to solution curve (E.L. Allgower, K.George, 1990).This algorithm was tested with several azetropic systems, obtaining

satisfactory results, which show in table 1, for the Acid acetic –Butanol-Butyl acetate-Water system.

An extension and logical application of previously mentioned procedure, consist of predicting the pressure to which appear new azeotropes or find the pressure to which disappear the azeotropes of the system, this prediction is known like computing **the bifurcation pressure** (N.Aslam, Aydin K. Sunol, 2003), and is very important for the modeling the possibilities of technological separation schemes.

Mixture	Phase	UNIFAC-DORTMUND HAYDEN-O'CONNELL MODELL	
		X^{az} (molar)	T^{az} (K/C)
Acetate Water	Heterogeneus	0.2847 0.7153	364.01 90.86
Alcohol Water	Heterogeneus	0.2572 0.7428	365.53 92.38
Alcohol Acetate	Homogeneus	0.8279 0.1721	390.15 117
Alcohol Acetate water	Heterogeneus	0.1043 0.1980 0.6976	363.53 90.38
Alcohol Acid Acetate	Homogeneus	0.3638 0.3705 0.2657	393.88 120.73
Alcohol Acid	Homogeneus	0.6258 0.3742	395.52 122.37

1.3 Characterization of fixed points: (Evaluation of eigenvalues)

Now the problem consists in how evaluating the behavior of a specific mixture in the simplex, since the equation (1.1) describes clearly a nonlinear system of type $X' = F(X)$, and what behavior will have in the vicinity of then singular points, that is , pure compounds and azeotropes. In order to make a transformation of nonlinear system to linear one is due to mention of Haltmann - Grossman theorem, (Parker and Chua, 1989) which considers that: If one has a nonlinear system of the type $X' = F(X)$ and a equilibrium or fixed point X_0, that is , such that $F(X_0) = 0$, so:

$$A = DF(X_0) = \begin{pmatrix} \left(\dfrac{\partial f_1}{\partial x_1}\right) \cdots \left(\dfrac{\partial f_1}{\partial x_n}\right) \\ \cdot \qquad \cdot \\ \cdot \qquad \cdot \\ \left(\dfrac{\partial f_n}{\partial x_1}\right) \cdots \left(\dfrac{\partial f_n}{\partial x_n}\right) \end{pmatrix}(X_0) \qquad (1.3.1)$$

If one has the $X' = AX$ system around the fixed point X_0. If all eigenvalues of A have real part $\neq 0$ the stability of both systems around X_0 is the same. (If those have null part, the stability of both systems could be different). This theorem is a consequence of first Taylor's theorem for a function linearization around a fixed or equilibrium point, thus:

$$F\left(\bar{X}\right) = \begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} \end{bmatrix} \begin{bmatrix} \bar{x}_1 \\ \bar{x}_2 \end{bmatrix} \tag{1.3.2}$$

To solve the derivates, replacing the respective function that describes the equilibrium phase's as:

$$\frac{\partial f_1}{\partial x_1} = \frac{\partial(x_1 - y_1)}{\partial x_1} = \frac{\partial(x_1(1 - K_1))}{\partial x_1} = (1 - K_1) - x_1\frac{\partial K_1}{\partial x_1} \tag{1.3.3}$$

Evaluating for a three components system:

$$F\left(\bar{X}\right) = \begin{bmatrix} -x_1\dfrac{\partial K_1}{\partial x_1} + (1 - K_1) & -x\dfrac{\partial K_1}{\partial x_2} \\ -x_2\dfrac{\partial K_2}{\partial x_1} & -x_2\dfrac{\partial K_2}{\partial x_2} + (1 - K_2) \end{bmatrix} \begin{bmatrix} \bar{x}_1 \\ \bar{x}_2 \end{bmatrix} \tag{1.3.4}$$

Therefore, the eigenvalues in the characteristic matrix in (1.3.4) will determine the behavior of the trajectories (residue curve) in the vicinity of these singular or fixed points, thus is known:
$$\lambda V = AV \tag{1.3.5}$$

If $\lambda\, and\, V$ satisfy this condition, for $V \neq 0$, so V is denominated eigenvector of "A" with eigenvalue λ. The last equation can be reorganized in the next form:

$$0 = AV - \lambda V$$
$$0 = (A - \lambda I)V \tag{1.3.6}$$

This equation will have a solution $\left(V \neq 0\right)$ if only:
$\det(A - \lambda I) = 0$, thus, the "A" eigenvalues λ are the roots of the equation:

$$0 = \det(A - \lambda I) = \det \begin{bmatrix} a_{11} - \lambda & a_{12} & \dots\dots\dots & a_{1n} \\ a_{21} & a_{22} - \lambda & \dots\dots & a_{2n} \\ a_{n1} & a_{n2} & & a_{nn} - \lambda \end{bmatrix} \qquad (1.3.7)$$

And the "A" eigenvalues are the solutions nonequal to zero of the equation (1.3.6); If we applied the last concepts and characterize the exposed systems we obtain the following results:

Compound	Composition	Eigenvalues	Characterization
IPA	0.704	0,962	
Water	0.296	0,929	**Unstable node**

