

Dr. Jordi Bonet Ruiz  
Dra. Alexandra Elena Bonet Ruiz  
*Departament d'Enginyeria Química i  
Química Analítica*



# Treball Final de Grau

**Contribution to the study of minimum extractor agent flow rate**

Oriol Yañez Gaya

*June 2019*



UNIVERSITAT DE  
BARCELONA



Aquesta obra està subjecta a la llicència de:  
Reconeixement–NoComercial–SenseObraDerivada



<http://creativecommons.org/licenses/by-nc-nd/3.0/es/>



*No great discover ever made without a bold guess.*

Isaac Newton

Agrair a tots els professors que he tingut, tant a la universitat com fora d'aquesta, per haver fomentat, encara que alguns més i altres menys, el desenvolupament de la meva curiositat. També agrair-los que m'hagin format com a professional i com a persona, realitzant una tasca que no es pot valorar mai suficient.

També a la meva família, la qual m'ha donat tot el seu temps, esforç i recursos per tal d'educar-me i formar-me el millor possible abans d'afrontar la vida



# CONTENTS

<b>SUMMARY .....</b>	<b>I</b>
<b>RESUM .....</b>	<b>III</b>
<b>1. INTRODUCTION .....</b>	<b>1</b>
<b>1.1 Extractive distillation .....</b>	<b>2</b>
1.1.1 Reflux ratio.....	4
<b>1.2 Isovatility curves .....</b>	<b>5</b>
<b>1.3 Relative volatility .....</b>	<b>7</b>
<b>1.4 Column Model .....</b>	<b>8</b>
<b>1.5 Pinch point.....</b>	<b>11</b>
<b>1.6 Studied Systems.....</b>	<b>16</b>
<b>2 OBJECTIVES .....</b>	<b>19</b>
<b>3 METHODOLOGY .....</b>	<b>21</b>
<b>3.1 Feasibility of Separations in Multifeed Columns.....</b>	<b>22</b>
<b>3.2 Material Balance Constrains for extractive Section. ....</b>	<b>23</b>
<b>3.3 Pinch Point Curves for the Middle Section.....</b>	<b>26</b>
<b>3.4 Minimum and Maximum Reflux Ratio.....</b>	<b>28</b>
3.4.1 Possible separation sequences for a given entrainer .....	29
3.4.2 Minimum entrainer ratio .....	31
3.4.3 Maximum reflux calculation.....	36
<b>3.5 Distillation sequence EFFICIENCY (DSE) .....</b>	<b>38</b>

---

<b>3.6</b>	<b>Obtention by lineal regression.....</b>	<b>44</b>
<b>4</b>	<b>CASE STUDIED WITH THE PROPOSED METHODOLOGY.....</b>	<b>45</b>
<b>4.1</b>	<b>Acetone-Methanol-Water .....</b>	<b>47</b>
<b>4.2</b>	<b>Acetone-Methanol-Chlorobenzene .....</b>	<b>49</b>
<b>4.3</b>	<b>Isopropanol-Ethylene glycol-Water.....</b>	<b>51</b>
<b>4.4</b>	<b>Acetone-Methanol-Ethanol .....</b>	<b>53</b>
<b>4.5</b>	<b>Acetone-Methanol-Isopropanol.....</b>	<b>55</b>
<b>4.6</b>	<b>Analysis of results.....</b>	<b>56</b>
<b>4.7</b>	<b>DSE comparision with the minimum feed ratio obtained .....</b>	<b>58</b>
<b>5</b>	<b>CONCLUSIONS.....</b>	<b>61</b>
	<b>REFERENCES AND NOTES.....</b>	<b>63</b>
	<b>ACRONYMS.....</b>	<b>65</b>



## SUMMARY

The extractive distillation is the most common used alternative when the mixture to separate has an azeotropic point or its components have close boiling points. Although most liquid separations are performed in the industry by distillation, the energy consumption of the distillation columns is very high, so any improvement achieved in that means energy and economic saving.

Shortcut methods have an important role in the conceptual design of distillation processes because they rapidly provide constraints for important design parameters such as minimum reflux ratio, number of stages, process feasibility, possible splits, and, specifically for extractive distillation, minimum solvent feed ratio and maximum reflux ratio. In this work, a simplified method using reversible distillation models has been applied to the conceptual design of double feed extractive distillation columns. As previously found by other authors, it is observed that these extractive distillation pinch curves, in addition to determining the feasibility region, are also useful for calculating an approximate minimum entrainer feed ratio independent of other parameters, as well as accurately pinpointing the minimum and maximum reflux ratios. Applications to example extractive distillation systems allow us to conclude that the method is reliable, fast, and much easier to implement than other methods.

**Keywords:** Double feed, extractive distillation, isvolatility curves, azeotropic mixture.



## RESUM

La destil·lació extractiva és l'alternativa més usada quan la mescla a separar és un azeòtrop o els seus components tenen punts d'ebullició semblants. Tot i que moltes de les separacions dutes a terme en la indústria es fan mitjançant la destil·lació, el consum energètic de les columnes de destil·lació és molt elevat, així que qualsevol millora en aquest camp significarà un estalvi tant energètic com econòmic.

Mètodes de simplificació tenen un rol important en el disseny conceptual de processos de destil·lació perquè et donen ràpid informació important de disseny com seria el mínim ratio de reflux, nombre de plats, la factibilitat del procés, possibles separacions i específicament per destil·lació extractiva, mínim ratio de solvent en 'aliment i màxim ratio de reflux. En aquest estudi, un mètode simplificat de la destil·lació reversible ha estat aplicat en disseny conceptual en doble aliment de destil·lació extractiva. Com trobat anteriorment per altres autors, s'observa que les corbes de pinçament de la destil·lació extractiva, en addició per determinar la regió de factibilitat, son útils per determinar un aproximat del mínim aliment ratio de reflux independentment dels altres paràmetres, com també determinar el màxim i mínim ratios de relax. Aplicat al nostre exemple de destil·lació extractiva podem concloure que el mètode es rapis i més fàcil que altres mètodes aplicats. Els sistemes son acetona-metà-aigua i etanol-aigua-etilènglicol, permetent una avaluació gràfica del mètode.

**Paraules clau:** Doble aliment, destil·lació extractiva, corbes de isovolatilitat, mescla azeotròpica



# 1. INTRODUCTION

In the specialty chemicals industry, distillation is one of the oldest and most widely used separation processes. The separation is based on the difference in the boiling temperature of the components. It consists on the attachment of connected stages in where two counter current flows interact, hence that there is mass transfer. It is necessary that all flows that enter a column plate are in non-equilibrium state, what originates the driving force for the mass transfer.[1]

The enrichment of the vapour phase takes part in every stage because the vapour from a previous stage has a minor concentration in the most volatile compound than the one that is in equilibrium with the liquid that goes in the mentioned stage. [1]

In some cases, the separation of the compounds in a mixture have similar boiling point or form azeotropes becoming infeasible to collect pure components by distillation. However, distillation is widely used, and enhanced distillation schemes are proposed to overcome this drawback. Complex flowsheets with recycle streams are required to separate the products. Sometimes an additional component, the so-called entrainer, is added to facilitate the separation, the entrainer-based extractive distillation and azeotropic distillation. On the other hand, entrainer-free enhanced distillation processes such as pressure-swing distillation are also sometimes used.[2]

Distillative separation is among the least expensive methods for separating mixtures that exhibit suitable volatility differences. Hence, continuous distillation columns, along

with their optimal operation and heat integration, constitute a major engineering activity in refineries and bulk commodity manufacturing. The common practice for distillation design often involves numerous trial-and-error experiments by means of state-of-the-art process flowsheet simulators. However, this time-consuming practice does not guarantee the production of successful designs; it might not provide any information about the feasibility of a specification in cases when the efforts do not converge. When the design-by-simulation approach is used, infeasibilities are often discovered only after extensive simulation studies

The principals types of distillation are.

- Simple distillation.
- Fractional distillation.
- Azeotropic distillation.
- Vacuum distillation.

## 1.1 EXTRACTIVE DISTILLATION

In simple terms, extractive distillation is a means of separating two substances with similar boiling points by adding a third substance to change the boiling point of one of compounds, thus making them easier to separate.

In the chemical world there are times when two substances become very difficult to separate using standard distillation, because their boiling points are so similar. The below flow diagram explains how extractive distillation works on a large scale. (A + B) are introduced into the first distillation column. Separately introduced in the first distillation column is a solvent (S). The solvent and B interact in such a way as to change the boiling point of B. The distillate from the first column (A) can then be effectively be separated from (B).

Once (A) is separated (B) you are left with the mixture of solvent and (B). These two chemicals are now pumped to a solvent recovery column to be separated. Once (S) and (B) are separated (S) is recirculated back into the first column and the process starts again. [3]

This type of enhanced distillation consists in the addition of an additional compound to the rectifying section of the column that modifies the relative volatility of the mixture. This way of adding the entrainer is what differentiates the extractive distillation from the azeotropic distillation. The extractive agent has a high boiling temperature and is miscible with one of the mixture compounds or it is more like some mixture compounds than to others, thus, the more similar compounds will have a lower activity coefficient in the dissolution than the others, what makes the separation easier.[1]

The most important thing when designing the extractive distillation system, is the choose of the entrainer because it must fulfil different properties. The entrainer boiling point has to be higher than the boiling point of the mixture compounds, thermal stable, economic and non-toxic if possible.

Extractive distillation is performed in a sequence of at least two columns, a two-feed column with an extractive middle section where the entrainer "breaks" the azeotrope followed by a single-feed entrainer recovery column. But can also be composed by three columns: a prefractionator to approach the azeotropic composition of the mixture, the extractive distillation column and the entrainer recovery column [2].

Extractive distillation is the most widely used type of enhanced distillation in the industry and this study focuses on it.

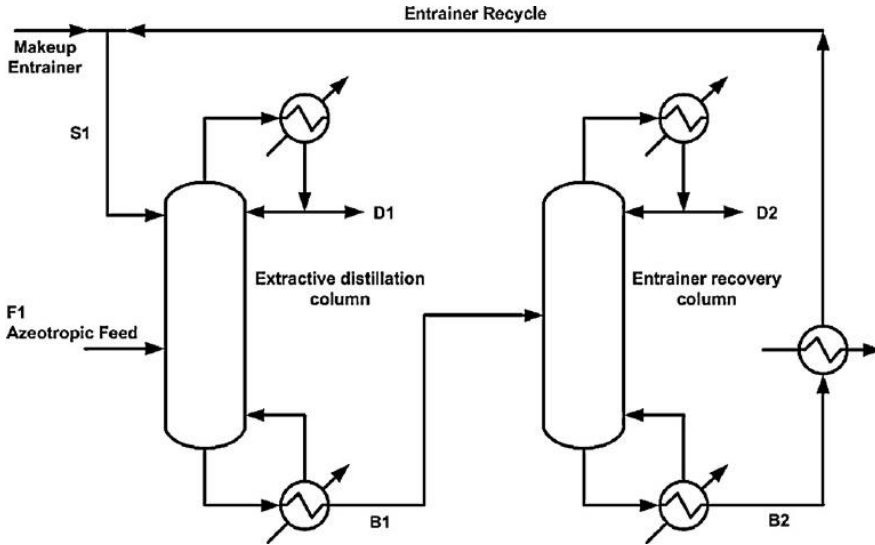


Figure 1. Typical extractive distillation scheme

### 1.1.1 Reflux ratio

It is the ratio of flow rate of liquid has returned to the distillation column from reflux drum to the flow rate of the amount of distillate is removed.

