



# Treball Final de Grau

**Optimal Pressure for Pressure Swing Distillation**

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## SUMMARY

Distillation is the most common unit operation for separation used in the industry. Many times, the mixtures to be separated have closely related boiling points or are azeotropic systems. In these cases, the conventional distillation doesn't work. In order to achieve the separation different forms have been developed to solve these cases. This work focus on azeotropic systems where the separation is achieved without the use of external agents. The pressure-swing distillation (PSD) allows the separation of the different components of the mixture making use of the sensitivity in the azeotropic composition which some mixtures have in front of different pressures.

An exhaustive bibliographic study is presented on no reactive binary mixtures where the separation is being achieved by PSD. Out of this search 180 articles were selected which in a first selection have been reduced to 140. Of these 140 a synthesis and a critical analysis was conducted of each article followed by a classification applying different criteria. As consequence of the analysis more articles have been excluded for not complying with the specific conditions of the search leading to a final number of 49 articles.

PSD has not been intensively studied, most of the publications in this field following the same criteria. This work will show that the majority of the investigations have been made following the criteria of the working pressure of the columns at 1 and 10 atmospheres and will be explained the considerations that have been taken in the investigations of the column pressures which have been optimized. Will also be explained the other classifications that have been applied at making the survey and will be concluded the general lines that have to be applied at selecting de PSD as method for the separation of the present mixture.

Once the study had been concluded was found that there are very few cases in which the selection of the pressures had been made optimizing the process according the energetic cost of the reboiler. From the articles that have followed this criterium has been selected one and made the simulation to compare the results: the ethyl acetate - ethanol mixture studied by Zhang et al. (2017) was selected to study. A simulation of the mixture was conducted, using the program

AspenPlus V10 with the parameters of the article and realizing the optimization with different pairs of pressures. Once the optimized values were obtained a total annual costs (TAC) was conducted in order to compare the results with those of the articles.

**Keywords:** Azeotropic distillation, ethyl acetate/ethanol, steam costs, optimization, AspenPlus

## RESUM

La destil·lació és la operació de separació més utilitzada en la indústria. Moltes vegades les mescles amb les que es treballa presenten punts d'ebullició molt propers o són sistemes azeotròpics. En aquests casos la destil·lació convencional no serveix. Per a poder dur a terme la separació s'han creat diferents formes per a poder assolir la separació que desitgem en aquests casos. Aquest treball es centra en sistemes azeotròpics on la separació es duu a terme en dos columnes sense afegir cap agent extern. La *pressure-swing distillation* (PSD) permet la separació dels diferents components d'una mescla aprofitant la sensibilitat en la composició azeotròpica que tenen algunes mescles als canvis de pressió.

Es presenta una cerca bibliogràfica exhaustiva sobre mescles binaries no reactives on la separació es duu a terme mitjançant la PSD. D'aquesta cerca s'han extret 180 articles dels quals després de fer una primera selecció s'han reduït a uns 140. D'aquest 140 s'ha realitzat una síntesis i anàlisi crític de cadascun d'ells classificant aquests segons diferents criteris. Després de fer l'anàlisi s'han anat descartant degut a què no complien les condicions específiques de la cerca fins arribar a una classificació final de 49 articles.

La PSD ha sigut fins ara un camp molt poc explorat on la majoria de treballs realitzats segueixen els mateixos criteris. En aquest treball s'exposa com la majoria d'investigacions s'han fet seguint el criteri de selecció de pressions de treball de les columnes a 1 i 10 atm i s'explicaran les consideracions que es fan en les investigacions on les pressions de les columnes es seleccionen optimitzant. També s'explicaran les altres classificacions que s'han fet a l'hora de fer la cerca i s'extrauran les directrius generals que es duen a terme a l'hora de seleccionar la PSD com a mètode per la separació de la mescla que es treballa.

Un cop feta la cerca, s'ha determinat que són molt pocs els casos en que la selecció de pressions es faci optimitzant segons els costos energètics del calderí. Dels articles que han seguit aquest criteri n'hem seleccionat un i hem fet la simulació per comparar resultats: la mescla etanol – etil acetat estudiat per Zhang et al. (2017) ha sigut l'elegit com a cas d'estudi. S'ha fet la simulació

de la mescla amb el programa AspenPlus V10 seguint els paràmetres dels articles i s'ha optimitzat per diferents parells de pressions. Un cop s'han obtingut els resultats optimitzats s'ha realitzat el TAC per poder comparar resultats amb l'article.

**Paraules clau:** Destil·lació azeotròpica, acetat d'etil/etanol, costos dels serveis calents, optimització, AspenPlus

# 1. INTRODUCTION

Among all the separation technologies, distillation is the most common unit operation used in the industry, and it consumes approximately 95% of the total energy used in the chemical separation industry. Many times, liquid mixtures are not amenable to ordinary fractional distillation. These mixtures have closely related boiling points and low relative volatility that make difficult and often uneconomical the distillation or are azeotropic systems that makes impossible to make the separation by ordinary distillation. These types of mixtures are widely found, and many industrial processes are in need for efficient and economical methods for their separation.

This study will focus on pressure-swing distillation. This technology consists in combining various distillation columns that operate at different pressures. Applying moderately different pressures in the different distillation columns some azeotropic mixtures can be separated.

## 1.1. AZEOTROPE

Vapor-liquid phase equilibrium (VLE) in a  $c$ -component mixture from low to moderate pressures can be represented by

$$y_i \cdot P = x_i \cdot \gamma_i \cdot P_i^{sat} \quad (1)$$

The activity coefficient ( $\gamma_i$ ) is a measure of the liquid-phase nonideality of a mixture and its value varies with both temperature and composition. When  $\gamma_i = 1$  the liquid phase is said to form an ideal solution and equation (1) reduces to Raoult's law. Nonideal mixtures ( $\gamma_i \neq 1$ ) can exhibit either positive ( $\gamma_i > 1$ ) or negative ( $\gamma_i < 1$ ) deviations from Raoult's law. Positive deviations are more common and occur when the molecules of the different compounds in the solution are dissimilar and have no preferential interactions between them. Negative deviations occur when there are preferential attractive forces between the molecules of the different species that do not occur in the absence of the other species. If these deviations are large enough, the pressure-composition (P-x,y) and temperature-composition (T-x,y) phase diagrams exhibit a minimum or maximum point. (Kirk-Othmer, 2004)

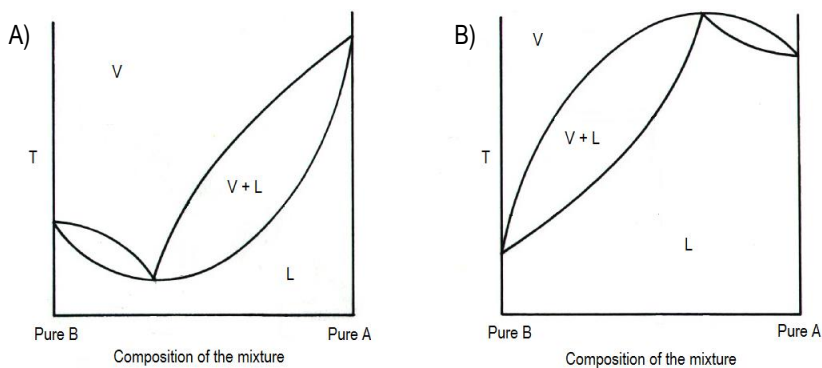


Figure 1. Boiling temperature diagrams for non-ideal mixtures of liquids showing A) positive and B) negative deviations from Raoult's law.

When the deviation is positive (case A)) the azeotropic mixture shows a minimum boiling temperature point. When the deviation is negative (case B)) the azeotropic mixture shows a maximum boiling temperature point.

At these minimum and maximum point the liquid phase and its equilibrium vapor phase have the same composition

$$y_i = x_i \quad \text{for} \quad i = 1, \dots, c \quad (2)$$

In this point the mixture boils at constant temperature, and the dew-point (vapor) and bubble-point (liquid) curves are tangent with zero slope making that the mixture passes directly from liquid to vapor phase without intermediate phase.

### 1.1.1. Ethyl acetate – ethanol azeotrope

Ethyl acetate and ethanol are some important solvents and both are important raw materials widely used in the chemical industry due to their excellent capacity as dissolvent. The mixture of them form a minimum azeotrope at atmospheric pressure that is impossible to separate by conventional distillation. To isolate these products several separation technologies are being used: azeotropic distillation, membrane separation, and liquid-liquid extraction as an example. The most widely technology used is the extractive distillation.

Due to the sensitivity that the composition presents to the changes of pressure, the possibility to separate the mixture by PSD has been studied. Having realized a bibliographic survey, a study made by Zhang et al. (2017) has been selected and used as basis for a comparison of our simulation results with those of Zhang et al. (2017).

## 1.2. DISTILLATION

Separation operations achieve their objective by the creation of two or more coexisting zones which differ in temperature, pressure, composition, and/or phase state. Each molecular species in the mixture to be separated responds in a unique way to differing environments offered by these zones. Consequently, as the system moves toward equilibrium, each species establishes a different concentration in each zone, and this results in a separation between the species. (Perry's, 2007)

The essential parameter for the enrichment is the relative volatility defined by:

$$\alpha_{ij} = \frac{y_i x_j}{x_i y_j} = \frac{\gamma_i \cdot P_i^{sat}}{\gamma_j \cdot P_j^{sat}} \quad (3)$$

The larger the value of  $\alpha_{ij}$ , the easier it is to separate component  $i$  from component  $j$ . From equation (2), at a  $c$ -component homogeneous azeotrope,  $y_i = x_i$  for all  $c$  components in the mixture. Therefore,  $\alpha_{ij} = 1$  for all components  $i$  and  $j$  and no enrichment of the vapor takes place during a partial vaporization. Thus, homogeneous azeotropes cannot be separated by ordinary fractional distillation. (Kirk-Othmer, 2004)

The feed material, which is to be separated into fractions, is introduced at one or more points along the column shell. Because of the difference in density between vapor and liquid phases, liquid runs down the column, cascading from tray to tray, while vapor flows up the columns, contacting liquid at each tray.