Compound	Composition	Eigenvalues	Characterization
N-Propanol	0.429	1.1478	
Water	0.571	-0.7916	**Saddle**

Compound	Composition	Eigenvalues	Characterization
N-Propanol	0,999	-2.0107	
Water	1,00E-06	-0.7575	**Stable node**
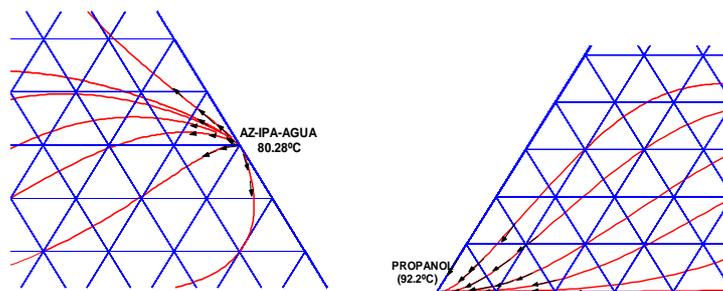
Figure 1.2) a) IPA-Water like an unstable node, **b)** pure propanol like a stable node.
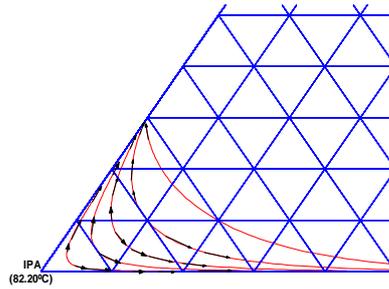
Figura 1.3) Pure Isopropanol like a sadle

1.4) Attraction regions and thermodynamic separatrix (Permissible regions of separation**)**

Attraction regions is a proper concept of non linear dynamic system, it can be extrapoled to previously exposed concepts. If L is an equilibrium point, so W_L^S, is a set of points, such that the flux $E(x)$ approximates to L when $\tau \to \infty$, (stable variety of L) , and W_L^μ is a set of points, such that the flux $E(x)$ approximates to L when $\tau \to \infty$,(unstable variety of L) . W_L^S , can be understood like **the border between attraction regions generated by two attractors.** This stables and unstable varieties are invariants by the flux $E(x)$, thus, for example around of a saddle fixed point, the stables and unstable varieties can be distinguished like tangents to stables varieties W_L^S or W_L^U . Attractors are the stables nodes these correspond to pure compounds and singular points, with the high boiling temperature.

If in a system exist several attractors, each one will have their own attraction region and will be separated for a stable nonlinear variety, denominated **thermodynamic separatrix**, which divides the separation region in permissible separation subregions, which are attraction regions in the separation by distillation. An important application is to draw up this stable variety, and know the possible regions where we can make the conventional separation analysis, since we have the imposed thermodynamics limitations.

1.4.1 Locating a point on W_L^U : Computing the thermodynamic separatix

Near the equilibrium point, $W_L^U \left(X_{eq} \right)$ is given, to first order, by unstable eigenvector uV , therefore, choose a point close to $\left(X_{eq} \right)$ that lies   on uV . More specifically, for some small $\in > 0$, choose the point:

$$X_s^0 = X_{eq} + \in u\vec{V} \qquad (1.4.1)$$

This first point will be the initial condition to integrating $E(x)$, thus:

$$p^{k+1} = X_s^0 + \Delta\tau\left(X_s^0 - Y\left(X_s^0\right)\right)$$

$$X_{W^U}^{K+1} = X_s^0 + \frac{\Delta\tau}{2}\left[\left(X_s^0 - Y\left(X_s^0\right)\right) + \left(X_s^0 - Y\left(p^{k+1}\right)\right)\right]$$

(1.4.2)

Integrating from this point in **forward** to obtain the separatrix.

Care should be taken when choosing $\in$. If $\in$ is too large X_s^0 might not lie close enough to $W_L^U\left(X_{eq}\right)$ in which case the trajectory through X_s^0 is not a good approximation to, $W_L^U\left(X_{eq}\right)$. If $\in$ is too small the trajectory may spend a large amount of time near $\left(X_{eq}\right)$ causing the integration error to accumulate with little motion along the trajectory. We implemented fourth Runge-Kutta mmethod, with optimal selection of $\in$, obtaining the following results :
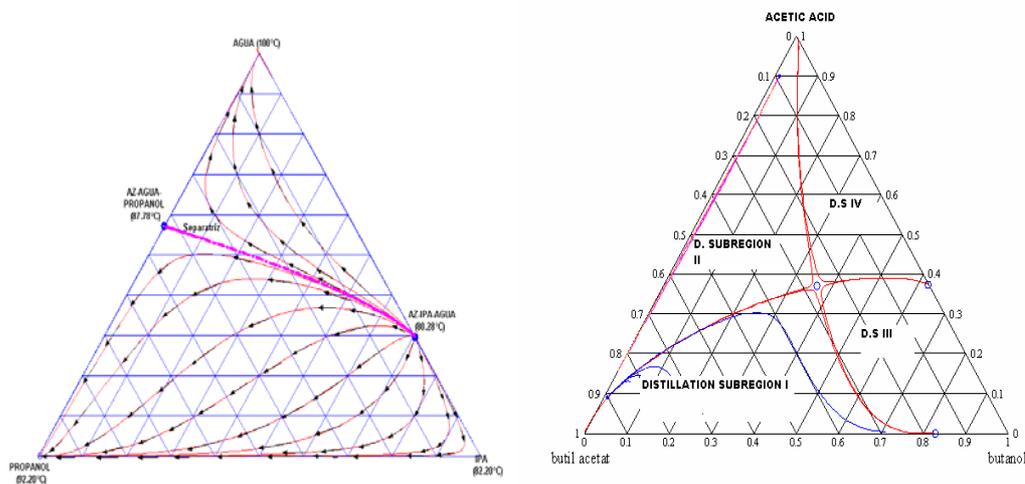
Figura (1.4) thermodynamic separatix of **(a)** Water – Propanol –IPA **(b)** Acetic Acid- Butyl Acetate- Butanol