For shortcut design of a distillation column, the minimum reflux calculation should be made first. For a refrigerated system, the optimal reflux ratio is one included between 1.1-1.2 times the minimum reflux ratio. For a hot system, the estimate optimum reflux ratio is 1.2-1.35 times the minimum one.



### 1.1.1.1 Minimum Reflux Ratio

If the reflux ratio is reduced the slope of the operating line is reduced and the number of stages required achieving for separation. Further reductions will increase infinite number of stages because the slope line will become closer to operating line.[4] This case is called a minimum reflux ratio. It is true that, reflux ratio decreases that the duty of reboiler and condenser decreases. In other hand, operating cost of distillation is decreased. Below the minimum reflux ratio, it is not possible to achieve required enrichment even it doesn't matter how many plates are you used.

## 1.2 ISOVOLATILITY CURVES

Isovolatility curves are used to define possible volatile orders in their respective regions, whereas RCM stable separatrices determine whether possible products could be obtained in their respective regions.[5]

Equivolatility curves are defined as the curves along which the relative volatility ( $\alpha_{ij}$ ) of two components is constant.[5] A special type of equivolatility curve is the isovolatility curve, where the relative volatility of two components is equal to one. Isovolatility curves have received attention because of their importance in the conceptual design of extractive distillation processes, for screening solvents. Laroche [5] demonstrated that these curves define the possible products in an extractive distillation process and subsequently used them for estimating the minimum reflux and feed ratios. Mathematically, the equivolatility (and in turn isovolatility) curves are defined using phase equilibrium distribution coefficients,  $K_i = y/x_i$ , as follows:

$$\alpha_{ij} = \frac{K_i}{K_j} = 1 \quad \text{for isovolatility} \quad (1)$$

Assuming an ideal vapor phase and a nonideal liquid phase described by an appropriate activity coefficient model:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i p_i^0}{\gamma_j p_j^0} \quad (2)$$

where  $\gamma_i$  is the activity coefficient and  $p^0$  is the saturation pressure. Is evident that in ideal systems the volatility order of the components ( $K_1 > K_2 > \dots > K_{n-1} > K_n$ ) is the same

throughout the composition diagram because of the absence of both azeotropes and distillation boundaries.

In the case of azeotropic systems the situation is very different because the volatility order depends on the number of isovolatility curves, which is equivalent to the number of binary azeotropes in the system. The isovolatility curve begins and ends at the binary edges of the ternary diagram and, therefore, divides the composition space into two regions, such that one of the components is the most volatile in one region while the other component is the most volatile in the other region. Also, by definition, each isovolatility curve for two components A and B must contain the azeotrope for these two components (if there is one). For a ternary azeotrope there can be three isovolatility curves, one for each binary system, with all three isovolatility curves connected at the ternary azeotrope. Residue have been used for determining graphically the isovolatility curves. [6]

The curve must be completed with knowledge of the location of the isovolatility curve  $\alpha_{AB} = 1$  (relative volatility is equal to 1), which splits the composition triangle into regions with an explicit order of volatility of the A and B components. The isovolatility

curve location is the core of a general feasibility criterion to infer which component is an attainable product and what the related column configuration is. To analyse the influence of pressure on the different entrainers, two binary azeotropic systems, ethanol-benzene and ethanol ethyl acetate, are used as case studies for separation by extractive distillation by combining pressure. The change in pressure results in a significant change in the selection of the entrainer. This discovery provides more possibilities for the choice of the entrainer and indicates the importance of pressure in extractive distillation, especially the pressure-sensitive system. [7]

### 1.3 RELATIVE VOLATILITY

Relative volatility is a measure comparing the vapor pressures of the components in a liquid mixture of chemicals. This quantity is widely used in designing large industrial distillation processes.

In effect, it indicates the ease or difficulty of using distillation to separate the more volatile components from the less volatile components in a mixture. By convention, relative volatility is usually denoted as  $\alpha$ .

Relative volatilities are used in the design of all types of distillation processes as well as other separation or absorption processes that involve the contacting of vapor and liquid phases in a series of equilibrium stages. [8]

$\alpha$  is a unitless quantity. When the volatilities of both key components are equal,  $\alpha = 1$  and separation of the two by distillation would be impossible under the given conditions

because the compositions of the liquid and the vapor phase are the same (azeotrope). As the value of  $\alpha$  increases above 1, separation by distillation becomes progressively easier. [4]

## 1.4 COLUMN MODEL

The column model for this work is based primarily on the Boundary Value Method (BVM) for double feed columns, with variations taking into account the column model proposed by Knapp and Doherty. In the current model the column equations are approximated by continuous differential equations rather than a set of discrete, stage-wise equations. The location of the lower feed is specified, and the middle section trays are counted upward starting from the lower feed tray. A partial condenser is used, and the feed qualities are considered. A conceptual schematic for the column is shown in Figure 2. [9]

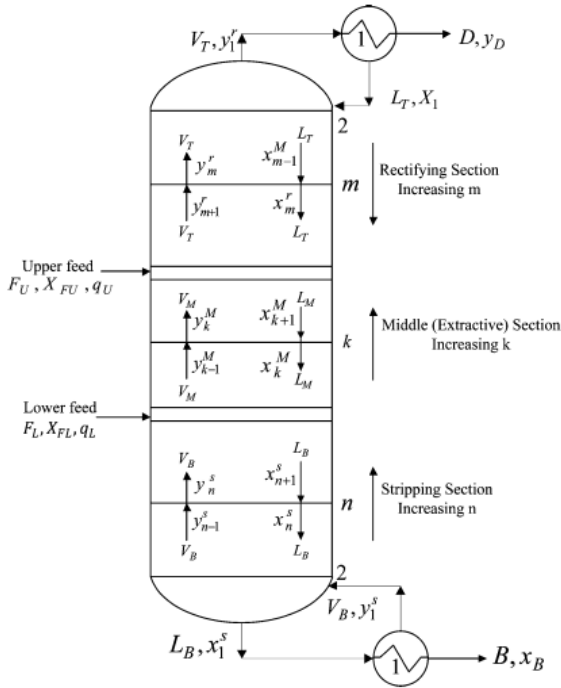


Figure 2. Schematic of a double-feed extractive distillation column.

In the current model, the middle section equations were described in terms of the reflux ratio, although they could just as easily be written in terms of the reboil ratio.

The component balance over the column gives

$$Fz_i = Bx_{Bi} + Dy_{Di} \quad (3)$$

A mass balance around the entire column gives

$$F_U + F_L = B + D \quad (4)$$

$$F_L X_{FL,i} + F_U X_{FU,i} = Bx_{Bi} + Dy_{Di} \quad (5)$$

with the overall feed rate ( $F$ ) defined by

$$F = F_U + F_L \quad (6)$$

$$Fz_i = F_U X_{FU} + F_L X_{FL} \quad (7)$$

The feed ratio ( $F_r$ ) is defined in terms of the two feed flow rates:

$$F_r = \frac{F_U}{F_L} \quad (8)$$

The Constant Molar Overflow (CMO) approximation was assumed for this model. Furthermore, pressure drop across the column was assumed to be negligible, and the column stages are assumed to be ideal. These assumptions allow the column mass balances to be developed in uncoupled form such that the mass balances for each section are independent of the other sections. Finally, a partial reboiler, and partial condenser were used, and as such the condenser and reboiler are designated as the first equilibrium stage in the rectifying and stripping sections, respectively. [10]

The application of the reversible distillation model for dual feed columns was presented

by Wahnschafft and Westerberg using the mass balances for the middle section. They found that the middle section has two pinch point trajectories defining both a lower and an upper bound for the reflux ratio. Therefore, for a specified design to be feasible it is necessary that the stripping profile ends inside the region limited by these two pinch point curves. Although Wahnschafft and Westerberg showed the importance of the pinch curves for double feed columns, some analysis was omitted. Wahnschafft and Westerberg's method used residue curve analysis for calculating the pinch points, which is a tedious and computationally expensive method. [6]

The composition profiles attainable in each column section are constrained by so called pinch point curves, which describe the compositions of the stationary points attainable at arbitrary reflux ratios. Thus, the course of the pinch point curves can be used to determine ahead of design calculations whether or not a given product specification is in principle feasible.[9][10]

## 1.5 PINCH POINT

The intersection of an operating line and the equilibrium curve is called a *pinch point*. A simple column will have two pinch points (because there are two operating lines). The points change when the operating lines do. An existing column can "pinch" if its operating line is too close to its equilibrium curve. This means that there are several stages doing very little separation and wasting resources. [11]

To cure a pinch, the most direct solution is to move the feed entry point. This is often an expensive proposition. In such cases, the reflux and boil up ratios can be increased to change the operating lines. This will increase operating costs and energy consumption but may be the only realistic option.

A pinch at the intersection of the feed line and the equilibrium curve indicates that the column is operating at *minimum reflux*.

The method relies on so-called fixed-point curves which are trajectories in the compositions space. These trajectories describe the possible compositions of pinch points in each column section as functions of the energy supplied to a column, i.e., for

all conceivable values of the reflux ratio. Pinch point trajectories may be determined analytically or, for ternary mixtures, can be located graphically using residue curve maps. Is mostly graphical analysis, using pinch point trajectories to establish separation feasibility ahead of design calculations. The analysis also provides information on the minimum entrainer supply for a specified separation and visualizes the phenomenon of the occurrence of a maximum reflux ratio for separation in a column with a separate, extractive agent feed. The analysis is analogous to that for single-feed columns, only the critical pinch trajectories may be those for the extractive column section between the feeds.[11]

A pinch point in a separation device is due to vanishing driving forces for mass exchange. In a distillation column, for example, a zone of constant compositions arises if the streams getting in contact on the trays approach equilibrium. If, and at which compositions, such pinch points occur depends on the energy supplied to the column, i.e., on the reflux and reboil ratio. A conventional adiabatic distillation column cannot be pinched throughout. However, the notion of a pinch point can be used to define the model of the thermodynamically optimum separation path. To minimize the occurrence

of irreversible processes, thermodynamic equilibrium must be approached throughout the column. Such operation could theoretically be attained in a column with an infinite

number of stages and heat exchange on each tray. Physically, this model implies that the internal vapor and liquid flows are adjusted by incremental heating and cooling at intermediate temperature levels to ensure that the vapor and liquid phase getting into contact at each stage are in equilibrium. The resulting separation path corresponds to the compositions of pinch points for continuously increasing condenser and reboil duties. [12]



In the equilibrium-based model of distillation, a pinch point can be calculated from the requirement that vapor and liquid compositions simultaneously satisfy the equilibrium relationship and the material balance equations. Instead of the rigorous mathematical model of such a process (e.g., Benedict, 1947; Petlyuk et al., 1965, Kaibel, 1987; Kohler, 1991; Kohler et al., 1991), we have used residue curve maps to graphically determine pinch point curves (Wahnschafft et al., 1992). The residue curve map of a ternary mixture is a convenient representation of the phase equilibrium behaviour, derived from the open distillation process. Such maps reveal the occurrence of boundaries for distillation at total reflux and indicate the direction of the vapor-liquid equilibrium vector as a function of the liquid composition.