Liquid reaching the bottom of the column is partially vaporized in a heated reboiler to provide boil-up, which is sent back up the column. The remainder of the bottom liquid is withdrawn as bottoms, or bottom product. Vapor reaching the top of the column is cooled and condensed to liquid in the overhead condenser. Part of this liquid is returned to the column as reflux to provide liquid overflow. The remainder of the overhead stream is withdrawn as distillate, or overhead

product. In some cases, only part of the vapor is condensed so that a vapor distillate can be withdrawn.

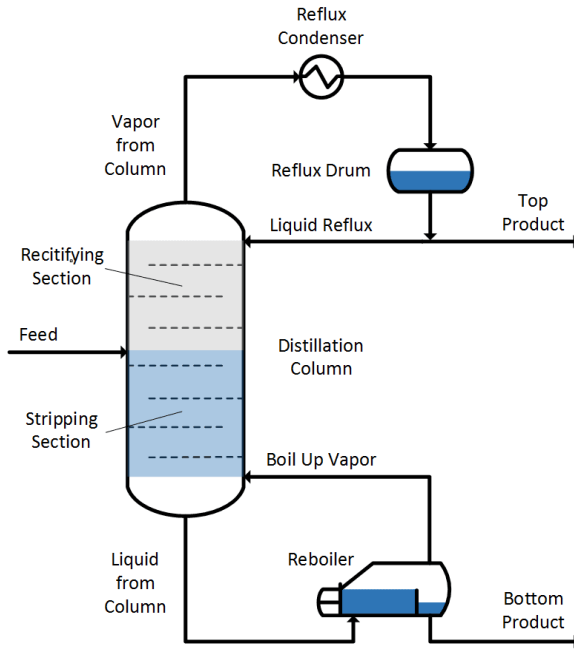


Figure 2. Schematic diagram for a simple continuous distillation column.  
(*Distillation Fundamentals*, 13/04/2018 via Neutrium)

This overall flow pattern in a distillation column provides countercurrent contacting of vapor and liquid streams on all the trays through the column. Vapor and liquid phases on a given tray approach thermal, pressure, and composition equilibria to an extent dependent upon the efficiency of the contacting tray.

The lighter (lower-boiling temperature) components tend to concentrate in the vapor phase, while the heavier (higher-boiling temperature) components concentrate in the liquid phase. The result is a vapor phase that becomes richer in light component as it passes up the column and a liquid phase that becomes richer in heavy components as it cascades downward. The overall separation achieved between the distillate and the bottoms depends primarily on the relative volatilities of the components, the number of contacting trays in each column section, and the ratio of the liquid-phase flow rate to the vapor-phase flow rate in each section.



If the feed is introduced at one point along the column shell, the column is divided into an upper section, and a lower section, which is often called the rectifying section, and a lower section, which is often referred to as the stripping section. (Perry's, 2007)

### 1.2.1. Azeotropic distillation

Various techniques have been developed facing the characteristics of azeotropic mixtures which include choosing an entrainer in order to create with the azeotrope specific distillation regions and node temperatures or to cause an azeotrope formation in combination with L-L immiscibility, exploiting changes in the composition with total system pressure and exploiting the curvature of distillation region boundaries.

#### 1.2.1.1. Pressure-swing distillation

Out of the numerous azeotropes only a fraction of them are sufficiently pressure-sensitive to be treated by PSD on an economical scale. In order to use this technique, the azeotropic composition must vary at least 5% (preferably 10 or more) over a pressure range, which preferably does not exceed 10 atm. A very large pressure range may result in the need of refrigeration for de condensation of the low-pressure distillate or a high reboiler temperature may result in the high pressure column (HPC).

For the application of the PSD three aspects must be considered:

- a. The azeotropic composition must be sensitive to pressure changes.
- b. The components of the mixture must not decompose with the increase of the pressure.
- c. In case of operation with on the vacuum, the pressure must be maintain in a pressure range that ensures that cooling water can be used. Any other cooling media will always cause higher operating costs.

For a binary mixture forming a pressure-sensitive, minimum-boiling azeotrope, the fresh feed,  $F$ , is mixed with the recycled stream from the second column to form the feed stream,  $F_1$ , to the first column, which operates at pressure  $P_1$ . (Alternatively, these two streams can be fed to separate points in the first column). Because  $F_1$  lies to the right of the azeotrope at pressure  $P_1$ , pure component A is removed as the bottom product,  $B_1$ , and a mixture near the azeotropic

composition at pressure  $P_1$  is the distillate,  $D_1$ . Stream  $D_1$  is changed to pressure  $P_2$  and fed to the next column as stream  $F_2$ . Because  $F_2$  now lies to the left of the azeotropic composition at pressure  $P_2$ , the other pure component, B, can be recovered in the bottom stream,  $B_2$ , and a near azeotropic mixture becomes the distillate,  $D_2$ , which is recycled to the first column. The greater the shift in azeotropic composition, the smaller the recycle flows rate will be relative to the product flow rates, and thus, the smaller the columns diameters and the more economical the process will be. An analogous procedure is used for binary maximum boiling azeotropes, except the pure component products are recovered as distillates and the near azeotropic streams come out of the bottom of each column. In processes with maximum azeotropes there is a risk of accumulation of high-boiling impurities in the recycle streams that makes the operation of the process more difficult. (Kirk-Othmer, 2004)

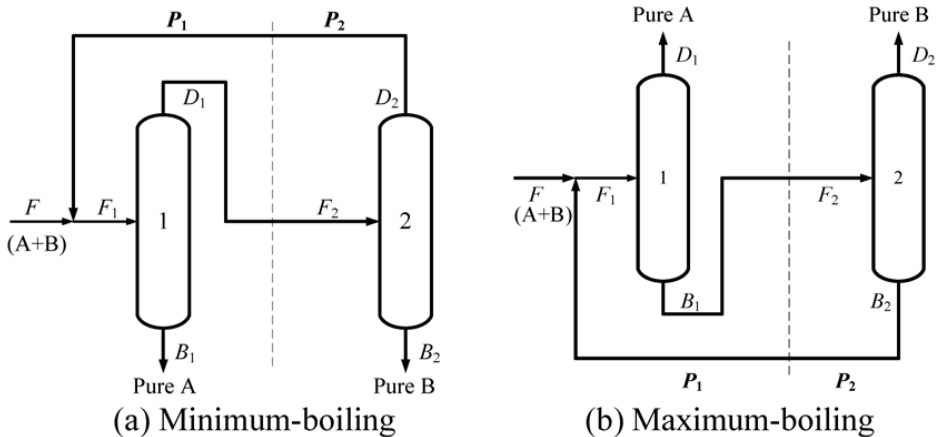


Figure 3. PSD sequence for (a) minimum-boiling azeotrope and (b) maximum-boiling azeotrope (extracted image from Fulgueras et al. 2016, Fig 2.)

## **2. OBJECTIVES**

The aim of this work is to conduct an exhaustive bibliographic revision of the different methods which are applied in order to select the pressures when conducting the distillation of an azeotropic mixture by means of the PSD. The review was intended to create a basis of articles classified by the criteria they have followed at selecting the pressures.

After finishing the search, a simulation was conducted of one of the articles. A comparison of the simulation with the article of Zhang et al. (2017) was conducted to show that the parameter that defines the optimum pressure of the columns depends essentially from the prices of the hot services of the reboiler by that avoiding to calculate the annual cost for each pressure.

Concerning the simulation of the mixture selected, the pressures had been optimized, and it was compared with the results of the article in order to verify if our theory coincides with their results.



### 3. LITERATURE REVIEW

Among all types of azeotropic distillation techniques, clearly, extractive distillation is the most widely used one. This technique is composed by 2 columns where an extractive agent is introduced with the azeotropic mixture to the first column. In this column the component A of the mixture will be separated, and a mixture of the agent and de component B will be fed to the second column. In this column component B will be separated from the agent and this will be recirculated to the first column. The process results in a loss of the agent and causes impurities in products A and B.

As explained before (1.2.1.1) PSD can only be used in certain azeotropic mixtures. This has let that PSD has not been widely investigated. In the majority of researches applied directly extractive distillation method.

In the past decades, PSD has gained some ground due to the advantages it presents in comparison to the extractive distillation. Society is advancing rapidly to a point where many resources are getting scarce and the PSD gives the opportunity to achieve the separation without the use of external components.

Due to the importance to reduce at maximum the losses of raw materials and at the same time optimizing the utilization of clean energy result in PSD being a very good alternative. An increasing number of investigators study the extractive distillation and the PSD in order to have a comparison between the costs of the two techniques. PSD clearly utilizes more energy due to the working pressures in the HPC and therefore the higher temperatures. Even when at first glance the extractive distillation appears to be more economical than PSD at a second glance and more profound study it may show the opposite. In the course of the study we will explain the method and the results of the articles of reference.

The research has been made in the search page Scopus with the following specifications: TITLE-ABS-KEY ("pressure swing") AND TITLE-ABS-KEY (distillation) AND NOT TITLE-ABS-KEY (adsorption) AND (LIMIT-TO (LANGUAGE, "English")). Also, it was based on the article

Liang et al. (2017). In addition, the following limitations have been applied: only binary-non-reactive systems will be studied, on continuous operation and without secondary entrainers.

It was decided to introduce these limitations after a first scrutiny of the articles since we considered that the adopted parameters were the most suitable ones for the mixture that was wanted to investigate.

Due to the great number of classifications which have been applied in each article, was decided to form to sections. The first section will be focused in the nature of the azeotropic mixtures and the second section will explain the criteria that have been followed at selecting the pressures of each column.

### **3.1. AZEOTROPIC NATURE**

In this section will be classified the different investigations that have been done according to the mixture that is being worked on. We will explain from every mixture the type of azeotrope, the system of columns used (HP-LP or LP-HP) and the authors who have published each one of these investigations.