The separatrix position in the simples could be displaced by changing the pressure, and we can observe more separation possibilities. The implementation of **Vresky's law** , permit know how the azetrope change with the pressure, later we computing the bifurcation pressure, how indicate the section (1.2).

2. Continuous Distillation and T.T.A to finite conditions operation

The residue curve map is usually divided into separate regions by simple distillation regions boundaries that characterize the simple distillation (open evaporation), which act as impassable barriers to the residue curves. How we mentioned before, the distillation regions are separated by thermodynamic separatrices. Each separatrix always begins and ends at either a pure component or an azeotrope. During an isobaric operation in a simple distillation the temperature of the liquid must increase

along a residue curve. In a continuous distillation have an increase in temperature from plate to plate going down the column, thus both have the same tendencies.

In continuous azeotropic distillation is would be desirable to have the same understanding, that opens evaporation on the characterization of the mixture relevant to distillation (D.B. Vandongen, 1985), generating the next questions:

1. Do simple distillation region boundaries act as barriers across which the continuous distillation profiles cannot pass?

2. Is it possible to use simple distillation diagrams for the purpose of devising sequences of azeotropic columns capable of separating the mixture into its pure components?

In the next sentences we will discuss the basis for the answers to these questions and we will enhance the vision of residues curves to analyze the possibilities of continuous distillation.

2.1 Analysis of a single Distillation Column:

The figure (2.1) show a simple distillation column with only one feed steam, which is governed under the next suppositions:

- Constant molar flow rates of liquid in both sections (stripping and rectifying) of the column
- Constant molar flow rates of vapour in both sections (stripping and rectifying) of the column
- Saturated liquid feed
- 100 % eficient
- The enthalpy of mixing is zero

This column model cannot be very accuracy, but supply a good qualitative approximation in the behaviour of the mixture, and observing the attractiveness between residue curve map and composition profiles in the continuous distillation.
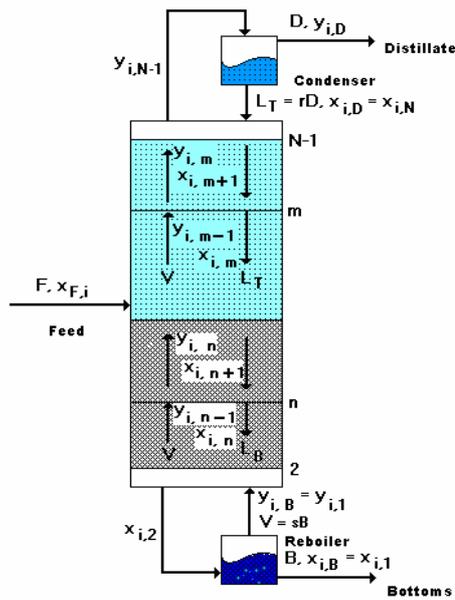
F**igure (2.1)** Schematic representation of a distillation column

If we make a material balance around an arbitrary plate **n** in the stripping section , a material balance around an arbitrary plate **m** in the rectifying section , where the distillate and bottoms compositionn ,and the same form the reflux and reboiler ratios are in relation by a global material balance, where each theoric tray is divide in a differential number of trays along the interval $[n \rightarrow n+1]$, obtaining a model that describes the composition profiles in both column sections (Sourrisseau and Doherty, 1980)

Rectifying Section:

$$\frac{dx_i'}{dh'} = x_i' - \left(\frac{r+1}{r}\right)y_i + \left(\frac{1}{r}\right)y_{iD}$$

$$x_i'\left(h' = 1\right) = x_{iD}$$

Stripping Section:

$$\frac{dx_i}{dh} = \left(\frac{s}{s+1}\right)y_i - x_i + \left(\frac{1}{s+1}\right)x_{iB}$$

$$x_i(h = 1) = x_{iB}$$

Restrictions and Conditions:

$$y_{iD} = \left(\frac{s+r+1}{s}\right)x_{Fi} - \left(\frac{r+1}{s}\right)x_{iB}$$