Pinch point trajectories may be determined as the compositions for which the material balance and the equilibrium line coincide. For single-feed columns, this procedure is equivalent to finding the compositions at which the equilibrium vectors, i.e., the tangents to the residue curves, point through the specified product compositions. As a reminder, the flows pertinent to the material balance around the top section of an adiabatic column. At any stage in the rectifying section, the compositions  $V_n$ ,  $L_{n-1}$ , and D must be on a straight line in a ternary diagram to satisfy the material balance.

$$V_n = L_{n-1} + D \quad (9)$$

Since a pinch point also requires the vapor and liquid to be in thermodynamic equilibrium, the composition  $V_n$  must be located on a tangent to the residue curve passing through  $L_{n-1}$ . Similarly, at any stage in the stripping section, the liquid composition must lie on a straight line between the bottoms difference point and the

composition of the vapor rising from the tray below and again, at a pinch point, the two phase compositions must be in equilibrium.

$$L_m = V_{m-1} + B \quad (10)$$

The criterion that the concentration profile regions determined for given product specifications must intersect is applicable regardless of the physical property behaviour of a mixture. However, in azeotropic systems, the application of the criterion can become more complicated, as pinch point curves may exhibit bifurcations and multiple branches. [6]

Consider, for example, the separation of a mixture of acetone, chloroform, and benzene shown in Figure 3. For the bottoms composition there are two branches of pinch point curves which represent possible stationary points for composition profiles originating at B. As long as the reboil ratio is not too high, the composition profile will terminate on the pinch curve branch that traverses into the neighbouring residue curve region. At too high values of reboil and reflux ratio, composition profiles will terminate on the disjointed pinch curve branch that ends at pure chloroform. Understanding the significance of the pinch point curves has enabled us to determine the maximum reflux ratio at which a separation across a residue curve or total reflux boundary may be possible, as well as the maximum extent of separation (Wahnschafft et al., 1992). The crossing of the total reflux distillation boundary is enabled by an extractive effect due to the influence of benzene on the relative volatility between acetone and chloroform. Thus, benzene acts like a heavy, extractive entrainer while it is present in the feed.[6]

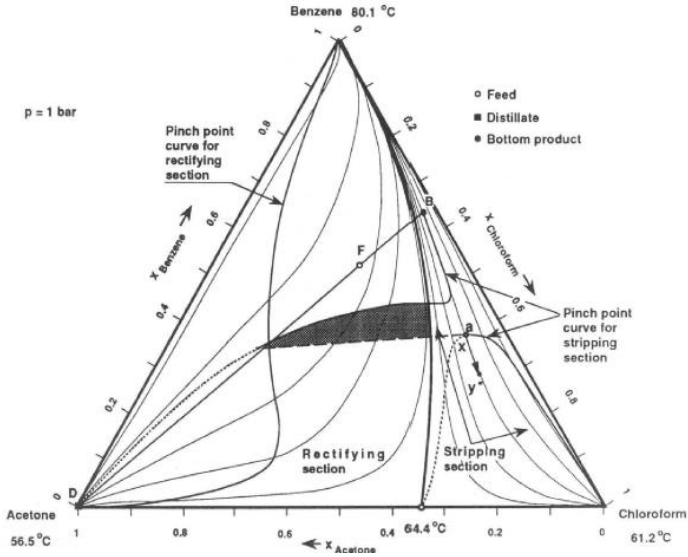


Figure 3. Separation of acetone/chloroform/benzene mixture. A total reflux boundary can be surpassed by distillation at finite reflux ratios, as long the pinch curve for the product beyond the boundary can extend into the neighbouring distillation region. In such cases the pinch point curve bifurcates into a branch describing stationary points for low values of the reflux ratio and one for higher reflux ratios.

The traditional extractive distillation process is just a special case of the situations where one should or has to consider designing a column with separate feeds. Whenever two streams which are mixtures containing the same components, only in different composition, are to be separated in a single column, they should generally not be mixed to avoid unnecessary irreversibilities. More importantly, however, certain separations of azeotropic mixtures may only be feasible when entrainers are supplied as separate feeds.

## 1.6 STUDIED SYSTEMS

The processes that will be carried out to calculate the minimum feed ratio will be those obtained from the studies of Mr. Stefan Brüggemann and Wolfgang Marquardt, on the one hand, and Libardo Estupiñan Perez, Greg P. Dechaine and Carlos A. Martinez Riascos.

The feed information about the process of Libardo Estupiñan Perez, Greg P. Dechaine and Carlos A. Martinez Riascos :[7]

system	feed mole fractions		product mole fractions	
	lower feed ( $X_{FL}$ )	heavy entrainer ( $X_{FU}$ )	distillate ( $y_D$ )	bottoms ( $x_B$ )
acetone–	0.5	0	0.98	0.00048
methanol–	0.5	0	$1 \times 10^{-4}$	0.45964
water	0	1	0.0199	0.53988
ethanol–	0.89	0	0.999	$4.8 \times 10^{-4}$
water–	0.11	0	$1 \times 10^{-6}$	0.11701
ethylene glycol	0	1	$9.99 \times 10^{-4}$	0.88241

Table 1. Design Specifications ( $q_u = 1$ )

They achieve the following minimum flow rate values

system	upper feed quality ( $q_u$ )	minimum feed ratio ( $F_{r,min}$ )	design feed ratio	reflux ratio ( $1.2r_{min}$ )
acetone–methanol– water	1	0.16	0.6	3.12
ethanol–water– ethylene glycol	1 1.1	0.26	0.8	1.32 1.2

Table 2. Final Design Specifications

As regards the other article, the conditions of food and minimum flow rate are determined in the following table. [13]

Component	$x_F$	$x_E$	$x_D$	$\frac{D}{F}$ $(E/F)_{min.bif}$
Isopropanol	0.62	0.0	1.0	0.62
Water	0.38	0.0	0.0	0.649
Ethylene glycol	0.0	1.0	0.0	
Acetone	0.7774	0.0	1.0	0.7774
Methanol	0.2226	0.0	0.0	0.740
Water	0.0	1.0	0.0	
Acetone	0.7774	0.0	1.0	0.7774
Methanol	0.2226	0.0	0.0	0.721
Ethanol	0.0	1.0	0.0	
Acetone	0.7774	0.0	1.0	0.7774
Methanol	0.2226	0.0	0.0	2.187
Isopropanol	0.0	1.0	0.0	
Acetone	0.7774	0.0	0.0	0.2226
Methanol	0.2226	0.0	1.0	0.788
Chlorobenzene	0.0	1.0	0.0	

Table 3. Design Specifications



## 2 OBJECTIVES

This work focuses on extractive distillation. The literature about calculation of minimum reflux ratio shows that when designing an extractive distillation process by rigorous simulations, the "try and error" method is used. This takes a lot of time to achieve optimum results of which is the optimum entrainer flow rate to use and if the use of a prefractionation column is worth.

Therefore, what we would like to achieve would be the search for methods of resolution of distillation systems with double feed with azeotropes.

The goal of the present work is to achieve some conclusions about the optimum entrainer flow rate to use, and the components from bottom or top of these two columns depending on the class of solvent used as entrainer and the volatility of the entrainer relative to the other components.

The focus of the present work is on homogeneous azeotropic distillation where the addition of an entrainer to an azeotropic mixture is intended to modify the relative volatility of the mixture without forming any new azeotropes or additional liquid phases such that the separation is possible in a two-column sequence. The first column is the extractive column producing one of the azeotropic components as a pure product, and the second column is the solvent recovery column producing the second component in pure form. The pure products are removed from the bottom or top of these two columns depending on the class of solvent used as entrainer and the volatility of the entrainer

relative to the other components (i.e., is the entrainer the heaviest, lightest, or intermediate of the three components).

Trying to achieve a simplification in such a way that graphically representing the curve of isovolatility and food conditions we can find a ratio in order to calculate the minimum feed flow rate.



### 3 METHODOLOGY

The design of distillation systems for the separation of given multicomponent mixtures always requires some knowledge about the feasible splits or, in other words, the theoretically possible product compositions. For ideal mixtures it is enough to know the order of normal boiling points or the relative volatilities to determine, at least qualitatively, which splits are feasible. However, for mixtures with nonideal equilibrium behaviour, i.e., composition- dependent relative volatilities, a more detailed analysis is required to determine existence and location of distillation boundaries. Because of its significance for synthesis and design of processes to separate azeotropic mixtures, the problem of determining the feasible separations of azeotropic mixtures has received much interest over the past three decades.[6]

Most publications about distillation boundaries have dealt with single-feed columns. Perhaps the most common approach has been to study the product composition limits of continuous distillation columns in comparison with residue curve and distillation line boundaries. These boundaries are determined for the limiting operating condition of total reflux. While it has been shown repeatedly that there are cases where the product composition boundaries derived for total reflux can be surpassed at finite reflux ratios, theoretical analyses to determine the separability limits based on more fundamental insight have been provided by Wahnschafft (1993), Wahnschafft et al. (1992) and Stichlmair and Herguiguera (1992).

The method presented by Wahnschafft et al. (1992) is based on the fact that, for the distillation of ternary mixtures, all degrees of freedom may be used to specify the desired product compositions rather than design parameters, such as the number of stages and the reflux ratio. Starting from the fixed product compositions, one can calculate suitable values of the design and operating parameters.

### **3.1 FEASIBILITY OF SEPARATIONS IN MULTIFEED COLUMNS**

To investigate separation paths and the question of separation feasibility in a two-feed column, we must start by specifying feed and product compositions. The objective is to obtain a quick feasibility assessment before trial-and-error calculations are used to determine the reflux and the number of stages needed in each column section. Rigorous simulations or the boundary-value procedure proposed by Levy (1985) can render such information. However, such iterative design calculations can be a tedious way to discover that a given design specification is simply infeasible. [10]

The ideas allow to conclude that there is a direct relation between the concepts of volatility curves and volatility order within the feasibility region for extractive distillation. The feasibility region will always be located inside the area where the distillate component has greater volatility. Although the feasibility region depends on the feed ratio, we have verified, for the cases studied, that the isovolatility curve is the limit when the feed ratio is infinite since the feasibility region is the area where the middle section profile must start and end. This guarantees that the rectifying section starts at a point on the light-entrainer edge but inside the feasibility region and ensures that the column rectifying section does not contain any of the intermediate boiling components.