Many of these articles are follow ups of previous studies where either the same pressures are applied and study other issues (most of them study the columns control) or optimize the process utilizing the data of the previous studies. The majority of the follow ups of these articles study other fields.

### 3.1.1. Type of azeotrope (Min-B or Max-B)

In the list that will be showed later appear 24 different mixtures. As can be seen in Figure 4 clearly the majority of azeotropic mixtures show a minimum boiling point.

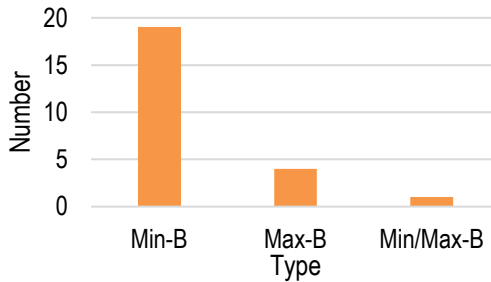


Figure 4. Type of azeotrope

Table 1 shows that the mixtures with positive deviations (minimum-boiling point) are much more common than the mixtures with negative deviations (maximum-boiling point), in accordance to the previously stated in 1.1..

### 3.1.2. Sequence of columns (LP-HP or HP-LP)

As can be seen in the *Table 1* the majority of the studies have selected a system of a LPC (low pressure column) followed by a HPC (high pressure column). Only a small number of studies execute a previous study to determine which combination is more advantageous (LP-HP or HP-LP). The majority chooses directly the LP-HP system if they work with a Min-B mixture and the HP-LP system if they work with a Max-B mixture.

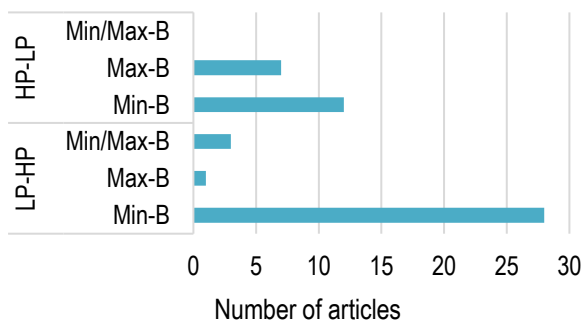


Figure 5. Sequence of columns

The literature studied did not give clues by which criteria the sequence of columns had been decided. After searching for the reasons why they do not conduct a study to find the optimum sequence of the columns, it was noticed the majority of the studies selects the LPC as the first column when the composition of the mixture at the feed is very different than the azeotropic composition at the selected pressures. When the composition of the feed mixture is very similar to the composition of the azeotropic mixture the HPC is selected as first column.

However, no conclusion was reached related to the use of the LPC as first column when the azeotrope is a Min-B azeotrope and the HPC as first column when the azeotrope is a Max-B azeotrope.

Table 1. Classification of the azeotropic nature

	<b>Mixture</b>	<b>Type</b>	<b>System</b>	<b>Reference</b>
1	<b>Acetic acid + DMAC (dimethylacetamide)</b>	Max B	LP – HP	Luyben (2012)
2	<b>Acetone + chloroform</b>	Max B	HP – LP	Luyben (2013a)
3a	<b>Acetone + methanol</b>	Min B	LP – HP	Modla and Lang (2012)
3b		Min B	LP – HP	Luyben (2012)
3c		Min B	LP – HP	Luyben (2008a)
3d		Min B	LP – HP	Fulgueras et al. (2016)
3e		Min B	LP – HP	Wang et al. (2016a)
4a	<b>Acetonitrile + water</b>	Min B	HP – LP	Repke et al. (2005)
4b		Min B		Huang et al. (2008)
4d		Min B	HP – LP	Repke et al. (2004)
5	<b>Acetonitrile + n-propanol</b>	Min B	LP – HP	Wang et al. (2016)
6a	<b>Chloroform + methanol</b>	Min B	LP – HP	Hosgor et al. (2014)
6b		Min B	LP – HP	Wang et al. (2016a)
7a	<b>Diisopropyl ether + isopropyl</b>	Min B	HP – LP	Luo et al. (2014)
7b	<b>alcohol</b>	Min B	LP – HP	Xia et al. (2017)
7c		Min B	HP – LP	Luyben (2018)
8	<b>Di-n-propyl ether + n-propyl alcohol</b>	Min B	LP – HP	Lladosa et al. (2011)
9	<b>Ethanol + toluene</b>	Min B	LP – HP	Zhu et al. (2015)



10a	<b>Ethanol + water</b>	Min B	LP – HP	Kiran and Jana (2015b)
10b		Min B	LP – HP	Mulia-Soto and Flores-Tlacuahuac (2011)
10c		Min B	LP – HP	Arifeen et al. (2007)
11	<b>Ethyl acetate + ethanol</b>	Min B	HP – LP	Zhang et al. (2017)
12	<b>Isoamyl acetate + isoamyl alcohol</b>	Min B	LP – HP	Rojas et al. (2016)
13a	<b>Isobutyl alcohol + isobutyl acetate</b>	Min B	HP – LP	Muñoz et al. (2006)
13b		Min B	HP – LP	Luo et al. (2016)
14	<b>Methanol + benzene</b>	Min B	HP – LP	Qasim et al. (2018)
15a	<b>Methanol + dimethyl carbonate</b>	Min B	HP – LP	Wei et al. (2013)
15b		Min B	HP – LP	Zhang et al. (2017)
16a	<b>Methanol + THF</b>	Min B	LP – HP	Wang et al. (2015b)
16b		Min B	LP – HP	Wang et al. (2014)
17a	<b>Methanol + trimethoxysilane</b>	Max B	HP – LP	Luyben (2014a)
17b		Max B	HP – LP	Luyben (2014b)
18a	<b>Methyl acetate + methanol</b>	Min B	HP – LP	Bonet et al. (2007)
18b		Min B	LP – HP	Zhang et al. (2016)
18c		Min B	HP – LP	Cao et al. (2016)
19	<b>Methylal + methanol</b>	Min B	LP – HP	Yu et al. (2012)
20a	<b>N-Heptane + isobutanol</b>	Min/Max. B	LP – HP	Wang et al. (2016b)
		Min/Max. B	LP – HP	
20b		Min/Max. B	LP – HP	Luyben (2017)
21a	<b>THF + ethanol</b>	Min B	LP – HP	Wang et al. (2015a)
21b		Min B	LP – HP	Wang et al. (2015c)
22a	<b>THF + water</b>	Min B	LP – HP	Abu-Eishah and Luyben (1985)
22b		Min B	LP – HP	Frank (1997)
22c		Min B	LP – HP	Luyben (2008b)
22d		Min B	LP – HP	Lee et al. (2011)
22e		Min B	LP – HP	Ghughe et al. (2017)
22f		Min B	LP – HP	Hamad and Dunn (2002)

23	<b>Toluene + 1-butanol</b>	Min B	LP – HP	Qasim et al. (2015)
24a	<b>Water + ethylenediamine</b>	Max B	HP – LP	Li et al. (2016)
24b		Max B	HP – LP	Fulgueras et al. (2015)
24c		Max B	HP – LP	Modla (2010)
24e		Max B	HP – LP	Modla and Lang (2007)

### 3.2. PARAMETER SELECTION

After a profound study of the different articles 4 criteria have been determined when the pressure has to be defined. Being the PSD a scarcely explored field many had applied the 1 – 10 atm heuristic. This tendency got less in the last years (as the change can be seen looking at the publication dates of the articles).

Many of the authors have realized that although the 1-10 atm heuristic is a valid choice and gives usable working range in the composition of the azeotrope not all the azeotropes respond equally to the changes of pressure. Even with a not too profound study of how the pressure affects the composition of the mixture results in a much more suitable selection of the pressure.

The task of an engineer lies among others in achieving the best cost, therefore, why just a small of articles dedicate themselves to optimize the pressure?

After a first review of the articles was decided to make an initial classification about which criteria the authors followed at the moment to select the pressures. Four criteria have been determined:

1. They select the pressure following the 1 – 10 atm heuristic
2. According to the working temperature of the condenser
3. According to the costs of the reboiler steam
4. Fixing a shift in the azeotropic composition

As previously stated the engineer intends (among other criteria) to minimize the costs, that's why for some time many of the studies apply a technique called HIPSD resulting in substantial savings of energy.

Separation techniques require the application of energy either the form of work or heat. The distillation operation requires energy in form of heat. Commonly, the heat is introduced in the lower part of the column, more specifically in the reboiler. Does the temperature is highest in the lower section of the column and lowest in the upper section. In the condenser energy is being removed. The result is a large energy input and a low overall thermodynamic efficiency which can be diminished by reutilizing the energy of the condenser. One way to reutilize the energy is applying the technique called Heat Integration Pressure-Swing Distillation (HIPSD).

The HIPSD can be applied by two ways:

- a. By integrating the condenser in the HPC with the reboiler in the LPC by means of a heat exchanger.
- b. By integrating the stripping section in the LPC with the rectifying section in the HPC.

Although a growing number of articles apply this technique representing many energetic and economic advantages, just a small number of articles apply the edge HIPSD by optimizing pressures. At using HIPSD for columns at which the pressures have been selected without optimizing or where the pressures have been selected in order to be able to use HIPSD the economic improvements may not represent the optimum.

When using HIPSD without applying the optimum pressure probably the working pressures will not be the most suitable ones and the process will not achieve the best cost due to the fact that only the energetic costs have been taken in account. The same occurs if the pressures are being defined in order to be able to apply HIPSD. Probably the selected pressures are not suitable for the specific mixture and the operation costs will be higher.

HIPSD simulation is not performed in this work due to time limitation, but it would be advisable as a further step of the research in order to analyse the costs and energy reduction due to its implementation.

### 3.2.1. Criteria

1. 1 – 10 atm heuristic
2. Working temperature of the condenser

If the LPC works at vacuum pressure, probably cooling water can not be used as refrigerating agent depending from the working pressure and therefore other cooling agents must be used, being much more expensive.