$$x_i\left(h = h_f\right) = x_i'\left(h' = h_f'\right)$$

$$1 < h_f, h_f' < \infty$$

$$0 < r < \infty$$

$$0 < s < \infty$$

How indicate the continuous distillation literature (Doherty and Perkins, 1979), the profiles that appear in both column sections, exhibit a similar form of residue curves, depending of feed localization each distillation profile will be contained in a simple distillation region Doherty and Van Dongen, 1985). For a ternary mixture case, we have to specify seven variables: P, X_F, X_B, r, s and start the integration of the model. The $h_f, h_f^/$ values are obtained after integration, the necessary condition, which occurs the distillation, is that the profiles must be intercepting, thus, $x_i(h = h_f) = x_i(h`=h_f)$, Figure (2.2) show the obtained profiles , for Ethanol-Methanol-Water system, where $X_F = \begin{bmatrix} 1/3 & 1/3 & 1/3 \end{bmatrix}$ and $X_B = \begin{bmatrix} 0.05 & 0.88 & 0.07 \end{bmatrix}$ bottoms composition. Therefore the reflux ratio will generate drastic changes in composition profiles, because a redistribution of concentration fields may be occur. All combination of the $(X_F), (X_B)$, reflux and rebioler ratios cannot be possible , These must be stay in the same distillation region, and satisfying the mass balance.
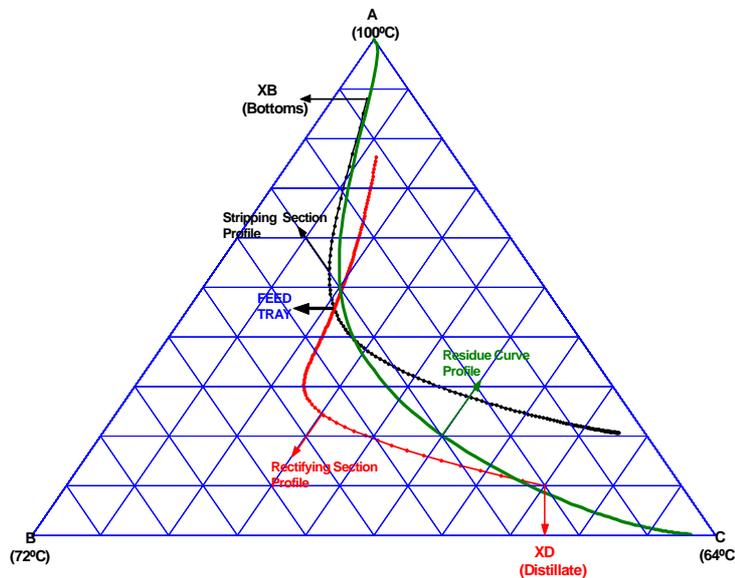
Figure **(2.2)** composition profile in both column section at finite reflux for methanol (B)-ethanol(C)-water (A) mixture.

If we examine the behavior of the compositions profiles for infinitely large reflux and reboil ratios, we can see that:

$$x_{i,m+1} = y_{i,m}$$
$$x_{i,n+1} = y_{i,n}$$
$i = 1,....c$

Besides,

$$\underline{Lim\,r_{\infty}}\left(\frac{dx_i}{dh'} = x_i - \left(\frac{r+1}{r}\right)y_i + \left(\frac{1}{r}\right)y_{iD}\right) \qquad = \frac{dx_i}{dh} = x_i - y_i \qquad (2.2)$$

The last equations coincide with residue curve expression near total reflux and reboil.

3) Pinch Points and columns to minimum reflux

Any excess in the reflux ratio can increase the energy demand in the distillation process, also the column diameter and heat interchange areas, being the key point to determine the optimal heat demand on the column. Minimum reflux is the least value at which can occur the separation by distillation, because is necessary a infinite number of stages to presence an infinitesimal change in the composition of the mixture, it is called "pinch points zone".

3.1) Tangent pinch points and computing minimum reflux.

When we implement de differential model of section (2.1) at some operations parameter to determine the composition profile, it is common find a trajectory that needs an infinite number of stage to vary the liquid composition, this profile is near to pinch point. If the reflux ratio is a little incremented, the profile changes drastically.
Is consequent to think, that a pinch point is a **bifurcation point,** and its jacobian matrix is singular, thus $\det(J) = 0$, and it is the initial criteria for the next analysis:

Under pinch conditions the equation that describes the rectifying section profiles in the section (2.1) model can be expressed how:
$$\frac{dx_i}{dh} = 0$$
If we linealized this function by Taylor's theorem, we obtain

$$\frac{dx_i}{dh} = x_i - \left(\frac{r+1}{r}\right)y_i + \left(\frac{1}{r}\right)y_{Di} = f(x_i, y_i) \quad \text{For } i = 1,2,....C\text{-}1 \qquad (3.1.1)$$

If

$$\alpha_{ij} = \frac{\partial\left(x_i - \left(\frac{r+1}{r}\right)y_i + \frac{1}{r}y_{Di}\right)}{\partial x_j} \qquad (3.1.2)$$

We have that:
$$\frac{dx_i}{dh} = \sum_{j=1}^{C-1}\alpha_{ij}x_j \qquad (3.1.3)$$

If we extend the before concepts, to a ternary mixture we obtain:

$$\frac{dx_1}{dh} = \left[1 - \left(\frac{r+1}{r}\right)\frac{\partial y_1}{\partial x_1}\right]x_1 + \left[\left(-\frac{r+1}{r}\right)\frac{\partial y_1}{\partial x_2}\right]x_2$$

$$\frac{dx_2}{dh} = \left[-\left(\frac{r+1}{r}\right)\frac{\partial y_2}{\partial x_1}\right]x_1 + \left[1 - \frac{\partial y_2}{\partial x_2}\left(\frac{r+1}{r}\right)\right]x_2$$