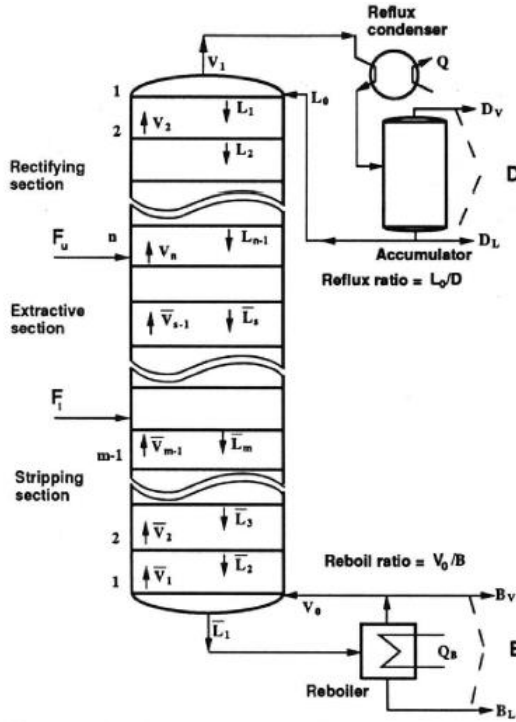


Figure 3. Flows in the sections of column with two feeds.

### 3.2 MATERIAL BALANCE CONSTRAINS FOR EXTRACTIVE SECTION.

Firstly is to establish mass balances for the whole column and for vapor and liquid flows in the three column sections. The balance equations for the flows in the rectifying and stripping section are the same as for a single-feed column. Hence, composition profiles in the rectifying and in the stripping section that are to lead to specified distillate and bottom products must be enclosed between the total reflux curves passing through these product compositions and the corresponding product pinch point curves. If these

two composition profile regions overlap, the assumed products can be obtained in a column without an extractive section or, in other words, in a simple column supplied

with the mixed feed. To determine if an extractive column can make a desired separation feasible when a single-feed design cannot, is needed to ask if the separation path in the extractive section can "connect" the composition profile regions of the rectifying and the stripping section. Hence, there must always be a maximum reflux ratio for a rational design of an extractive column.[14]

To evaluate the mass balance constraints for the extractive section between the two feeds, must decide which of the feeds should be the upper one and which the lower one. While normally a feed with a lower bubble point temperature is supplied closer to the top of a column, introducing the streams in reverse order of the volatilities can expand the range of feasible separations when an extractive effect occurs. There are also situations in which feeding streams in reverse order of bubble points reduces the reflux requirement to accomplish the same separation (Levy, 1985). If the order of the feeds is not obvious, the following analysis may have to be performed for both possible configurations.

Overall mass balance:

$$F_u + F_l = D + B \quad (11)$$

Balance for extractive section around the top part of the column:

$$V_{s-1} - L_s = D + F_u \quad (12)$$

Balance for extractive section around the bottom half of the column:

$$V_{s-1} - L_s = F_l - B \quad (13)$$

Note that the index  $s$  for the stages in the extractive section is assumed to increase from 1 at the lower feed tray upward. Equations around top and bottom of the column

are valid at any stage in the extractive section. Since the right-hand sides of these equations are not a function of the tray number, there is a difference point with constant composition also for this column section. From combining the two equations, it is apparent that, in a ternary diagram, this difference point must be the intersection point of the line that connects the compositions for  $F_u$  and  $D$  with the line that connects those for  $F_l$  and  $B$ . However, unlike the difference points for the rectifying and the stripping section which correspond to the specified product compositions, the difference point  $A$  for the graphical construction of the composition profile in the extractive section is located outside the composition diagram. [14]

From the material balances around individual column sections it can be concluded that in the rectifying section the net vapor flow must be higher than the net liquid flow. Conversely, in the stripping section the net molar liquid flow is larger than the vapor flow. To decide which of the flows is larger in the extractive section, however, it's needed to make a distinction. We can distinguish:

$$1. \quad D > F_u \quad V_{s-1} = L_s + (D - F_u) \quad (14)$$

$$2. \quad D < F_u \quad L_s = V_{s-1} + (F_u - D) \quad (15)$$

The difference point is found by continuing the connection line between  $F_u$  and  $D$  beyond  $D$ , whereas in the second case it is located on the continuation beyond  $F_u$ . Accordingly, it is either the composition of the vapor rising from below that must be situated on the line between the difference point and the liquid composition or the liquid composition that is between the difference point and the composition of the vapor. Thus, it's possible to locate the difference point and analyse qualitatively how the

composition profile calculation would have to proceed in the extractive section, as determined by the material balance constraints and the vapor-liquid equilibrium behaviour indicated by the residue curves.

### 3.3 PINCH POINT CURVES FOR THE MIDDLE SECTION.

A ternary system used as an example [6], namely the system 2-propanol, water, and ethylene glycol, shall serve to illustrate the role of the difference point for the extractive section. Assume there are two separate feeds,  $F_u$  and  $F_l$ , whose hypothetical total inlet composition is  $F_t$ . It's needed to know if it is theoretically possible to produce  $D$  as distillate and  $B$  as bottoms. Because the concentration profile regions for the stripping and the rectifying section do not overlap, these products cannot be realized in a single-feed column.

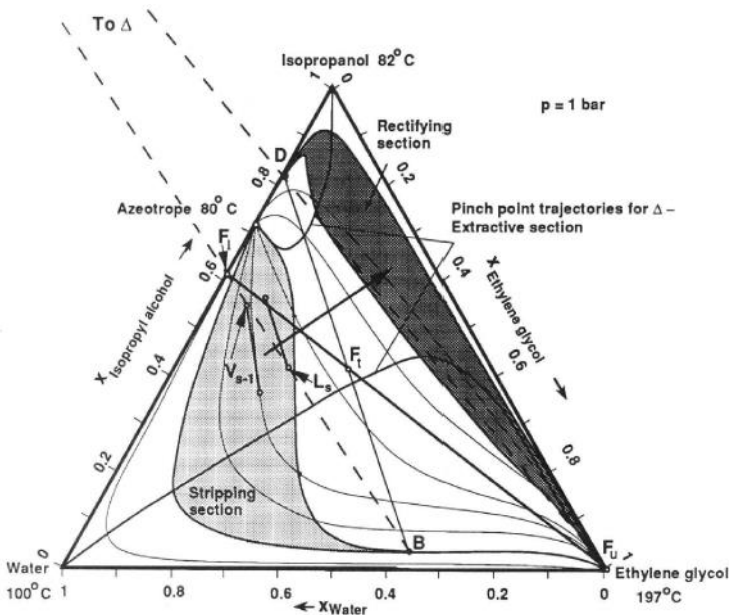


Figure 4. Residue curve diagram of 2-propanol/water/ethylene glycol system.

Since for the given feed and product specifications the distillate flow rate  $D$  is greater than the supply of the assumed upper feed ( $F_u$ ), the difference point  $A$  is found on the extension of the line connecting  $F_u$  and  $D$  beyond  $D$ . In Figure 4 it is indicated that this difference point will be rather far out to the upper left of the composition triangle. The point corresponds to the intersection of two balance lines: one that includes the upper feed and the distillate and one which includes the lower feed and the bottoms product.

As discussed before, the composition profiles in the rectifying and in the stripping section that are to lead to specified products are confined by total reflux curves and by pinch point trajectories determined for the specified product compositions. These pinch point curves were found as the trajectories of compositions at which the tangents to the residue curves aim at the composition of the difference points. By analogy, knowing the location of the difference point for the extractive section, it's possible to determine graphically whether and where there are pinch trajectories along which the equilibrium vectors point at  $A$ . As sketched in Figure 4, in the case of our example problem, one can find two such trajectories. As for the rectifying and the stripping section [12] these trajectories originate at the nodes and saddles and the residue curve map, i.e., at pure components and azeotropic compositions.

The pinch point trajectories divide the composition space into regions in which the separation paths that could conceivably be accomplished in the extractive section are qualitatively different.

Let first consider the composition region between the two pinch trajectories for the extractive section. Because  $D > F_u$ , the graphical construction of the composition

profile requires that the composition of the vapor rising from below is located between the liquid composition and the difference point. Thus, an arbitrary composition must be pick in the region between the pinch trajectories and visualize how the calculation of the composition profile would have to proceed. Following alternate equilibrium and material balance steps beginning in the composition region reachable by the stripping profile. In the example, stepping up the hypothetical trays in the extractive section leads to compositions that move toward the 2-propanol-ethylene glycol axis. This separation path is consistent with those achievable in the bottom stripping section and in the top rectifying section the separation can proceed from the high-boiling bottoms composition toward the distillate along a path with constantly decreasing temperature. Hence, the given product specifications are in principle feasible when ethylene glycol is added as an extractive agent (feed  $F_u$ ).

### 3.4 MINIMUM AND MAXIMUM REFLUX RATIO.

The composition profiles in the rectifying and in the stripping section, determined by starting from the specified product compositions for a specific reflux and reboil ratio, must reach into the region between the extractive section pinch trajectories. This requirement defines lower and upper bounds for the reflux ratio at which the specified separation could possibly be accomplished. At too high a reflux, the composition profile in either the stripping or the rectifying section will end at a pinch outside the composition region for which the extractive section can make the desired separation feasible.



### 3.4.1 Possible separation sequences for a given entrainer

In extractive distillation, it's possible to find the statement that a high-boiling entrainer will allow one to produce the lighter-boiling component as pure distillate. It is known

now that this is not generally correct. Which component(s) can appear in the distillate depends not only on the pure component boiling points, but also on the nonideal molecular interactions between the entrainer and the components to be separated [6]. By increasing the relative volatility of the heavier azeotropic constituent, it is quite possible that an entrainer takes the lighter component to the bottom. However, it has not been shown how the existing design options can be inferred from the trajectories of residue curves, and one may even wonder if both options could be feasible for a certain entrainer. Laroche used rigorous simulations to study designs of extractive distillation columns. For a selected entrainer, they found that it was only possible to design a column that would produce either the lighter- or the intermediate-boiling component as pure distillate. Using pinch point analysis, it's possible now investigate which design could be realized without having to rely on simulations. Moreover, the question of how much of the entrainer will be needed to accomplish a specified separation of an azeotropic mixture it's possible to resolve. As an example, let us consider the separation of the acetone/methanol azeotrope with water as an entrainer.[16]