That is why many studies select the working pressures of the columns in order than the LPC is in condition to utilize cooling water as refrigerating agent. Other studies select a pressure of 1 atm for the LPC because for economic reasons: working at vacuum pressure is much more expensive than operating at atmospheric pressure.

Was not founded a study comparing the costs between utilizing a more expensive cooling agent than water working the LPC at atmospheric pressure or utilizing cooling water with LPC operated at vacuum. We think it should be studied more profoundly whether the equipment cost of a column operated in vacuum results in higher of lower operating costs comparing with a column operated at atmospheric pressure and maybe therefore not being capable to use water as cooling agent.

Most of the studies select a cooling water temperature in order to provide a temperature difference of 10 to 20 degrees between cooling agent and distillate. Within this range of 10 to 20 degrees the studies determine a given temperature e.g. 15°C resulting in a boiling point of the azeotrope (in case of a Min-B azeotrope) or the boiling point of one of the components of the mixture (in case of a Max-B azeotrope). They obtain the working pressure of the column since every boiling temperature corresponds to a determined pressure.

From this point on they can select the pressure of the HPC by 4 different ways:

- A. Selecting the pressure when an important shift in the composition occurs.
- B. Selecting the pressure of the HPC with a goal to minimize the costs while the working pressure of the LPC is fixed.
- C. Selecting the pressure of the HPC in order to be able to use a certain type of steam in the reboiler.

The reboiler works with a steam (normally evaporated water) that work at different levels: low-pressure (LPS), medium-pressure (MPS) or high-pressure steam (HPS).

Each one of this work at different temperature ranges being LPS working at lower level, MPS working at medium level and HPS at higher level. As we change from one type of steam to another the costs rise and finally reach a local minimum and at the end to reach an absolute minimum with HPS.

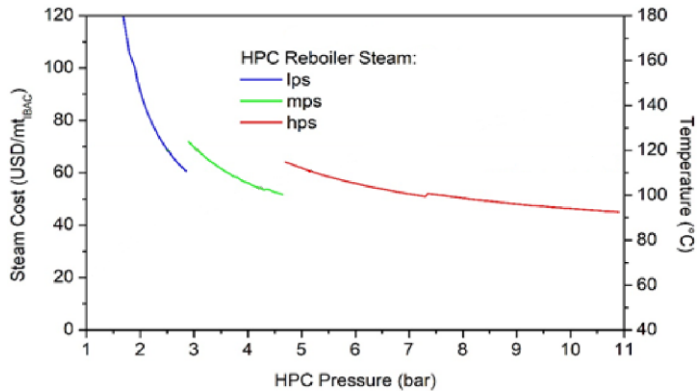


Figure 6. Steam cost example

The operating pressure of the columns have a high impact to the operating costs due to the fact that as the pressure raises the cost of the steam generation also raises but at the same time the working costs diminish because working the columns at higher pressures the difference in the azeotropic composition is larger and less recirculation flow is necessary.

The majority of these studies select one type of steam and stay in one of these minimums without conducting a global study of the cost of operation.

D. Selecting the pressure in order to be able to use HIPSD.

### 3. Costs of the steam for heating the reboiler

It is well known that distillation consumes high amounts of energy, which leads directly to the emission of carbon dioxide into the atmosphere. As exposed before, due to the environmental issues and also the surge of the cost of energy the engineers are obliged to explore new techniques in order to reduce and make the best use of the consumed energy.

Due to the elevated price of the generation of steam for the reboiler, there is clearly a direct relation between the minimum costs and the minimum use of steam. Therefore, in order to find the optimal pressures in some cases an economic study is being executed called total annual

costs (TAC). The aim of the TAC is to find out the optimum of the separation process and is being calculated like:

$$TAC = \text{total capital costs} / \text{payback period} + \text{operating costs} \quad (4)$$

Where

$$\text{Capital cost} = \text{column vessel cost} + \text{plate cost} + \text{heat exchangers cost} \quad (5)$$

$$\text{Operating cost} = \text{annual steam cost} + \text{annual cooling water} \quad (6)$$

As can be shown the operating costs (as is hot utility = steam) are very important at selecting the pressure. When a study of the economical costs of the column is being realized in fact a study of the operating cost of the reboiler is being realized because if these are the minimums for conducting the separation the columns will be run at the minimum pressure of the operation.

When realizing the TAC it can be seen which is the optimum working pressure utilizing the optimum of the steam pressure level and consumption.

The study of the pressures is large and tedious and therefore many times LPC is being chosen starting the cooling water and TAC only is conducted for the HPC (studies classified as 2.B.). If in the contrary a global study of the TAC is being conducted there are 2 different ways to be followed:

- A. They find the optimum pressures following the simulated annealing algorithm (SAA).
  - B. Initially a minimum pressure for the LPC is being selected in order to be able to use cooling water as refrigerating agent. Then a TAC is being conducted for the HPC and the optimum pressure for this column is being fixed. With this fixed pressure a TAC for the LPC is being conducted to determine the optimum pressure for the LPC.
  - C. Different working pressures are being selected which are known to result in a good separation and conduct the TAC for each one of the possible combinations.
4. Fixing a variation in the composition and determining the pressures according to these variations.

Table 2. Criteria classification

	LP (atm)	HP (atm)	T - LP (K)	T - HP (K)	Criteria
1	1	5	333,9	389,7	4
2	0,77	10	334,8	431,6	2c
3a	1	10	-	-	1
3b	1	5	329,4	370,8	4
3c	1	10	345	418	1
3d	1	10	-	-	1
3e	0,66	10,32	327,34	418,13	3a
4a	1	3,1	-	-	-
4b	1	10	-	-	3b
4c	1	2,8	-	-	2a
5	1	7	375,04	431,74	-
6a	1	10	341,1	426,6	1
6b	0,79	10,89	-	-	3a
7a	1	10	357,48	436,1	1
7b	1	4	359,1	394	2a
7c	1	4	359,1	394	2a
8	0,3	1	341,02	363,13	2c
9	0,5	11	343,8	495,81	3c
10a	1	10	371	424	1
10b	1	10	371	424	1
10c	1	10	369,63	422,82	1
11	0,5	6	342,2	403,9	2b
12	1	3,5	417,8	469	-
13a	0,2	1	344,15	398,5	2c
13b	0,19	1	347,2	395,61	2c
14	1	8	336,47	432,02	2c
15a	2	12	358	463	4
15b	1	13,1	342,38	471,17	-
16a	1	10	337,7	433	2c

16b	1	10	337,7	433	2c
17a	0,25	7	397	439	2b
17b	0,25	7	397	439	2b
18a	1	8,7	-	-	-
18b	1	11	341,3	422	2b
18c	1	10	-	-	-
19	1	12	340,63	409,77	4
20a	1	4	383,71	429,51	3c
	1	12	384,55	509,33	3c
20b	0,2	2	347	397	2b
21a	1	10	351,4	433,1	1
21b	1	10	351,4	433,1	1
22a	1	6,8	373	420	-
22b	1	6,8	373	420	-
22c	1,1	7,9	379,2	421,1	2c
22d	1,1	7	370,9	417,1	2c
22e	1	10	370,59	432,94	2b
22f	1	7,8	373	419	-
23	1	10	390,47	488	1
24a	0,1	2	348,6	419,2	4
24b	0,1	6,6	354,89	463,19	3b



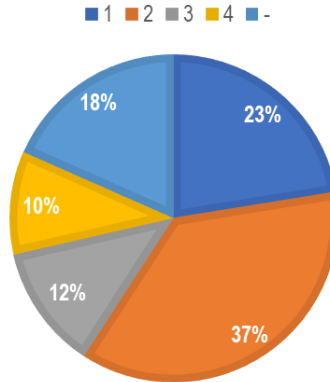


Figure 7. Percentage of articles that follow each criteria

As can be seen in Fig. 7 in the majority of the articles the pressures have been chosen according to the cost of the condenser. As this Fig. 7 shows just the general classifications of each criteria it was decided to create a logic diagram of each classification of each criteria. This is shown in Fig. 8.

Although it resulted in some of the articles impossible to determine which criteria was applied a scheme have been established of the ones that could be determined to see more clearly which criteria was applied. The order of the following classification is by letter and number of each article (first column of the Table 1 and Table 2).

As one can see the before said is confirmed. The majority of the articles fix the pressure at 1 and 10 atm without having realized any type of optimization. Following those the majority selects the pressure of the LPC in order to use cooling water and with a determined type of steam they select the pressure of the HPC. This results that they remain in one of these local minimums without realizing an analysis of the global cost.

After having studied all the articles is has been found that no article was done having in account all the options. Further onwards a logical diagram will be shown which has to be followed in order to find the optimal operational values.