(3.1.4)

And this is a $X^{/} = AX$ system, thus:

$$J = \begin{bmatrix} 1 - \left(\frac{\partial y_1}{\partial x_1}\right)\left(\frac{r+1}{r}\right) & -\frac{\partial y_1}{\partial x_2}\left(\frac{r+1}{r}\right) \\ -\left(\frac{\partial y_1}{\partial x_1}\right)\left(\frac{r+1}{r}\right) & 1 - \left(\frac{\partial y_2}{\partial x_2}\right)\left(\frac{r+1}{r}\right) \end{bmatrix}$$

(3.1.5)

Or in equivalent form:

$$\det J = \det\left(I - \frac{r+1}{r}Y\right) = 0$$

(3.1.6)

Where:

$$Y = \left[\frac{\partial y_i}{\partial x_j}\right]_{P,X_i}$$

The minimum reflux calculation generates a system of C unknowns $(r, x_{ei}, i = 1,..C-1)$ and C equations, so:

$$\det J = 0$$

$$x_i - \frac{r+1}{r}y_i + \frac{1}{r}y_{Di} = 0 \quad i = 1,....C-1$$

(3.1.7)

Where x_i will be the pinch composition and r will be the minimum reflux.

We implemented an algorithm based in the Broyden –Householder Method (Holland, 1981) to resolve (3.1.7) equation system.

4) Determination of possible operation zones

When the minimum reflux ratio is computing, for some operation conditions, it proceed to increase gradually this reflux ratio to values near to infinte, thus

$r \to \infty$ ó $s \to \infty$, in such case a residue curve is obtained, and represent the limit value that the distillation could be take. The region delimited by this set of trajectories will determine the zone where the separation cans occur, because it is enclosed by the zones of maximum and minimum possible work, and in the same sense for the reboils ratios, this region is called "operation leaf" (Dennis Y.C. Thong et al,1998)

4.1. Construction of operation leaf:

4.1.1 Rectifying Section:

Given the desire bottoms composition , it is specify some reflux ratio ,such $r > r_{min}$, and it integrate the equations (2.1), subject to their restrictions, until $\left| x_i^{j+1} - x_i^j \right| \approx 0$, in this moment it obtain a pinch composition. The locus of this points is called "pinch point lines" (O.M. Whanschafft et al, 1992) . j represents some rectifying tray.

4.1.2 Stripping Section:

Given the desire distillate composition , it is specify some reboil ratio ,such $s > s_{min}$, and it integrate the equations (2.1), subject to their restrictions, until $\left| x_i^{k+1} - x_i^k \right| \approx 0$, in this moment it obtain a pinch composition. The locus of this points is called "pinch point lines" for the stripping section (O.M. Whanschafft et al, 1992) . k represents some stripping tray.

4.1.3 Tray composition line

This represents the locus of obtained composition for *the same tray,* the generated trajectory
by the joint of his point is called "Tray composition line". The intersection of a couple of these lines (stripping and rectifying), represent a possible separation and a possible column configuration to specific operation conditions and specifications.

Figure (4.1) show the development of before concepts for Acetic acid –isopropanol-isopropyl acetate system. And figure (4.2) for MTBE-isobutene-methanol system.
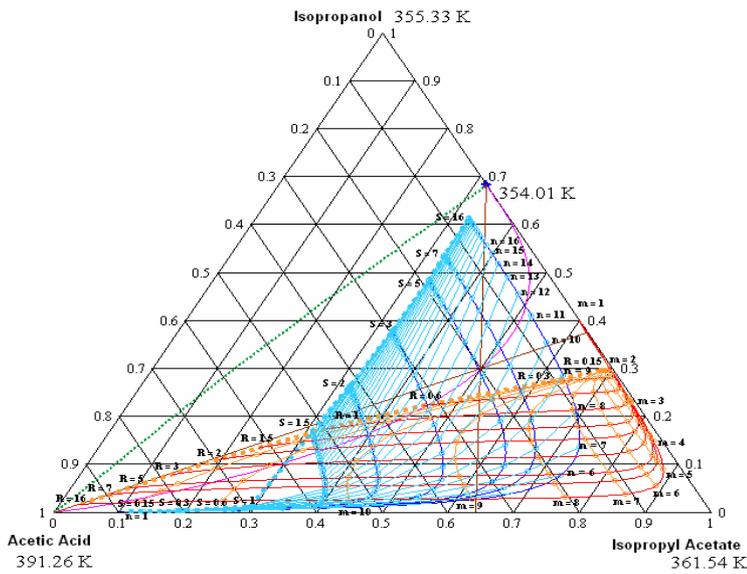
Figure (4.1) Analysis of separation possibilities to finite operation conditions for IP acetate
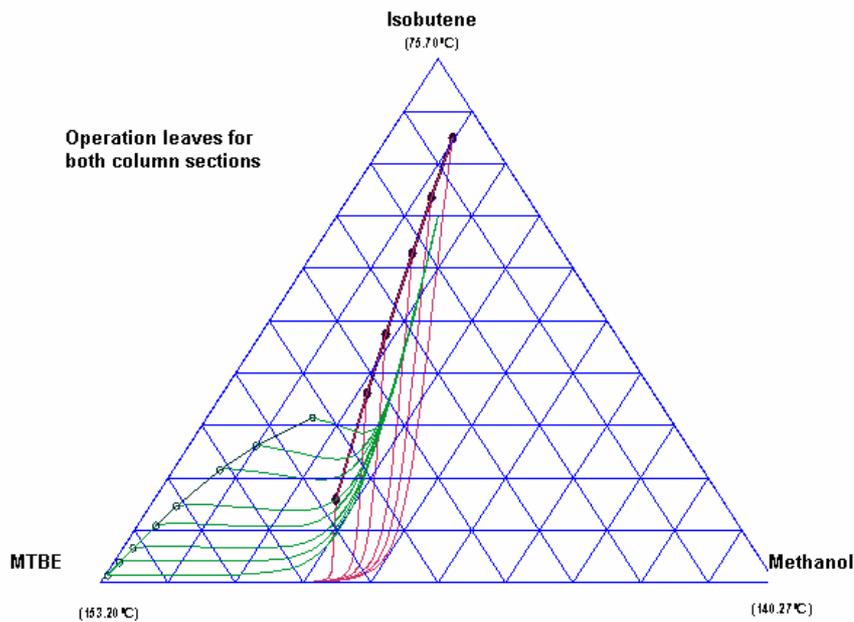