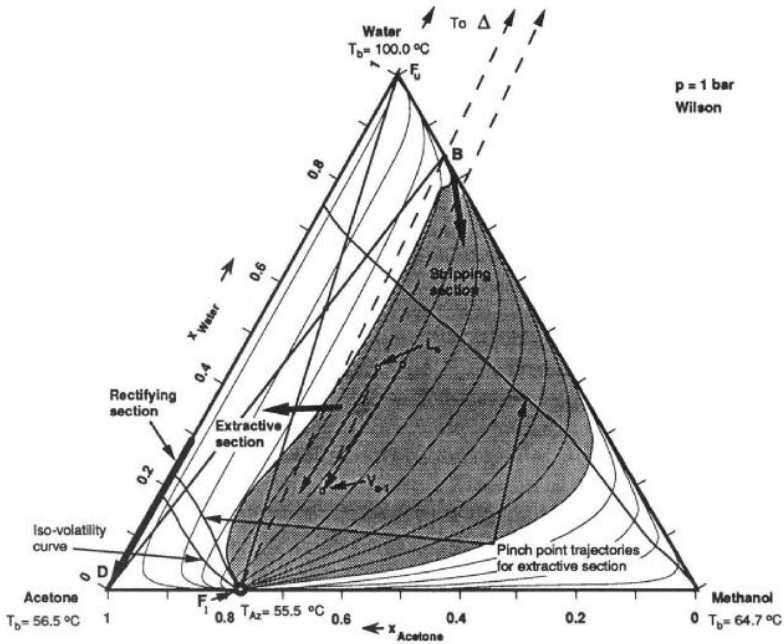


Figure 5. Separating an azeotropic mixture of acetone and methanol using water

The profile region for the stripping section allows for removal of acetone, so that water and methanol can be produced as bottoms. On the other hand, the separation in the rectifying section that can lead to acetone as distillate is restricted to a path along the acetone/water axis. In other words, if methanol appears above the upper feed tray, it cannot be separated from acetone in the rectifying section—it will escape into the distillate. Thus, the extractive section must accomplish the separation through the composition region between the pinch curve for the stripping section and the acetone/water axis.[6]

From the feed and product specifications, this time the difference point A for the extractive section is on the entrainer-rich, upper right side of the composition diagram. There are again two pinch trajectories for this difference point. Since the distillate flow rate is smaller than that of the upper feed, the composition profile in the extractive

section must be constructed such that the liquid composition on a stage  $s$  is located between the difference point and the composition of the vapor rising from below. By testing some arbitrary liquid and vapor compositions in the region between the pinch curves for the extractive section, one can verify that the composition profile in the extractive section must traverse toward the water-acetone axis. Thus, there is a path from the assumed bottoms composition all the way to the postulated distillate along which the boiling temperature decreases monotonically the specified products are feasible.

### **3.4.2 Minimum entrainer ratio**

#### *3.4.2.1 Minimum entrainer feed ratio with isovolatility curve*

The minimum entrainer feed ratio ( $Fr, \min$ ) is one of the most important design variables for extractive distillation processes because it has direct implications on the size of the column, the operating cost, and the solvent circulation rates. Methods have been developed for estimating the minimum feed ratio although these methods are tedious and complicated. Such complicated methods are unlikely to find widespread use among chemical engineering practitioners, and as such, a simpler algorithm for determining ( $Fr, \min$ ) is desirable.[16]

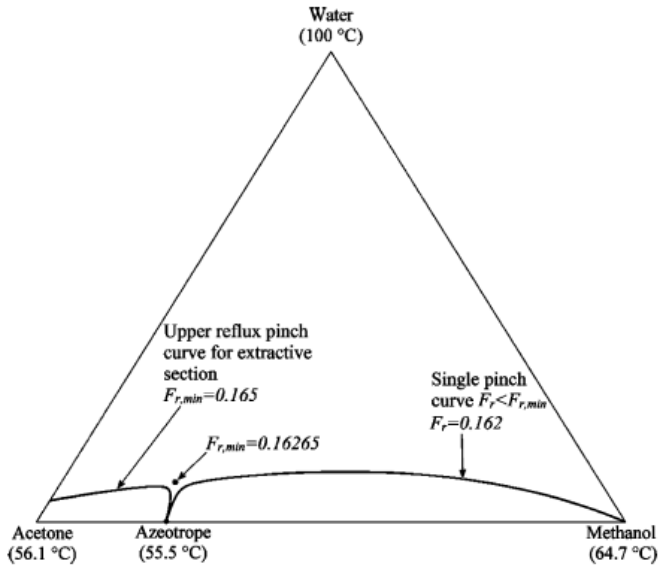


Figure 6. Pinch curves for two entrainer feed ratios, one above and one below the minimum entrainer feed ratio, for the acetone–methanol–water system at 1 atm.

Using the pinch curves for the middle section, it is possible to find an approximate solution for the minimum feed ratio. The pinch point curves for the extractive section of the acetone–methanol–water system at two different feed ratios in the vicinity of the minimum are shown in Figure 6. Upon inspection of this figure it is apparent that a bifurcation point exists at a specific feed ratio. Wahnschafft and Westerberg pointed out that as the feed ratio approaches its minimum value ( $F_r, \min$ ) the region between the upper and lower pinch curves decreases. In this work it was observed that once the limiting value has been reached or exceeded ( $F_r \leq F_r, \min$ ) the upper and lower reflux pinch curves merge into a single curve.[9] Consequently, only one pinch point curve will exist, thus indicating that the design is no longer feasible. As Figure 6 shows for the system acetone–methanol–water, the minimum feed ratio for this set of column

specifications is 0.163. This point corresponds to a pitchfork bifurcation point for the map of the upper reflux pinch curves.[17]

The method proposed by Knapp and Doherty accurately determines the minimum reflux ratio ( $r_{\min}$ ) and the minimum feed ratio ( $Fr_{\min}$ ) simultaneously, using a very complex and mathematically intense algorithm. Method, for determining  $r_{\min}$  and  $Fr_{\min}$  using the maximum reflux pinch curve. When the feed ratio is lower than  $Fr_{\min}$ , the maximum reflux pinch curve changes direction and will instead move toward the opposite vertex as shown in Figure 6. Therefore, it is possible to determine the approximate minimum feed and reflux ratio by varying the feed ratio and determining the value at which the curve flips.

An effective method for reducing the number of iterations and/or calculations required to locate the approximate minimum feed ratio is to use the isovolatility line as a guide. If the pinch curve corresponding to a given feed ratio lies close to the isovolatility line, then it can be argued that the chosen feed ratio is much higher than the minimum feed ratio since it is approaching its limit. As the pinch curve begins to diverge significantly from the isovolatility line, it is clear that the feed ratio is approaching the minimum value and will soon flip as the feed ratio is reduced. In this manner, the isovolatility line acts as a visual guide to help reduce the number of iterations needed to determine the exact location of the minimum feed ratio (i.e., the point where the pinch curve “flips”). [7]

A natural extension of the above analysis is to use the isovolatility curves as a fast and very effective solvent screening tool. Laroché found that “the higher the achievable relative volatility is the easier the separation and the lower the minimum reflux ratio”. Obviously, it is also desirable that the entrainer can be easily recovered in the second column. An extractive column requires less entrainer when (1) the

isovolatility curve ends nearest to the overhead product edge and (2) when the relative volatilities between the entrainer and the azeotropic components are high since high volatilities require lower feed and reflux ratios.[7]

#### 3.4.2.2 *Minimum entrainer feed ratio with relative volatilities*

This is another method founded without using the iteration to try pinching curves, but working with the ternary diagram for the ridge between the extractor agent and the compound that would be absorbed by the extractor of the first column

It would be to take different fraction values from the extractor agent (E), once a set of fractions determined, it's possible calculate the fraction of the compound that would be extracted with the extractor making the difference to the value of 1 (100%).

Next, is to carry out the study of the liquid-vapor equilibrium of these two compounds that are working binary. Once is studied this study of the liquid-vapor equilibrium, it's necessary study the relative volatilities of the two substances.

The next step is to represent the relative volatilities of the compounds with respect to the fraction of the extractor agent.

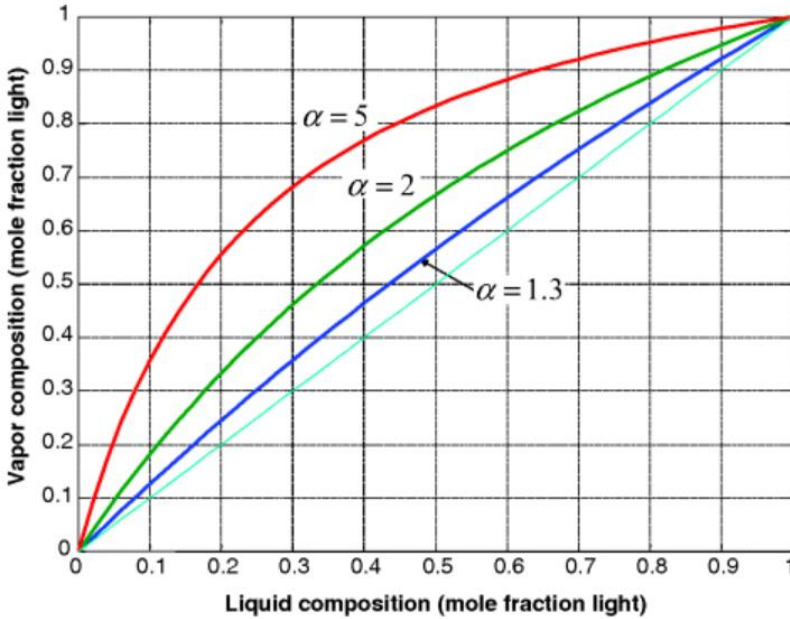


Figure 7. xy curves for relative volatilities of 1.3, 2, and 5.

After all these previous steps a fraction of the compound that will come out by column 1 purely. Therefore, it's needed to go through the previous steps of changing the fraction of the pure component of the first column to the point where a diagram emerges that presents higher points and inferiors to a relative volatility ( $\alpha$ ) of 1, because when  $\alpha = 1$  there is no possible separation, since it means that the two compounds have the same volatility. The greater the value of  $\alpha$  above 1.0, the greater the degree of separability, i.e. the easier the separation. Recall that when a system has reached an equilibrium, no further separation can take place - the net transfer rate from vapor to liquid is exactly balanced by the transfer rate from liquid to vapor.

Once this fraction is fixed of the first compound to distil itself, it must find the fractions of the extracting agent and the thickened that make the relative volatility of the system ( $\alpha$ ) the same, because as mentioned earlier it means that it is not feasible the separation. Therefore it would be already have the minimum foot fraction of the first column and assuming that any other composition would already have pure compost for the head of the first column, the thinned agent of the first column would come out pure by the second column and the foot. From the second column, the pure extractor would come out.

Finally, having these compositions found it's possible to obtain through the balances of matter the flow rate of the minimum extract agent.

### 3.4.3 Maximum reflux calculation

Extractive distillation processes exhibit a maximum reflux ratio beyond which the separation is no longer feasible. When the reflux ratio exceeds this upper limit, the middle section profile will end in an azeotrope or on the maximum reflux pinch curve. A straightforward but accurate method for calculating the maximum reflux ratio is to use the maximum reflux pinch curve. In this case, a reflux vs pinch mole fractions (of any component) plot will display the exact value.[6]

Two possible scenarios can arise during this analysis. The simplest case is when the maximum reflux corresponds to the intersection between the maximum reflux pinch curve and one of the edges of the ternary composition diagram, using the azeotropic



composition as the starting point. In contrast, there are nonideal mixtures for which the maximum reflux is controlled by a tangent pinch (turning point). Therefore, the maximum reflux is located by any point on the maximum reflux pinch curve. [9]

For example, the acetone–methanol–water system shown that the pinch point determines the maximum reflux ratio for this separation.