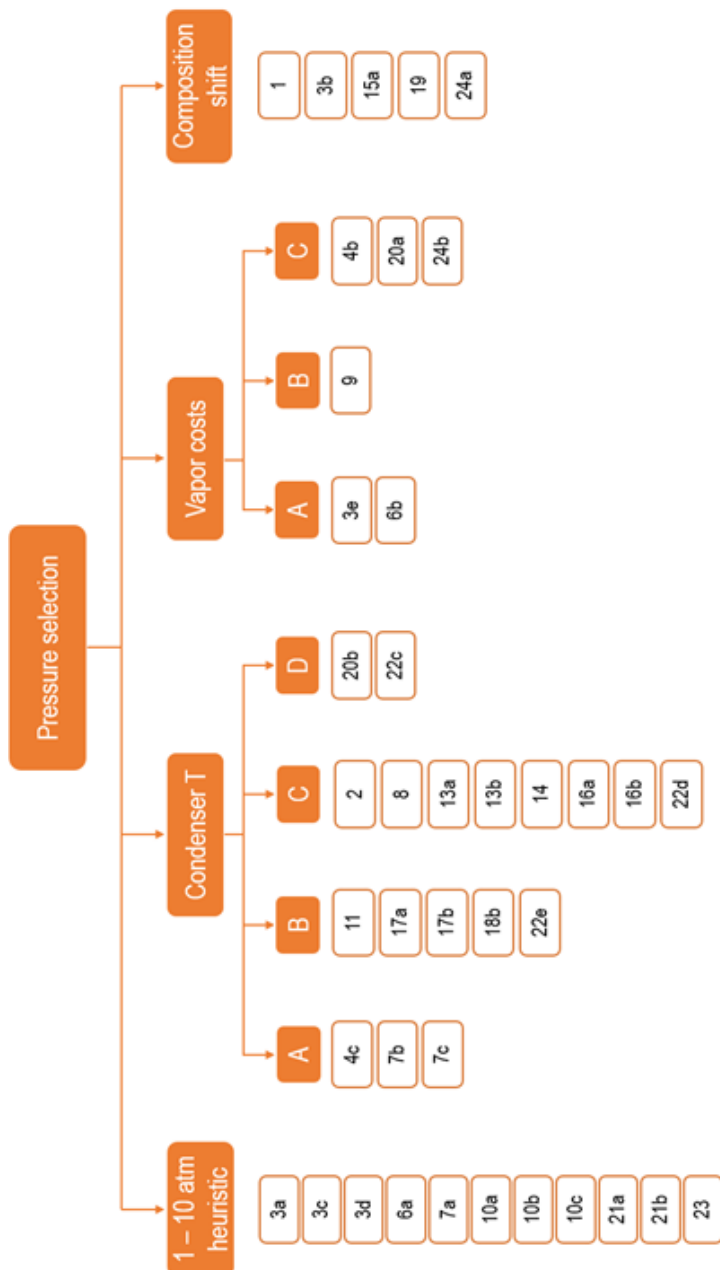


Figure 8. Articles that follow each criteria

## 4. SIMULATION

In this section is being intended to undergo a basic simulation of the PSD with a mixture of ethyl acetate + ethanol using the simulation program AspenPlus V10. Once the simulation is done a comparison of the obtained results is being made with the article of Zhang et al. (2017) as reference.

### 4.1. PRESSURE OPTIMIZATION

Having classified the articles and having determined the criteria they follow; some steps have been determined to be followed when realizing a valuable study of the PSD.

The schematic steps that must be followed are shown in the Figure 9.

In the following lines will be explained more profoundly the steps of the Figure 9:

1. To know if the composition of the mixture is sensible to the pressure changes the 1-10 atm heuristic must be applied. If the composition varies more than 10% the PSD may be considered.
2. Once the feed composition is selected the best distribution of the columns (HP-LP or LP-HP) can be known. Although the figure provides the selection of one or the other option it's preferable to do the optimization with both combinations.
3. It was considered that fixing the pressure of the LPC according to the temperature of the cooling water was a good option to start the optimization process. As has been explained before the temperature of the cooling water must be lowered between 10-20°C (to be chosen by the investigators) in order to have the established necessary difference.
4. First the pressure of the HPC will be selected and the following step is the optimization of the LPC. The TAC will be realized for the LPC and if in case the minimum isn't achieved higher pressures will be studied. As has been explained before there are no studies which determine whether working at determined pressures of vacuum and cooling water results in less costs than working at higher pressures with other cooling agents.

The TAC of the LPC will be done in order to study this.

5. Once the LPC has been optimized the following step is to optimize the HPC and do the TAC of the HPC. In case the TAC does not achieve the minimum the pressure will be augmented. It must be emphasized not to remain in local minimums which show when using different types of steam (LS, MS and HS).
6. After realizing the TAC of the pair of columns the result has to be compared with studies of other methods of distillation. If the TAC is minimum the optimum has been achieved if not, the separation has to be realized by other means of distillation.

#### 4.1.1. PSD vs. DSE

As explained in point 1 and 6 if the TAC does not result in a minimum or the composition is not sensible to pressure changes other options must be considered. The majority of the azeotropic distillations are made with the extractive distillation because of this.

In order to find the optimum conditions different types of distillation must be studied. Although a profound study is not executed it is necessary a basic study. An option of a basic study is shown.

The distillation sequence efficiency (DSE) model has been applied in order to see if it is more economic to separate the azeotrope of a binary mixture (with components A and B) by PSD instead extractive distillation. This DSE model assumes distillation columns as Carnot thermal machines that produce separation instead of work.

Hypothesis:

The available hot sources in the plant limit the maximum temperature that can be achieved (TM).

In both cases (PSD and extractive distillation) it is preferable to operate at the maximum (available) temperature, thus achieving the maximum effectivity and therefore the reboiler should be operated at TM. Since we aim to operate at TM, the pressure of the HPC must be set at the point where the boiling point will be the TM. Once the pressure has been defined in the head of the column (in case of a Min-B) or in the bottom (in case of a Max-B) a composition and a temperature  $x_{az,P1}$  y  $T_{az,P1}$  will be obtained.

In accordance with the TFG of del Castillo (2017) the DSE of the extractive distillation will be 78% of the efficiency when operating with an infinite flow of extraction agent. Since the columns of the extractive distillation are not pressurized, the temperatures of the distillates will correspond to the boiling temperatures of the components A and B at 1 atm.

Using the PSD, the pressure will be lowered to the minimum temperature ( $T_m$ ), which permits the use of cooling water, this means, when the boiling temperature of the azeotrope AB corresponds to  $T_m$ . This pressure defines the composition of the distillate (in case of a Min-B) or the bottom product (in the case of a Max-B) a  $x_{az,P2}$  and the temperature of the pure component B which is obtained in the second column  $T_{b,P2}$ .

- Resolution:

Dividing the DSE of the PSD by the DSE of the extractive distillation shows, that the PSD is a better option if this division is greater 1.

Extractive distillation DSE:

$$DSE_E = [x_A \cdot \eta_1 + x_B \cdot \eta_2] \cdot 0.78 \quad (7)$$

Pressure-Swing distillation DSE:

$$DSE_{PSD} = x_A + x_B \cdot \eta_1 + \frac{D_2}{F} \cdot (\eta_1 \cdot \eta_2 - 1) \quad (8)$$

Resulting (in case of a sequence HP-LP):

$$\frac{x_A + (1 - x_A) \cdot \frac{TM - T_{az,P1}}{TM} + (1 - x_A) \frac{x_{az,P1}}{x_{az,P2} - x_{az,P1}} \cdot \left( \frac{TM - T_{az,P1}}{TM} \cdot \frac{T_{B,P2} - Tm}{T_{B,P2}} - 1 \right)}{0.78 \cdot \left( x_A \cdot \frac{TM - TA}{TM} + (1 - x_A) \cdot \frac{TM - TB}{TM} \right)} \quad (9)$$

Simplifying:

$$\frac{T_{B,P2} \cdot Tm(x_{az,P2} - x_{az,P1}) + (x_A - 1)(T_{B,P2} \cdot T_{az,P1} \cdot x_{az,P2} + Tm \cdot x_{az,P1}(TM - T_{az,P1}))}{0.78 \cdot T_{B,P2}(TA \cdot x_A - TB)(x_{az,P1} - x_{az,P2}) - (TM - TB \cdot x_A)(x_{az,P1} + x_{az,P2})} \quad (10)$$

As was said before (Chapter 3.2.) the PSD permits the use of HIDIC. HIDIC can be used when  $T_{az,P1} > T_{b,P2}$  (in case of a column sequence: HP-LP)

$$\frac{Tm \cdot x_A + (1 - x_A)(TM - T_{az,P1} - 20)}{0.78 \cdot x_A(TM - TA) + (1 - x_A)(TM - TB)} \quad (11)$$

If this division is higher than 1 the HIDIC should be considered.

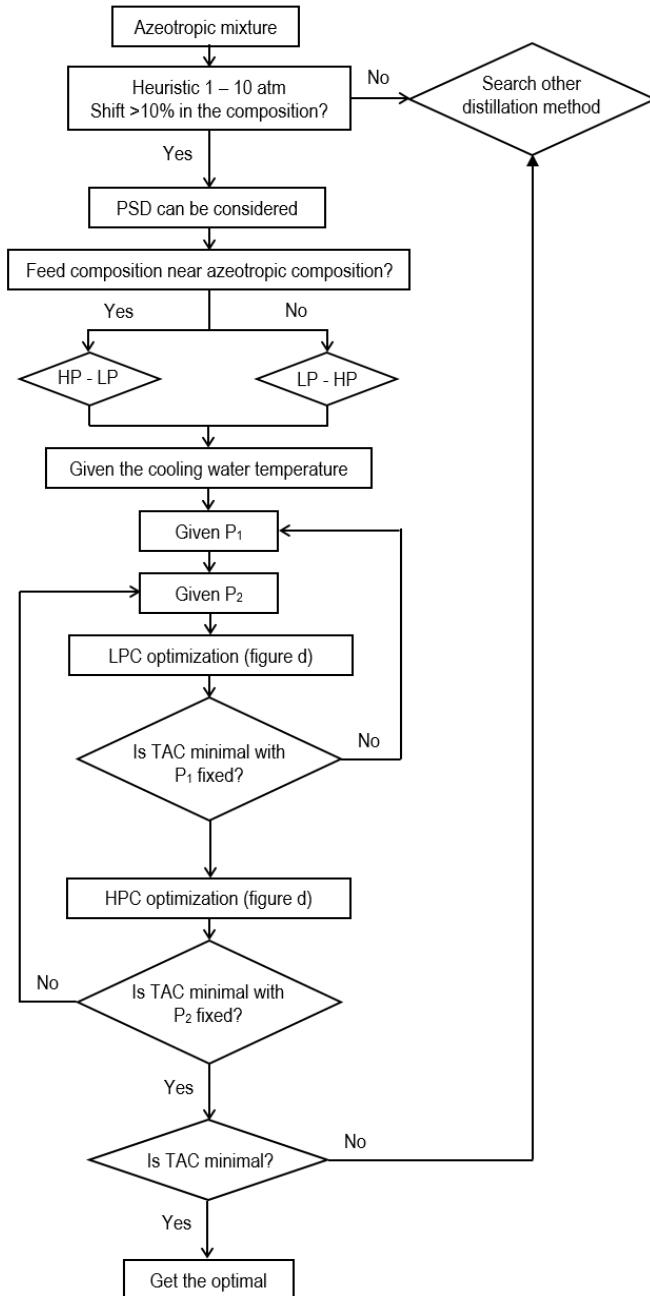


Figure 9. Sequential iterative pressure optimization for PSD process

## 4.2. CASE STUDY

This article is classified as 2B, which means that fix the pressure of the LPC in order to use water as cooling media and optimizes the pressure of the HPC. It also realizes a study on the best combination (LP-HP or HP-LP). After the optimization of the HPC the author decides that the best option is that to work the LPC at 0.5 atm and the HPC at 6 atm and the combination HP-LP. The results of this optimization are linked to the minimum operational cost that is produced at 6 atm. The results of the simulation are:

Table 3. Characteristics of the article

	HP-LP
<b>P<sub>1</sub> [atm]</b>	6
<b>P<sub>2</sub> [atm]</b>	0.5
<b>NT<sub>1</sub></b>	55
<b>NT<sub>2</sub></b>	30
<b>RR<sub>1</sub></b>	2.027
<b>RR<sub>2</sub></b>	1.474
<b><math>\Delta x_{\text{spec}}</math> [mol% EA]</b>	3.5
<b>Capital cost [10<sup>6</sup> \$]</b>	3.339
<b>Operated cost [10<sup>6</sup> \$/year]</b>	1.083
<b>TAC [10<sup>6</sup> \$/year]</b>	1.751



These results are obtained for a feed flow of 100 kmol/h and a composition of 50/50 mol% ethanol/ ethyl acetate. The flow sheet of the optimized process without HIPSD is:

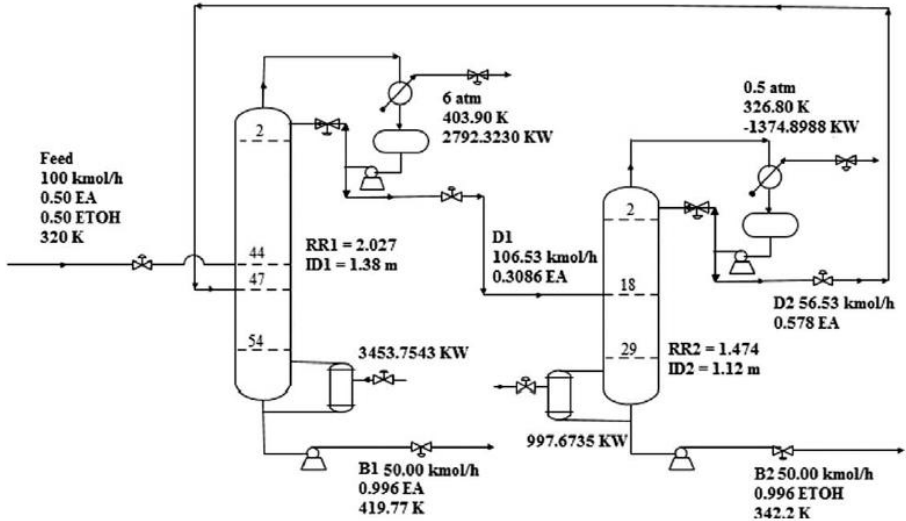


Figure 10. Flowsheet of the process without heat integration (extracted image from Zhan et al. 2017, Fig. 4)

The following table shows the necessary parameters for the simulation.

Table 4. Parameters necessary for the simulation

<b>Feed T [K]</b>	320
<b>Purity of bottoms [mol%]</b>	99.6
<b>Activity coefficient model</b>	UNIQUAC
<b>LP steam (6 bar, 433K) [\$/GJ]</b>	7.72
<b>MP steam (11 bar, 457K) [\$/GJ]</b>	8.22
<b>HP steam (42 bar, 527K) [\$/GJ]</b>	9.88

### 4.3. METHODOLOGY

In order to conduct the simulation and to be able to compare with the results of the article a couple of parameters have been set. The reference article utilizes different VLE data than will be used here. It has been decided not to conduct the simulation with the same data since in previous versions of the Aspen applied in its data base an erroneous VLE and as consequence at simulating the mixture ethyl acetate + ethanol this erroneous VLE data have been used.

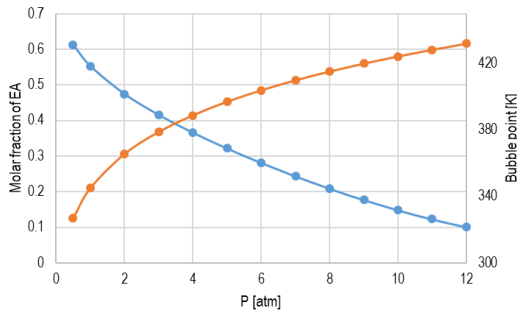


Figure 11. Effect of the pressure on the azeotropic composition and temperature

It was considered to be necessary to actualize the VLE data and conduct the simulation with the correct VLE because it corresponds to the real azeotrope. In continuation, the composition and the feed flow have been fixed, utilizing the same values that are being used in the article (as show in Figure 10) and by this way proceeding to the manufacture of the macroscopic material balances (BMM) of each one of the columns.

For the description of the BMM the same terminology as in Figure 3 has been utilized:

- General system:

$$F = B_1 + B_2 \quad (12)$$

$$F \cdot z_F = B_1 x_{B1} + B_2 \cdot x_{B2} \quad (13)$$

- First column:

$$F + D_2 = D_1 + B_1 \quad (14)$$

$$F \cdot z_F + D_2 \cdot x_{D2} = D_1 x_{D1} + B_1 \cdot x_{B1} \quad (15)$$

- Second columns:

$$D_1 = D_2 + B_2 \quad (16)$$

$$D_1 \cdot x_{D1} = D_2 x_{D2} + B_2 \cdot x_{B2} \quad (17)$$

Once the BMM of the system have been solved for a composition and feed flow is deduced that the exit flows  $B_1$  and  $B_2$  are both equal at 50 kmol/h.

Table 5. Feed composition and flow and purities

	Quantity
$F$ [kmol/h]	50
$z_F$	0.5
$x_{B1}$	0.996
$x_{B2}$	0.996

The reference article fix the pressure of the LPC at 0.5 atm because is the pressure that allows to utilize water as cooling agent. In order to make achieve the best possible comparison, having in mind that the VLE is different, it is being decided to set the same pressure of the LPC. Once the pressure of the LPC is fixed it was decided to execute the simulations exclusively with integer numbers, because the article studied only combinations with integer numbers. This way 9 simulations will be realized, being 4 atm the minimum pressure studied because at this pressure the azeotropic composition varies little and clearly the energetic costs will be much higher. The pairs of pressures utilized and the resolution of the BMM allow to know how the distillate flows vary.

Table 6. Distillation mole flows

Pressure LP-HP [atm]	0.5 - 4	0.5 - 5	0.5 - 6	0.5 - 7	0.5 - 8	0.5 - 9	0.5 - 10	0.5 - 11	0.5 - 12
Distillate mole flow - HP [kmol/hr]	123.42	104.59	91.76	82.44	75.36	69.86	65.54	62.15	59.47
Distillate mole flow - LP [kmol/hr]	73.42	54.59	41.76	32.44	25.36	19.86	15.54	12.15	9.47

As can be seen, as the difference of the pressures increases and therefore the difference of the composition of the azeotrope, the distillate flow diminishes.

In the next table the variables that had been set and the optimized variables for each one of the simulations are displayed.

Table 7. Operating conditions for the rigorous simulation system

		HPC	LPC
<b>CONFIGURATION</b>	Set-up Options	Calculation type: Equilibrium Number of stages: <b>Optimized variable</b> Condenser: total Reboiler: Kettle Valid phases: Vapor-Liquid Convergence: Azeotropic or Strongly non ideal liquid	
	Operating Specifications	Reflux ratio: <b>Optimized variable</b>	
		Bottom rate: 50 kmol/h	Bottom rate: 50 kmol/h
<b>STREAMS</b>	Feed Stream	Stage of recirculated stream: <b>Optimized variable</b> Stage of feed stream: <b>Optimized variable</b>	Stage of feed stream: <b>Optimized variable</b>
<b>PRESSURE</b>	Top stage / Condenser pressure	<b>Selected variable</b>	Fixed at 0.5 atm

It was decided to follow a logic structure in order to optimize the variables, shown in orange. With this aim the logic diagram Fig. 12 was created, which shows the steps taken in all the simulations for the optimization of the columns

The structure for the execution of the simulation is the following:

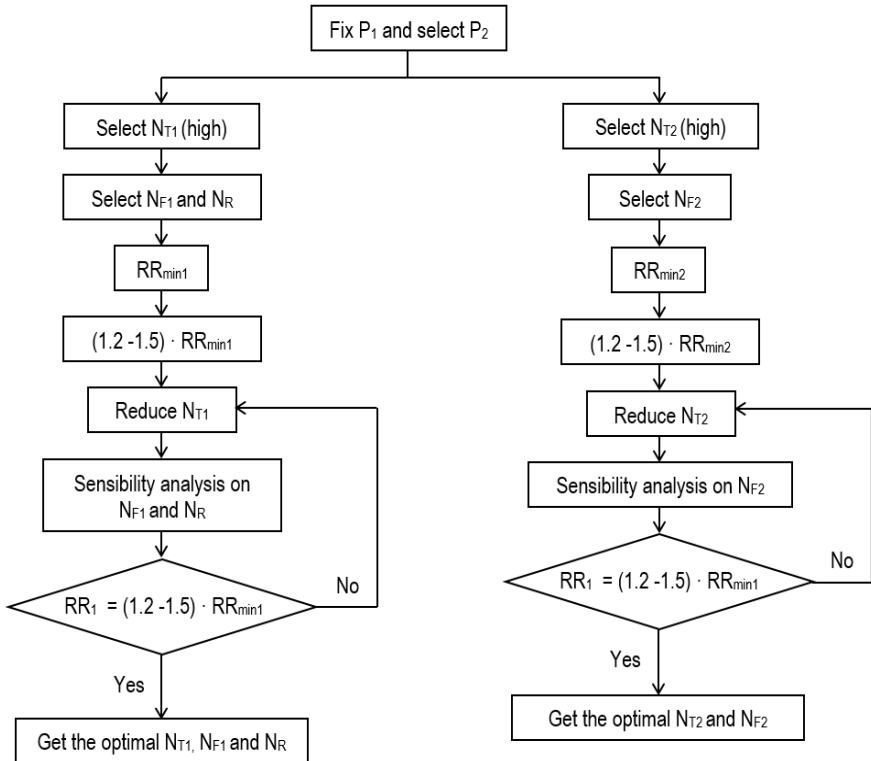


Figure 12. Sequential iterative optimization procedure for PSD process

In order to find the minimum reflux a column with a very high number of stages was selected and the  $(1.2 - 1.5) \cdot RR_{\min}$  heuristic was applied, this means the optimum reflux will be found between 1.2 and 1.5 of the minimum reflux.