Figure (4.2) Operation Leaf for MTBE-Isobutene-Methanol

5) Reactive mixtures. Simultaneous chemical and physical equilibrium for reacting systems

For a system of one phase or multiple phases can be in equilibrium G (free energy function) must be in a minimum (global) in addition to fulfill the material balance restrictions to thermodynamic established conditions $(T \, y \, P \, fixes)$, therefore:

$$dG_{T,P} = 0 \qquad (5.1)$$

It is , a necessary condition , but no sufficient condition. The fundamental problem is express G in function of initial mol number. In this work we resolve this minimization problem implemented a non estequiometric formulation. We implemented the Lagrange multipliers for avoid the restriction imposed for the material balance, thus:

$$\ell(\eta, \lambda) = \sum_{i=1}^{N} n_i \mu_i + \sum_{k=1}^{M} \lambda_k \left(b_k - \sum_{k=1}^{N} a_{ki} n_i \right) \qquad (5.2)$$

Equation (5.2) represents the lagrangian where λ is a vector of M unknowns Lagrange multipliers, therefore the necessary conditions give a set of $(N+M)$ equations, for $(N+M)$ unknowns $(n_1, n_2, \dots n_N, \lambda_1, \lambda_2, \dots \lambda_M)$. We implemented the two-phase reactive flash operation (E.S. Cisneros , et al,1996) for modeling eq.(5.1 and 5.2) rewriting the equations in terms of component mole fractions and the corresponding constraint equations for the phase compositions ,thus:

$$\theta_V \sum_{i=1}^{N} a_{ki} y_i + \theta_L \sum_{i=1}^{N} a_{ki} x_i - b_{kf} = 0 \qquad (5.3)$$

para $k = 1, \dots, M$

$$\sum_{i=1}^{N} y_i - 1 = 0$$
$$\sum_{i=1}^{N} x_i - 1 = 0 \qquad (5.4)$$

Where θ_V, θ_L are the phases fractions defined in terms of molar flow and b_{kf} is the elemental composition vector for any phase, in addition the conditions of chemical and physical equilibrium will be defined by the equality of chemical potentials in both phases:

$$\mu_{ii}^{L} = \mu_{i}^{V} \qquad (5.5)$$

And in the problem solution we have M+2 equations, whit M+2 unknowns $([\lambda_1, \dots, \lambda_M], \theta_V, \theta_L)$.

5.1) Reactive Bubble point (reactive liquid – vapor equilibrium)

This problem consist in determining the temperature when the liquid composition x_i are in reacting equilibrium , besides must be forming the first vapour bubble, where this incipient phase have a y_i composition such that $y_i = k_i x_i$ assuming quickly rate of reaction.

The incipient phase limit condition, (it forms a infinitesimally vapor quantity) is represented by:

$$\theta_V \rightarrow 0 \tag{5.6}$$

Here, the eq.(5.6) is not affect the material balance , and those restriction will be described by:

$$\sum_{ii=1}^{N} a_{ki} x_i - b_{kf} = 0 \tag{5.7}$$

In this case, we are computing a chemical equilibrium over one phase, but the temperature is unknown.
.
5.2) Residue curve maps in presence of chemical reactions