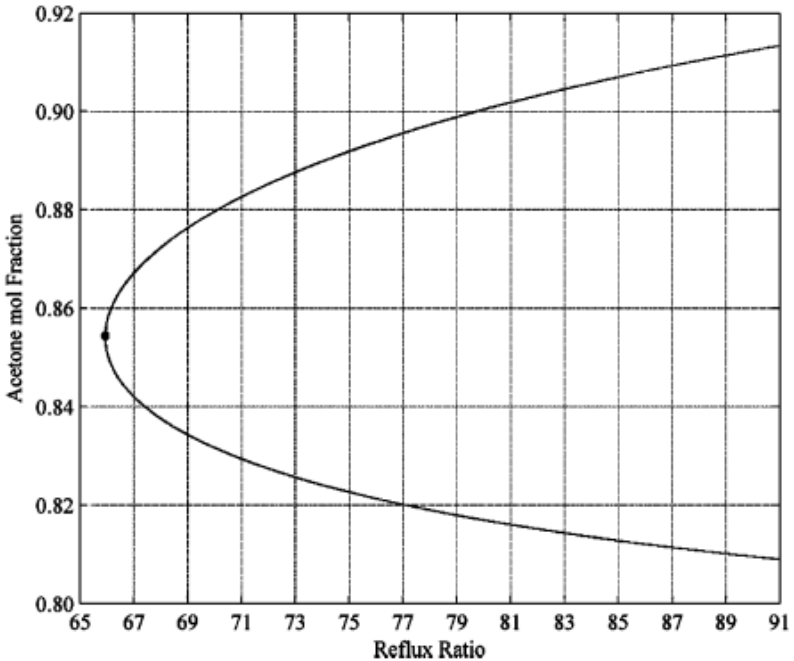


Figure 8. Maximum reflux controlled by a turning point for the acetone–methanol–water system. Entrainer feed ratio = 0.6, pressure = 1 atm

### 3.5 DISTILLATION SEQUENCE EFFICIENCY (DSE)

There are multiple alternatives to achieve a mixture separation, thus it is essential to evaluate them and choose the most efficient one. These choices have important influence on attainable costs, compared to the choices made in later design stages. The improvement of one process unit can negatively influence some others and, of course, the overall process efficiency. Therefore, the process should be considered as a whole. Consequently, all these aspects imply that proposing an efficient process is not an easy task. [18]

One of the most used methods are the process heuristics, which are sentences commonly accepted for the design and based on the experience. Despite being very used, sometimes provide contradictory guidelines. For that reason, some studies appeared to provide an equation inspired by the existing heuristics with the goal to provide a numerical value to decide when the heuristics do not point to a clear situation for column sequencing. At this point and having into account the proposed equation by Nadgir and Liu the CES-Coefficient of Ease of Separation, the Distillation Sequence Efficiency number (DSE from now on) equation was proposed.[19]

The DSE describes how good a distillation sequence is. It is based on the number of columns, the feed flow-rate, the exit streams from each column and the temperatures of the top and the bottom of each column. In addition, it does not rely on process heuristics therefore it avoids any contradictions.

The DSE number is evaluated by a simple equation to use in calculation because it requires a small number or readily available data input, such as boiling composition, and low computing effort. The DSE is calculated based on the feed composition and efficiency of each distillation column.

$$DSE = \sum_i x_i \cdot \prod_C \eta_{iC} \cdot 100 [\%] \quad (16)$$

In equation 16 the DSE is shown, where  $x_i$  is the molar fraction of each compound in the feed and  $\eta_{iC}$  the Carnot efficiency of the column, a dimensionless magnitude defined in equation 17 where  $T_{Bottom}$  and  $T_{Top}$  are the temperatures (in Kelvin units) of the streams coming out from the bottom and the top of the column respectively.

$$\eta_C = \frac{T_{Bottom} - T_{Top}}{T_{Bottom}} \quad (17)$$

The Carnot efficiency value is equal to the column efficiency when the desired product is collected as distillate, and the efficiency is equal to 100% for the columns in which the desired compound is collected as a bottom product.

Instead of using each composition, the DSE number is calculated as the sum of efficiencies of the output flows of each column, divided by the mixture feed flow rate. Thus, the DSE equation turns into equation 18.

$$DSE = \sum_i \frac{F_i}{F_{Feed}} \cdot \prod_c \eta_{ic} \cdot 100 [\%] \quad (18)$$

DSE is a parameter useful to determine how much efficient is a distillation sequence. It considers the molar fraction of the compounds in the feed stream and the Carnot efficiency of the column. As many streams are closed in the system, the DSE is calculated from the sum of efficiencies of output and recycling streams flow rate divided by the crude feed flow rate.

The efficiency depends on the path followed by the stream. An output stream efficiency depends on the columns efficiency from its path that is form feed and for the recycles the path forward is from the point where the recycled is mixed to where is recycled back and the path backwards is the recycle itself. The recycle flow rate has a negative efficiency of one for the path backwards.

The DSE definition for a sharp split sequence is presented in equation 19:

$$DSE = \sum_i x_i \cdot \prod_c \eta_{ic} \quad (19)$$

where,  $x_i$  = molar fraction of the compound in the feed of the sequence.

$\eta_{iC}$  = Carnot efficiency of the column C.

In this work, general DSE presented in equation 20 is used.

$$DSE = \sum_i W_i \cdot \prod_c \eta_{ic} \quad (20)$$

where,  $W_i$  = stream depending on the feed.

$\eta_iC$  = Carnot efficiency of the column C

The Carnot efficiency of the three columns are presented in equation 21 to 23.

$$\eta_1 = \frac{T_{B1} - T_{D1}}{T_{B1}} \quad (21); \quad \eta_2 = \frac{T_{B2} - T_{D2}}{T_{B2}} \quad (22); \quad \eta_3 = \frac{T_{B3} - T_{D3}}{T_{B3}} \quad (23);$$

The DSE number is used for the assessment of the distillation sequence efficiency. The DSE general expression for the studied processes schemes becomes equations 24 and 25 for the three and two columns process scheme respectively.

$$DSE = \frac{B_1}{F} + \frac{D_2}{F} \cdot \eta_1 \cdot \eta_2 + \frac{D_3}{F} \cdot \eta_1 \cdot \eta_3 \quad (24)$$

$$DSE = \frac{D_2}{F} \cdot \eta_2 + \frac{D_3}{F} \cdot \eta_3 \quad (25)$$

One data not provided in the articles, and required to calculate the DSE number, are the stream temperatures. Therefore, the column output streams at their boiling temperatures are determined using vapor liquid equilibrium binary diagrams generated with Aspen Plus®.

In order to provide some guideline about which is the optimum entrainer flow in an extractive distillation scheme, for each case the DSE number has been evaluated and also the corresponding DSE number for an infinite entrainer flow ( $DSE_\infty$ ). A stream with an infinite flow rate of entrainer has a boiling point close to the pure entrainer boiling point. A simple expression able to correlate the values of  $DSE_\infty$  and DSE is fitted. This

relation provides an equation with one unknown: The second column Carnot efficiency. This value provides the second column bottom temperature, which becomes related

with a fixed composition of the bottom stream. Finally, for a fixed crude flow rate and composition, the optimum entrainer flow rate can be easily determined.

In this case, better results are obtained. The multiple correlation coefficient has a value of 0.97, higher than the previous one. The determination coefficient is also higher. It has a value of 0.94, what indicates that the fitting to the regression is fairly good. A lower typical error is obtained, specifically of 1.44. Finally, equation 26 is obtained, with a slope of 0.78 and the interception in 0.00.

$$DSE = 0.78 \cdot DSE_{\infty} \quad (26)$$

Distillation Sequence Efficiency of an extractive distillation:

$$DSE = x_A \cdot \frac{(T - T_A)}{T} + x_B \cdot \frac{(T_E - T_B)}{T_E} \quad (27)$$

Assuming an infinite flow rate of extractive agent as limit condition, then  $T = T_E$ .

The maximum distillation efficiency:

$$DSE_{\infty} = x_A \cdot \frac{(T_E - T_A)}{T_E} + x_B \cdot \frac{(T_E - T_B)}{T_E} \quad (28)$$

Once this relation is established, it is possible to calculate the optimum entrainer flow for a process that must be designed. The optimum DSE value can be obtained, thus the  $\eta_2$  value too. What will provide the temperature of the bottom stream for the

extractive column and consequently its composition. This calculation process is described by equations 29 and 30.

$$\eta_2 = 0.78 \cdot \eta_{2,\infty} + \frac{D_3}{D_2} \cdot \eta_3 \cdot (0.78 - 1) \quad (29)$$

$$T_{BE} = \frac{T_A}{(1 - \eta_2)} \quad (30)$$

An easy way to get the molar fractions of a mixture starting from its boiling temperature is by liquid-vapour binary diagrams.

Finally, with a mass balance on the extractive column, the entrainer flow is obtained by equation 31, where B and E are molar flows and x is the molar fraction of entrainer in the output stream.

$$E = \frac{B \cdot x}{1 - x} \quad (31)$$

The main problem of the analysis of DSE is that when calculating the index of flow of optimum extractive agent, because it's not possible to know if it's working within the zone of feasibility of the system, then, what will carry out is the analysis explained previously with knit curves and isovolatility. Curves to calculate within the maximum and minimum values that can work on, and then calculate the optimum through DSE and see if it is within the feasible area. In the following point we will carry out some practical case.

### 3.6 OBTENTION BY LINEAL REGRESSION

By wanting to obtain results on the minimum agent flow rate, what we will try will be to obtain a valid proximation to the value of this rate using the composition of the feed and the fraction of the distillate of the first column.

This approach is carried out by means of the linear regression of the values of minimum agent flow rate relative to the feed and the value of the curve.

The purpose is that with this regression we will obtain an equation that will allow us to calculate from two data in a fast and simple way.



## 4 CASE STUDIED WITH THE PROPOSED METHODOLOGY

The case studied are the acetone-methanol-water, acetone-methanol-chlorobenzene, isopropanol-ethylene glycol-water, acetone-methanol-ethanol and acetone-methanol-isopropanol.

The design procedure is laid out in a step by step manner yielding a feasible design including its design parameters. The design specifications for the systems are listed in Table 3.

Component	$x_F$	$x_E$	$x_D$	D/F (E/F) <sub>min,bif</sub>
Isopropanol	0.62	0.0	1.0	0.62
Water	0.38	0.0	0.0	0.649
Ethylene glycol	0.0	1.0	0.0	
Acetone	0.7774	0.0	1.0	0.7774
Methanol	0.2226	0.0	0.0	0.740
Water	0.0	1.0	0.0	
Acetone	0.7774	0.0	1.0	0.7774
Methanol	0.2226	0.0	0.0	0.721
Ethanol	0.0	1.0	0.0	
Acetone	0.7774	0.0	1.0	0.7774
Methanol	0.2226	0.0	0.0	2.187
Isopropanol	0.0	1.0	0.0	
Acetone	0.7774	0.0	0.0	0.2226
Methanol	0.2226	0.0	1.0	0.788
Chlorobenzene	0.0	1.0	0.0	

Table 3. Design Specifications

The starting point in the extractive distillation design procedure is to perform the isovolatility curve calculation because it provides the necessary knowledge for determining which components will be removed as either a bottom or distillate product. Furthermore, the isovolatility curves provide a rapid and easy means for screening through a list of candidates entrainers in order to select the best one without taking into account economics. Finally, as was explained previously, the isovolatility curve provides an upper limit when the feed ratio tends to infinite values, and therefore, it provides a guide for the calculation of the minimum feed ratio.