As can be observed in Figure 12 the optimization of each of the columns is independent. This is proved that once solved the general BMM and fixed  $F$ ,  $B_1$ ,  $B_2$  and the column pressures  $D_1$  and  $D_2$  will be held fixed and will be independent from the parameters of the optimization of the column.

After realizing the simulation for each of the pairs of values one proceeded to the optimization of the economics of each simulation. The simulation was done with the program AspenPlus V10,

introducing the prices of the steam giving automatically the result. This means, that the prices stipulated in the article were used instead the ones pre-established in AspenPlus V10. This is the only variation of the economic parameters, that has been made, since the aim of this TFG was not an exact simulation of the cost but, to show, if the cost of the reboiler are the ones, that at the end define the cost of the process.

It is assumed, that the ones, that define the operating cost, is the temperature of the HPC, and by this the pressure of the HPC. Although the temperature is higher, the reflux is less (See chapter 3.2.1.) and therefore the cost will decrease as the pressure rises. It is intended to show, that by simply multiplying the costs of the different types of steam with the kW necessary in form of heat it is possible to determine which will be the most suitable pressure of the HPC.

Following this theory, it can be concluded that increasing the temperature is advantageous and therefore the cost will arrive at a minimum by increasing the pressure to a maximum (the maximum will be that one that the steam can achieve). One has to bear in mind, that the azeotropes have a point where the changes in composition are minimal and that the components will decompose at extreme temperatures.

Therefore, it has to be considered, if the minimum is at HS (where the absolute minimum is) or if it is impossible to reach it (because the study does not consider the number of pressures or for what has been explained in the previous chapter) and the minimum will be located in steams of lower pressure.

In order to be able to conduct the comparison, what will be done is exchanging the prices of the steam in the program AspenPlus V10 with the ones, used in the article. By this could be observed if the minimum costs are really linked to the costs of the reboiler and if the results are comparable with those of the article.

## 5. RESULTS AND DISCUSSION

In this chapter the results of the rigorous simulation are discussed. Once the simulation had been established one proceeded to calculate the economic cost according to each one of the simulations and having discussed the best option (of pressures) for the mixture. At the end of the chapter a comparison with the article is presented.

### 5.1. SIMULATION RESULTS

In Table 7 the optimized results of every pair of pressures are shown. The number of plates resulted constant for all pressures in the HPC, in contrary to the LPC, where the number of plates has diminished, ruled by a diminishing difference in the azeotropic mixture.

As the pressure of the LPC is fixed as well as the feed composition it is clear, that the feed plate will not undergo a variation if the number of plates stays constant. On the contrary, the feed plate will be lower, due the fact that the feed will have an increasingly major different composition to the previous, and in order to achieve the optimum column, the feed plate must be lowered.

As has been explained before, as the pressure is augmented, the temperature rises and hence the caloric demand of the reboiler. At the same time, at higher pressure higher difference in the composition of the azeotrope and therefore less distillate flow. At a reduced flow rate of the distillate results less energetic demand at the condenser, but a higher reflux ratio is necessary to reach the composition of the azeotrope.

Table 8. Results of the simulation

Pressure (atm)	0.5 - 4	0.5 - 5	0.5 - 6	0.5 - 7	0.5 - 8	0.5 - 9	0.5 - 10	0.5 - 11	0.5 - 12
Number of stages - HP	70	70	70	70	70	70	70	70	70
Number of stages - LP		35	33	31	30	28	26	25	24
Feed stage location R - HP	64	64	64	65	65	65	65	65	65
Feed stage location - HP	58	59	59	60	60	60	61	61	61
Feed stage location - LP		28	26	23	22	20	18	18	17
Reboiler heat duty - HP [kW]	3595	3676	3778	3823	3870	3897	3897	3871	3828
Reboiler heat duty - LP [kW]		1329	1043	855	701	624	581	523	477
Reboiler temperature - HP	399.3	408.8	417.0	424.2	430.7	436.6	442.0	447.0	451.7
Reboiler temperature - LP		334.7	334.7	334.7	334.7	334.7	334.7	334.7	334.7
Condenser heat duty - HP [kW]	-4521	-4201	-4027	-3868	-3757	-3659	-3556	-3447	-3333
Condenser heat duty - LP [kW]		-1682	-1382	-1182	-1019	-935	-886	-824	-776
RR <sub>min</sub> - HP	2.4	2.8	3.1	3.5	3.9	4.1	4.4	4.6	4.7
RR <sub>min</sub> - LP	2.3	1.6	1.7	2.0	2.4	3.0	3.8	4.7	6.0
RR - HP	3.1	3.6	4.0	4.4	4.8	5.2	5.5	5.7	5.8
RR - LP		2.2	2.4	2.7	3.1	3.8	4.8	5.9	7.4



Having activated the costs and fixed the prices of the steams according to those of the article we have arrived at the following results. In the second, third and fourth column of the table the cost/second of the reboilers of the two columns are shown.

Table 9. Energy costs

Pressure [atm]	Reboiler heat duty - HP [\$/s]	Reboiler heat duty - LP [\$/s]	Total reboiler heat duty [\$/s]	Capital cost [\$]	Operating cost [\$/year]	Total Utilities Costs [\$/year]
0.5 -- 4	27.8	12.8	40.6	6,502,880	3,075,520	1,475,280
0.5 -- 5	28.4	10.3	38.6	6,280,730	3,134,690	1,544,850
0.5 -- 6	29.2	8.0	37.2	6,255,810	2,900,920	1,331,690
0.5 -- 7	29.5	6.6	36.1	6,223,610	2,857,780	1,291,750
0.5 -- 8	29.9	5.4	35.3	6,917,430	2,865,010	1,258,990
0.5 -- 9	32.0	4.8	36.9	7,832,990	3,029,410	1,360,260
0.5 -- 10	32.0	4.5	36.5	6,037,100	2,843,200	1,289,750
0.5 -- 11	38.3	4.0	42.3	6,118,920	3,056,250	1,482,090
0.5 -- 12	37.8	3.7	41.5	6,365,770	3,046,660	1,460,060

In order to show more clearly the comparison of the results we have established a graphic diagram of the cost of the reboiler with the temperature/pressure and the total utility cost/pressure.

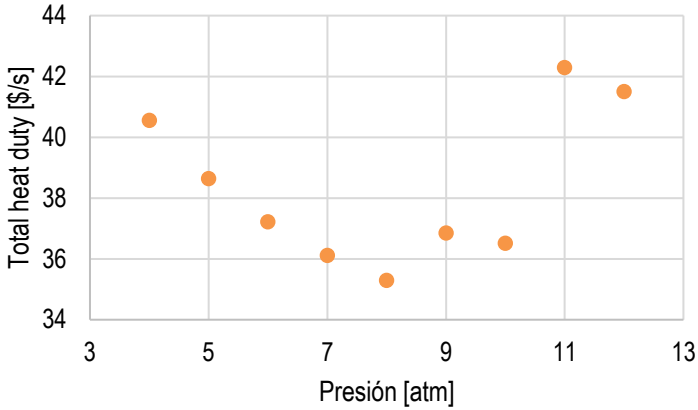


Figure 13. Total heat duty costs

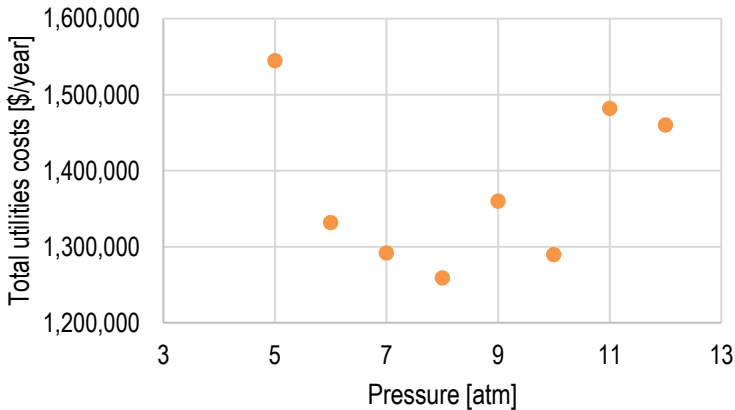


Figure 14. Total utilities costs

As can be seen in the diagrams: the results are comparable. Both studies arrive at the conclusion, that the optimum pressure of the HPC is 8 atm. Thus it is demonstrated, that the parameter that really decides the optimum pressure is the temperature of the hot services for the HPC.

The simulation does arrive at 12 atm and even at this pressure the absolute minimum is not reached. If we had continued to increase the pressure up to the maximum of the HP steam, we would have reached the absolute minimum. As we didn't continue up to higher pressures, we

have remained in one of these relative minimums which we mentioned in (Chapter 3.2.1.) The minimum corresponds to 8 atm, by which it is possible to use MPS.