The Figure (5.1) represents an open evaporation ,like for non reactive systems, but now in terms of element 'mole' fractions (Michelsen, et al, 1995) ; If we represent a material balance for the *M elements* that conform the *N species we have:*
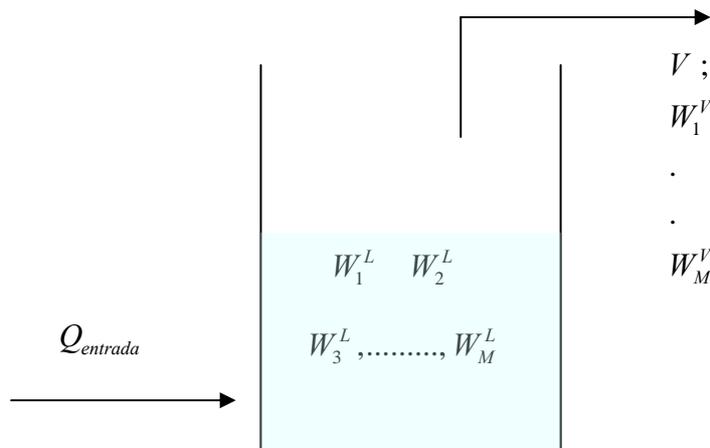
Figure (5.1) Open evaporation stage, in function of the element mole fraction in the chemical reaction.

$$-VW_j^V = \frac{d\left(H(t)W_j^L\right)}{dt} \ , \ para \ j = 1,.....M \tag{5.8}$$

By mean a global balance:

$$-V = \frac{dH(t)}{dt} \tag{5.9}$$

Replacying eq. (5.9) in eq. (5.8) , we have

$$\frac{dW_j^L}{d\tau} = W_j^L - W_j^V \tag{5.10}$$

Solving eq. (5.10) we obtain the *residue curve map when chemical reactions are present.* These profiles could be approximate to $\left(\infty\!/\!\infty\right)$ regime in a single reactive distillation column.

5.3) Feasibility design in reactive distillation processes in equilibrium controlled columns.

When is implemented the residue curve map in elemental mol fractions terms, these maps contain the same functional form than residue curve map without chemical reaction for conventional distillation (C.A.Rivera, J.Grievink, 2004), for non reactive mixtures in molar fractions. The fixed points in the equation (5.10) appear when $W_j^L = W_j^V$ .reactive azeotrope is of importance in reactive separation systems in order to identify the reactive distillation boundaries (or separation feasibilities). Barbosa and Doherty (1988) defined a reactive azeotrope as an equilibrium phenomena where the rate of vaporization and condensation coupled with the rate of reaction of each species are such that vaporization and condensation occurs without change of composition in either phase.

The main difference with respect to non-reactive azeotropes is that in this case the condition of equality of mole fractions for each species in the respective phases is not needed. Recently, Ung and Doherty (1995b) proposed the necessary and sufficient conditions for the existence of a reactive azeotrope using their set of transformed composition variables. In this paper, we are introducing an *element azeotrope,* which is identical (in principle) to the azeotropes found in non-reactive systems. Thus, with the element balance approach, the conditions for the existence of *element azeotropes* are: The point where the compositions of element j (j = 1 . . . . . M) in all coexisting phases are identical, or, equivalently, the element elative volatility of element j (j = 1 . . . . . M –1) with respect to element R is unity.