## 4.1 ACETONE-METHANOL-WATER

What is being done now is to first make the graphical representation of the ternary diagram with the isovolatility curve.

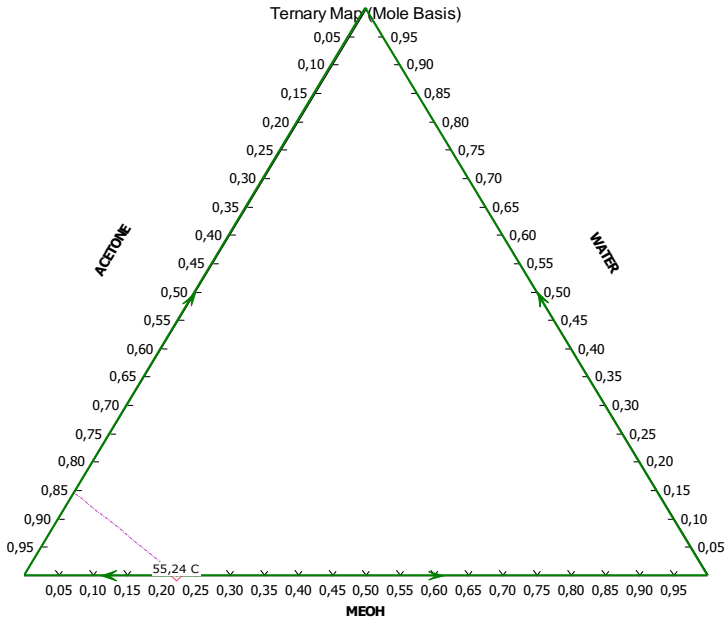


Figure 9. Ternary diagram with the isovolatility curve

Once we have the representation we find the composition of the compound that will be produced by the first column, in which case it is the acetone. This composition is on the edge between the composition of the extractor agent and the column head compound, exactly where it is cut with the isovolatility curve.

After having this value, we will take the food composition value of the case that we are studying, the information of this food is in the previous table. We also obtain the value of the minimum extractor agent flow rate. After having these three values, we have to move on to the next example until you have the results of all the cases studied.

Compositions	Minimum extractor flow rate	Feed fraction	Fraction on isovolatility curve
Acetone/MeOH/H <sub>2</sub> O	0,74	0,7774	0,86

Table 4. Acetone/MeOH/H<sub>2</sub>O

## 4.2 ACETONE-METHANOL-CHLOROBENZENE

As I said before, we have represented again the ternary diagram with the curve of isovolatility.

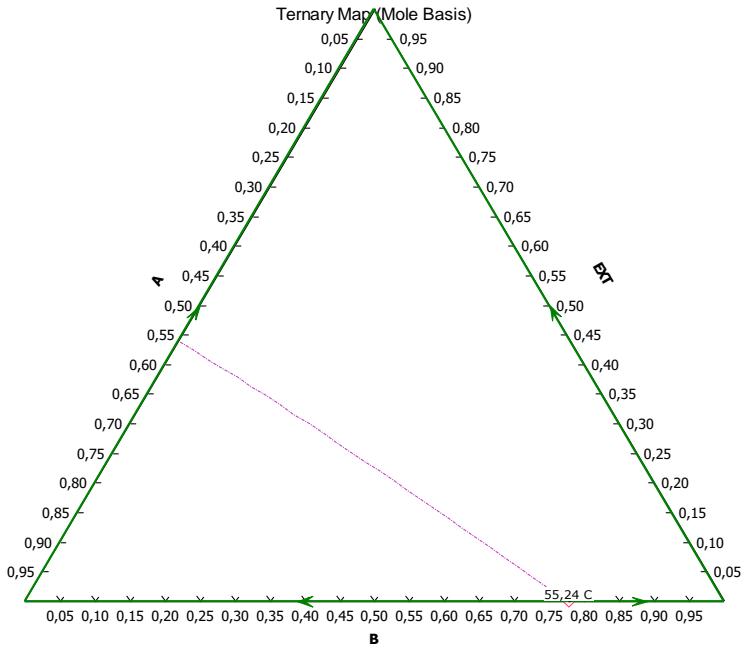


Figure 10. Ternary diagram with the isovolatility curve

In this diagram, compound A is acetone, compound B, methanol, and extractor chlorobenzene.

Once we have the representation we find the composition of the compound that will be produced by the first column, in which case it is the acetone. This composition is on

the edge between the composition of the extractor agent and the column head compound, exactly where it is cut with the isovolatility curve.

After having this value, we will take the food composition value of the case that we are studying, the information of this food is in the previous table. We also obtain the value of the minimum extractor agent flow rate. After having these three values, we have to move on to the next example until it's known have the results of all the cases studied.

Compositions	Minimum extractor flow rate	Feed fraction	Fraction on isovolatility curve
Acetone/MeOH/Chlorobenzene	0,788	0,7774	0,56

Table 5. Acetone/MeOH/Chlorobenzene

### 4.3 ISOPROPANOL-ETHYLENE GLYCOL-WATER

As I said before, we have represented again the ternary diagram with the curve of isovolatility.

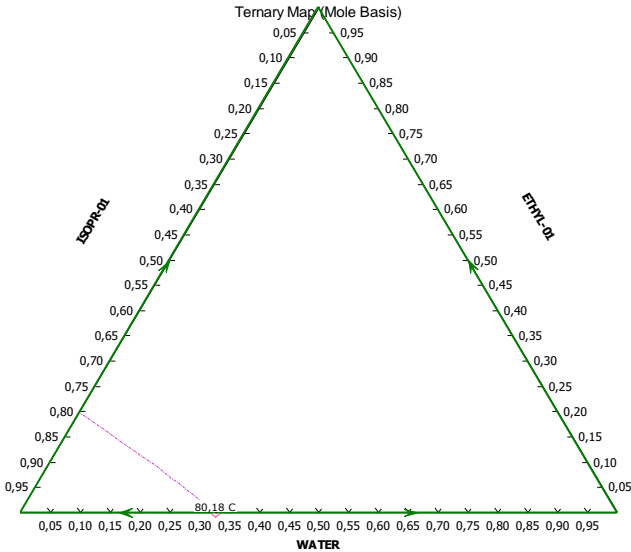


Figure 11. Ternary diagram with the isovolatility curve

In this diagram, compound A is i-propanol, compound B, water, and extractor ethylene glycol.

Once we have the representation we find the composition of the compound that will be produced by the first column, in which case it is the i-propanol. This composition is on

the edge between the composition of the extractor agent and the column head compound, exactly where it is cut with the isovolatility curve.

After having this value, we will take the food composition value of the case that we are studying, the information of this food is in the previous table. We also obtain the value of the minimum extractor agent flow rate. After having these three values, we have to move on to the next example until it's known have the results of all the cases studied.

Compositions	Minimum extractor flow rate	Feed fraction	Fraction on isovolatility curve
i-propanol/ethylene glycol/water	0,649	0,62	0,8

Table 6. i-propanol/ethylene glycol/water



#### 4.4 ACETONE-METHANOL-ETHANOL

As I said before, we have represented again the ternary diagram with the curve of isovolatility.

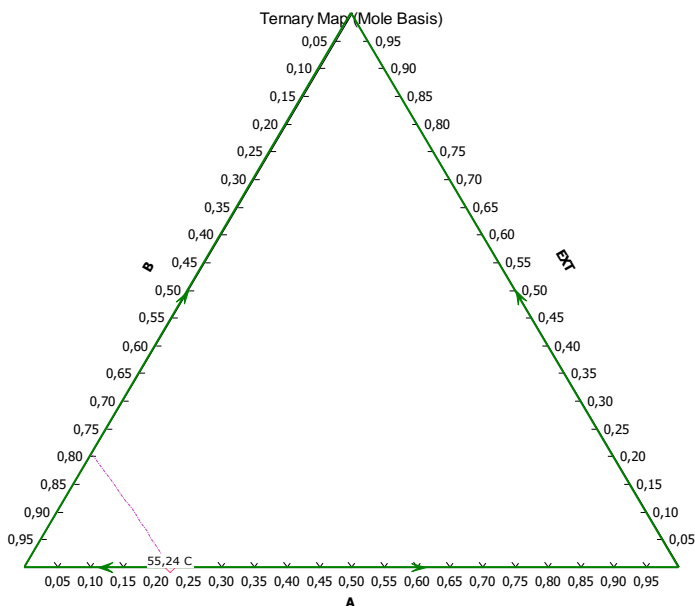


Figure 12. Ternary diagram with the isovolatility curve

In this diagram, compound B is methanol compound A, acetone, and ethanol as a extractor agent.

Once we have the representation we find the composition of the compound that will be produced by the first column, in which case it is the methanol. This composition is on

the edge between the composition of the extractor agent and the column head compound, exactly where it is cut with the isovolatility curve.

After having this value, we will take the food composition value of the case that we are studying, the information of this food is in the previous table. We also obtain the value of the minimum extractor agent flow rate. After having these three values, we have to move on to the next example until it's known have the results of all the cases studied.

Compositions	Minimum extractor flow rate	Feed fraction	Fraction on isovolatility curve
Acetone/MeOH/Ethanol	0,721	0,226	0,8

Table 7. Acetone/MeOH/Ethanol

## 4.5 ACETONE-METHANOL-ISOPROPANOL

As I said before, we have represented again the ternary diagram with the curve of isovolatility.

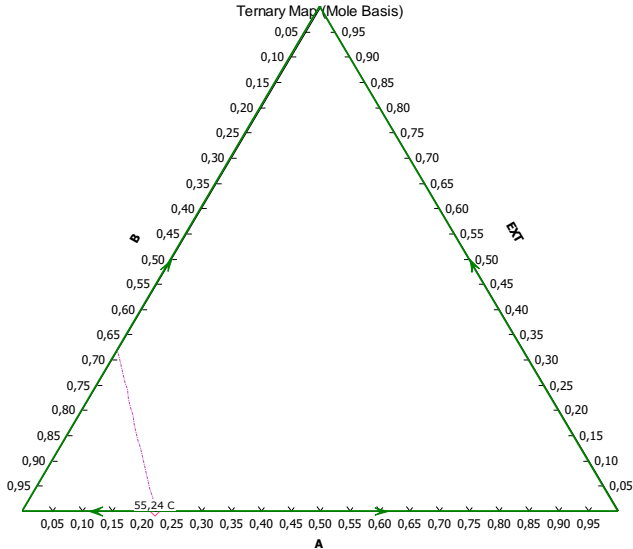


Figure 13. Ternary diagram with the isovolatility curve

In this diagram, compound B is methanol compound A, acetone, and isopropanol as a extractor agent.