All information contained in these residue curve map can be explained and extrapoled in the same form, how we indicated in the above section in this paper when chemical reaction is not present, like show the next figures:
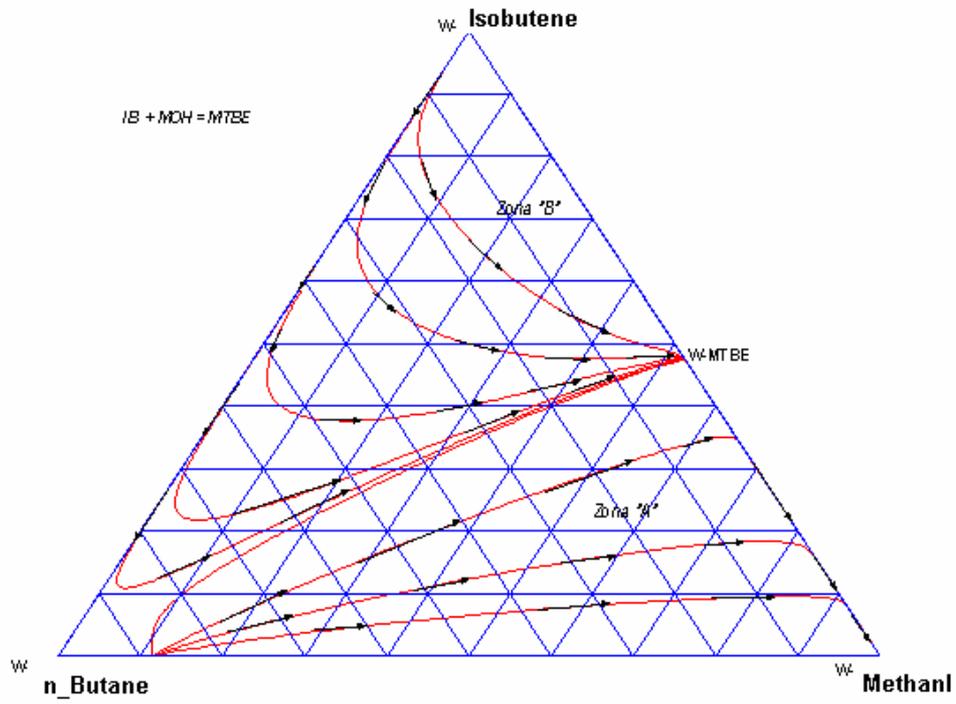
Figure 5.2) Residue curve map in presence of chemical reactions (P=10 atm) .
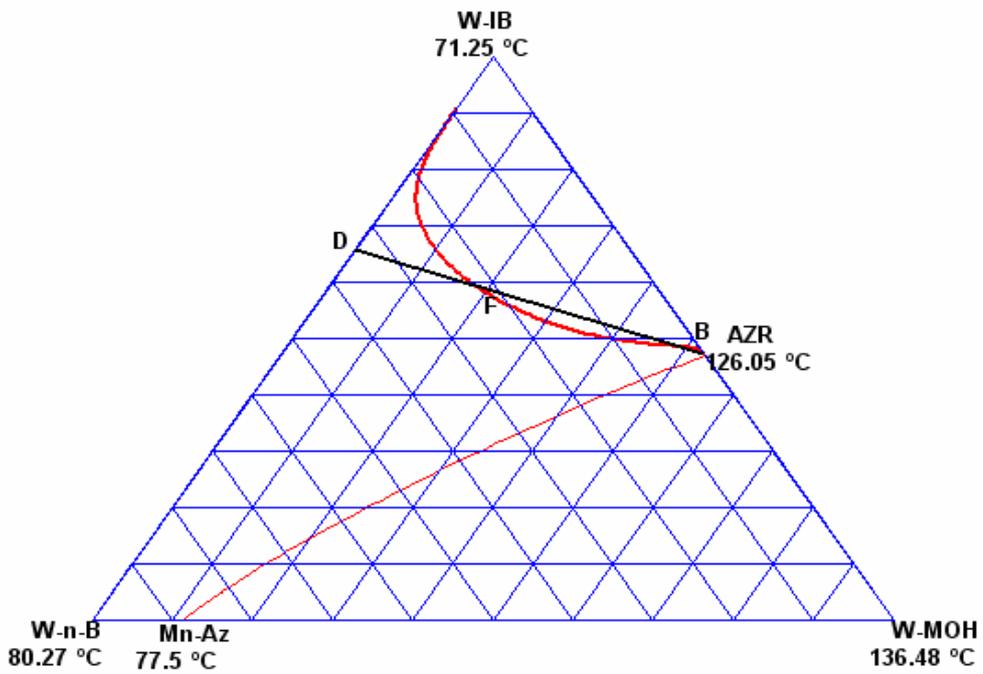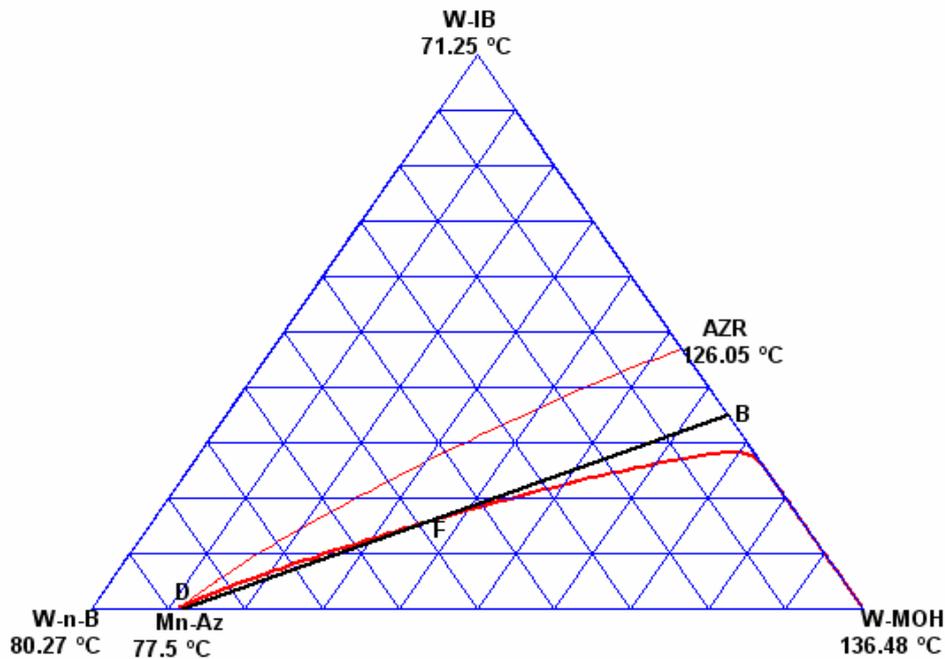

Figure 5.3) Feasibility separation for zone B. According to figure (5.2)(P=10 atm) .

Figure 5.4) Feasibility separation for zone A. According to figure (5.2)(P=10 atm) .

6. Conclusions

Has been a proposed new criterion for determination of separation possibilities for conventional and non conventional distillation from existent methods and make emphasis in the simplex topology, founding news topological points like bifurcation points, obtaining more accuracy results and reducing the time consumption.

The residue curve map and the static analysis is the first step in all conventional or reactive distillation design process. The study made in this work about the non conventional variables of design such as, reflux or energy supply to reboiler, has shown that these variables enhance the separation possibilities.

The concept of distillation regions and thermodynamic separatices, could be extended to continuous distillation since, they limits separation possibilities in the same way that in differential distillation. The algorithm illustrated in this work ensure the sufficient and necessary conditions for a possible separation

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