Once we have the representation we find the composition of the compound that will be produced by the first column, in which case it is the methanol. This composition is on

the edge between the composition of the extractor agent and the column head compound, exactly where it is cut with the isovolatility curve.

After having this value, we will take the food composition value of the case that we are studying, the information of this food is in the previous table. We also obtain the value of the minimum extractor agent flow rate. After having these three values, we have to move on to the next example until it's known have the results of all the cases studied.

Compositions	Minimum extractor flow rate	Feed fraction	Fraction on isovolatility curve
Acetone/MeOH/isopropanol	2,187	0,226	0,68

Table 8. Acetone/MeOH/Isopropanol

#### 4.6 ANALYSIS OF RESULTS

In the following table we express all the results obtained:

Compositions	Minimum extractor flow rate	Feed fraction	Fraction on isovolatility curve
Acetone/MeOH/H <sub>2</sub> O	0,74	0,7774	0,86
Acetone/MeOH/chlorobenzene	0,788	0,7774	0,56
i-propanol/ethylene glycol/water	0,649	0,62	0,8
Acetone/MeOH/ethanol	0,721	0,226	0,8
Acetone/MeOH/isopropanol	2,187	0,226	0,68

Table 9. Information about any system

With this information, what we will carry out will be a linear regression in order to obtain the values of the coefficients that relate the values to obtain a function of the food fraction and the information obtained from the isovolatility curve, if we can simplify all calculation methods for minimum agent flow rate and achieve these results.

Compositions	Minimum extractor flow rate	Feed fraction	Fraction on isovolatility curve	Lineal regression aprox
Acetone/MeOH/H <sub>2</sub> O	0,74	0,7774	0,85	0,81884
Acetone/MeOH/chlorobenzene	0,788	0,7774	0,56	0,902244
i-propanol/ethylene glycol/water	0,649	0,62	0,8	0,786
Acetone/MeOH/ethanol	0,721	0,226	0,8	0,6678
Acetone/MeOH/isopropanol	2,187	0,226	0,68	2,42268

Table 10. Final results

With these results after the regression we can see that they have quite a few results and that it is a quick and easy way to have an approximation of the values of the minimum agent flow rate

#### 4.7 DSE COMPARISON WITH THE MINIMUM FEED RATIO OBTAINED

Once we have the minimum feeds ratio of the systems we must calculate the DSE of these, then, we will see if the DSE calculated will be in the feasible zone, otherwise if the feed ratio it's between the maximum and minimum reflex ratios searched before.

Now we have to do same for the acetone-methanol-water system:

We will start calculation for the system.

$$DSE_{\infty} = x_A \cdot \frac{(T_E - T_A)}{T_E} + x_B \cdot \frac{(T_E - T_B)}{T_E}$$

Where:  $T_E = T_{Water} = 373K$ ,  $T_A = T_{Acetone} = 329 K$ ,  $T_B = T_{Ethanol} = 351K$

Result:  $DSE_{\infty} = 0,106$

So, after calculating  $DSE_{\infty}$  we must calculate the temperature that makes:

$$DSE = 0,78 * DSE_{\infty} = 0,0829$$

Knowing:

$$DSE = x_A \cdot \frac{(T - T_A)}{T} + x_B \cdot \frac{(T_E - T_B)}{T_E}$$

This temperature is  $T = 354 K = 81 \text{ }^{\circ}\text{C}$

Finally, we have the calculated Temperature, graphically the binary diagram Tx-y of the methanol water system will calculate the methanol fraction of the system and from the material balance we will find the fraction of feed.

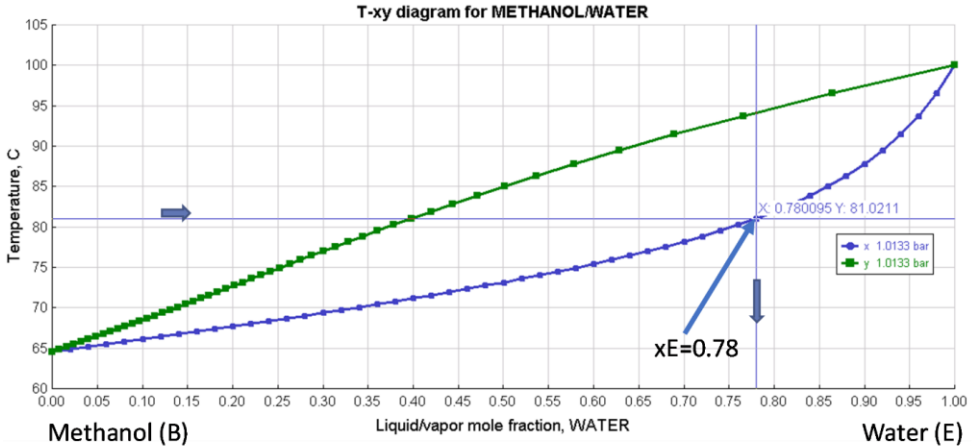


Figure 14. T-xy diagram for methanol/water

So, from the Figure 14, we obtain  $x_E = 0,78$ . Then we calculate the optimum feed ratio.

$$F_r = \frac{x_B \cdot x_E}{1 - x_E} = 1,81$$

With this result we obtain a  $F_r$  above the minimum found too so we are working in a feasible area.





## 5 CONCLUSIONS

A method for the conceptual design of dual feed columns was presented. The method extends the concepts proposed by Wahnschafft and Westerberg. Using the middle section pinch curves, it is possible to determine the feasibility region for extractive distillation. The concept of isovolatility curves is exploited to determine a priori which components can be recovered as distillate and bottoms products.

However, the BVM is inconvenient for mixtures with more than four components because of the lack of graphical representations for composition trajectories in higher dimensions.

Pinch point curves have been identified as the limiting trajectories, which mathematically are uniquely defined through the mass balances and the requirement that the vapor and liquid getting in contact at any stage must be in equilibrium. By determining these limiting trajectories, either by calculation or graphically using reasonably detailed residue curve maps, it is thus possible to decide without column simulations or design calculations whether the specified products are in principle feasible.

Furthermore, the isovolatility concept is very important in the screening of potential entrainers for extractive distillation because it shows which entrainer(s) will result in increased relative volatility of the azeotropic components. The methods developed in this work facilitate the direct determination of the minimum feed ratio, which in turn can

be used to determine the minimum reflux ratio, the number of stages, and the feed tray location for a given set of product and operating specifications. Using bifurcation theory and the features of the extractive pinch curves, the current method provides an alternative methodology for the determination of the design parameters of double-feed extractive distillation columns.

In extractive distillation, there are three important decisions to make at the time of optimizing a process; the entrainer selection and the entrainer flow rate.

The feasibility of a specified separation in a column with more than one feed can be examined without trial-and-error calculations.

## REFERENCES AND NOTES

- [1] McCabe, W. L., Smith, J. C., Harriot, P. *Operaciones unitarias en Ingeniería Química*. Editorial: McGraw Hill, 1991. ISBN: 0-07-044828-0
- [2] Górák, A., Sorensen, E. *Distillation: Fundamentals and principles*. Editorial: Elsevier, 2014. ISBN: 978-0-12-386547-2.
- [3] [https://en.wikipedia.org/wiki/Extractive\\_distillation](https://en.wikipedia.org/wiki/Extractive_distillation)
- [4] [http://www.separationprocesses.com/Distillation/DT\\_Chp04n1.htm](http://www.separationprocesses.com/Distillation/DT_Chp04n1.htm)
- [5] Laroche, L.; Bekiaris, N.; Andersen, H. W.; Morari, M. Homogeneous Azeotropic Distillation – Comparing Entrainers. *Can. J. Chem. Eng.* 1991, 69, 1302–1319
- [6] Wahnschafft, O. M.; Westerberg, A. W. The Product Composition Regions of Azeotropic Distillation-Columns. 2. Separability in 2-Feed Columns and Entrainer Selection. *Ind. Eng. Chem. Res.* 1993, 32, 1108–1120.
- [7] Estupiñán Perez, L., Dechaine, G. P., & Riascos, C.A.M. (2015). Simplified Conceptual Design Methodology for Double-Feed Extractive Distillation Processes. *Ind. Eng. Chem. Res.*, 54 (20), pp 5481–5493. DOI: 10.1021/ie501781p
- [8] Laroche, L.; Bekiaris, N.; Andersen, H. W.; Morari, M. Homogeneous Azeotropic Distillation - Comparing Entrainers. *Can. J. Chem. Eng.* 1991, 69, 1302–1319.
- [9] Knapp, J. P.; Doherty, M. F. Minimum Entrainer Flows for Extractive Distillation - a Bifurcation Theoretic Approach. *AIChE J.* 1994, 40, 243–268.
- [10] Levy, S. G.; Doherty, M. F. Design and synthesis of homogeneous azeotropic distillations. 4. Minimum reflux calculations for multiple-feed columns. *Ind. Eng. Chem. Fundam.* 1986, 25, 269-279.
- [11] Van Dongen, D. B.; Doherty, M. F. Design and synthesis of homogeneous azeotropic distillations. 1. Problem formulation for a single column. *Ind. Eng. Chem. Fundam.* 1985, 24, 454–463.
- [12] Fidkowski, Z. T.; Malone, M. F.; Doherty, M. F. Nonideal multicomponent distillation: Use of bifurcation theory for design. *AIChE J.* 1991, 37, 1761–1779.
- [13] Bruggemann, S.; Marquardt, W. Shortcut methods for nonideal multicomponent distillation: 3. Extractive distillation columns. *AIChE J.* 2004, 50, 1129–1149.
- [14] Tanaka, S.; Yamada, J. Graphical Solution of Operating Region in Extractive Distillation. *Kagaku Kogaku (Abridged Ed.)* 1965, 3 (1), 40-43.
- [15] Levy, S. G. Design of Homogeneous Azeotropic Distillations. Ph.D. Dissertation, The University of Massachusetts, Amherst, 1985.
- [16] Berg, L.; Yeh, A. The Unusual Behavior of Extractive Distillation-Reversing the Volatility of the Acetone-Isopropyl Ether System. *AIChE J.* 1985, 31 (3), 504-506.
- [17] Knapp, J. P.; Doherty, M. F. Thermal Integration of Homogeneous Azeotropic Distillation Sequences. *AIChE J.* 1990, 36, 969–984.

- 
- [18] Plesu, V., Bonet Ruiz, A. E., Bonet, J., Llorens, J., Iancu, P. (2014) Shortcut assessment of alternative distillation sequence schemes for process intensification; *Computers and Chemical Engineering*, 83, pp. 58-71.
- [19] Nadgir, V., Liu, Y. *Studies in chemical process design and synthesis: Part V: a simple heuristic method for systematic synthesis of initial sequences for multicomponents separations. AIChE J.* 1983; 29 (6): 926-34.

## **ACRONYMS**

(F<sub>r</sub>) Feed ratio

(D) Distillate

(F) Feed

(DSE) Distillate Sequence Efficiency

(x) Molar fraction

(y) Vapor fraction