Both graphics show, that the optimum operating pressure is 8 atm. In the following figures the different diagrams are shown and in the tables are the parameters that define the simulation.

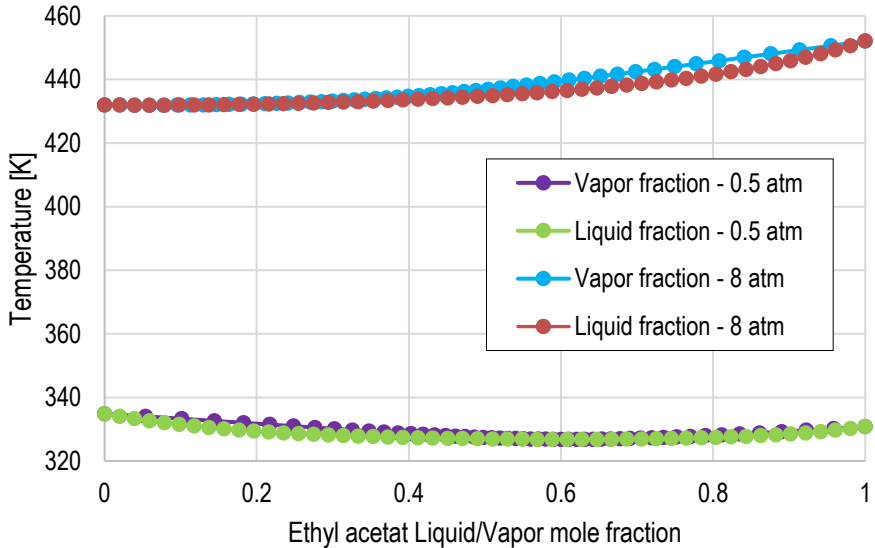


Figure 15. Azeotrope ethyl acetate/ethanol at 0.5 and 8 atm

As can be seen in Figure15 the composition has a large shift when the pressure changes from 0.5 atm to 8 atm. This indicates that the reflux rates will be lower.

Table 10 shows the flows and compositions of each stream:

Table 10. Characteristics of the streams

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320	415.2	430.7	326.8	334.7
<b>Pressure [atm]</b>	49.3	8	8	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100	75.4	50	25.4	50
<b>Ethanol</b>	50	59.6	0.2	9.8	50
<b>Ethyl acetate</b>	50	15.7	49.8	15.5	0
<b>Mole Fractions</b>					
<b>Ethanol</b>	0.5	0.791	0.004	0.388	0.996
<b>Ethyl acetate</b>	0.5	0.209	0.996	0.612	0.004

Table 11, Table 12 and Table 13 show the characteristic parameters of every column:

Table 11. Optimized parameters

		HPC	LPC
<b>Number of stages</b>		70	30
<b>Feed stage location</b>		60	22
	<b>Recirculated</b>	65	
<b>RR<sub>min</sub></b>		3.9	2.4
<b>RR</b>		4.8	3.1

Table 12. Values of the reboiler

	HPC	LPC
<b>Temperature [K]</b>	430.7	334.7
<b>Heat duty [kW]</b>	3870	701
<b>Distillate rate [kmol/h]</b>	50	50
<b>Reflux rate [kmol/h]</b>	548.2	62.7

Table 13. Values of the condenser

	HPC	LPC
Temperature [K]	334.7	326.8
Heat duty [kW]	-3757	-1019
Distillate rate [kmol/h]	75.4	25.4
Reflux rate [kmol/h]	363.9	78.9

Figure 16 and Figure 17 show the composition profile of the HPC (Figure 16) and the LPC (Figure 17).

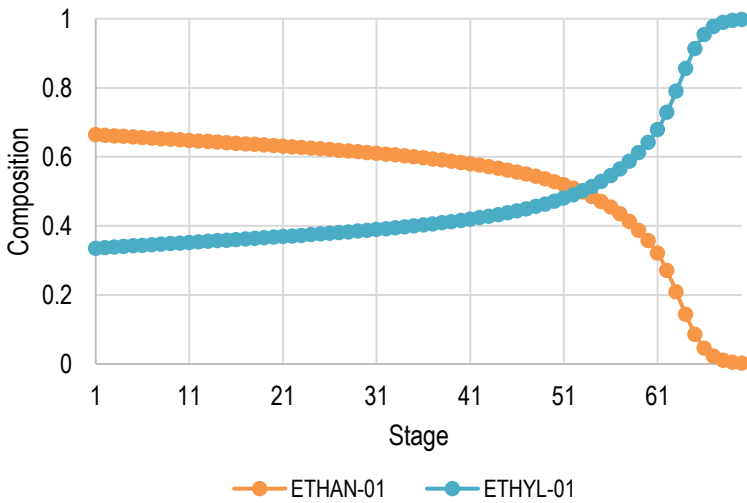


Figure 16. Composition profile of the HPC

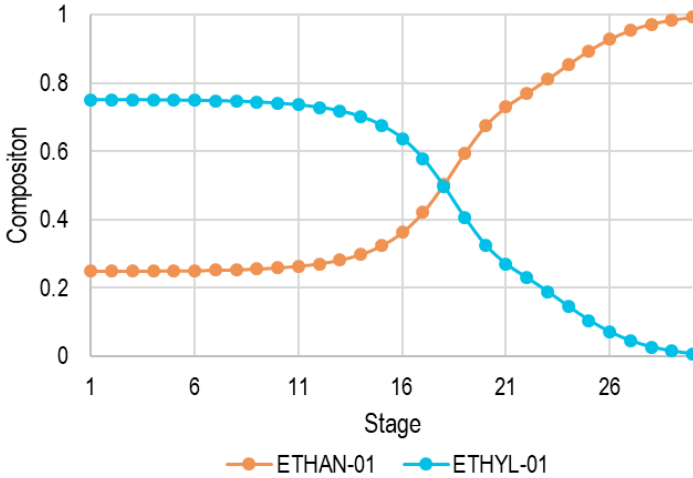


Figure 17. Composition profile of the LPC

## 5.2. COMPARISON WITH ZHANG ET AL. (2017)

Table 14. Article vs. Simulation

	ARTICLE		SIMULATION	
	HPC	LPC	HPC	LPC
<b>Pressure [atm]</b>	6	0.5	8	0.5
<b>Number of stages</b>	55	30	70	30
<b>Feed stage</b>	44	18	60	22
<b>Refluxed stage</b>	47		65	
<b>RR</b>	2.027	1.474	4.8	3.1
<b>Operated cost [\$/year]</b>	1,083,000		2,865,010	

The number of plates increases with respect to the number of plates in the article. This is owed to our decision to do the simulation effecting that both column reach the azeotropic composition, as can be seen in Figure 16 and Figure 17 the composition varies only a bit in the

last stages. In order to reduce costs, in many articles it is decided, that the composition is approximately 1% less, probably this being the reason for the difference of plates.

The difference of the reflux has mainly two reasons: 1. The heuristic  $RR = (1.2 - 1.5) \cdot RR_{\min}$  allows a pretty large space to select the RR, 2. The azeotropic composition (VLE varies) is not the same, whilst we have higher compositions of EA in each pressure. The greater the difference of the composition is, the greater the reflux has to be. Therefore, the reflux applied in this simulation will always be higher than the one in the article for a given pressure.

The position of the feed plates is quite similar (having in mind the difference in size and the RR) and the feed compositions are quite similar too. The same occurs with the heat duty of the respective reboilers.

The sequence of the columns is important for finding the optimum operating conditions, the sequence HP-LP was selected, because the feed composition is similar to the azeotropic composition. If, in the contrary, one would have selected the sequence LP-HP, the operating cost would have been higher, because one would not have taken the advantage of the proximity of the compositions (feed and azeotropic) causing a higher consumption of energy due to the higher distillate flow.

After analysing the operating cost in the simulation, was observed, that the optimum pressure is 8 atm. Was tried to find out the reason, for which the optimum pressure in the article does not coincide with the result of our optimization and concluded, that the reason is, that AspenPlus V10 does not take in consideration the difference of 10 - 20 °C that has to be selected between the steam and the columns temperature. As this difference of 20 °C does not exist, AspenPlus V10 utilizes MPS up to 8 atm, whereas the article utilizes MPS up to 6 atm.

After taking in account, that AspenPlus V10 does not apply the established difference of temperature was observed, that one arrives at the same conclusion in the article and in the simulation, this means that the optimum pressure will be the higher one at which it is possible to use MPS, being 6 atm in the article and 8 atm in the simulation.

After conducting the comparison using these elementary tools of the design of the columns, was concluded that the obtained results are comparable to those of the article.





## 6. CONCLUSIONS

This study presents an extensive bibliographical review about the Pressure Swing Distillation and shows the different criteria that have been taken in consideration when selecting the pressures.

In the beginning, it was intended to identify all those studies, that selected the optimum pressures according to the cost of the reboiler. The search showed, that there were only a small number of studies and hence it was decided to execute a broad and profound study of the different methods for selecting the pressures.

Having conducted the survey, a logic diagram was designed of what is considered to be the optimum selection of the pressures. Once the survey was completed, it was decided to analyse one of the articles, which select the pressures according to the cost of the reboiler.

Although the article didn't undergo a TAC for the two columns when selecting the pressures, it was assumed, that it represented a good option for the comparison. With the simulation is showed, that the decisive variable for finding the optimum pressure are the costs of the steam of the reboiler.

The simulation led to the following conclusions:

- A good starting point for the optimization of the pressures is taking the temperature of the cooling water as temperature of the services of the LPC (having in consideration the difference of 10 to 20 °C that the temperatures must have).
- The sequence of the columns (HP-LP or LP-HP) is an important variable in order to reach the operational optimum.
- It is of eminent importance to conduct a good optimization of the columns in order to reach the operational optimum.
- What defines the optimum pressure, is the cost of the steam for the reboiler, which means, that this pressure which results in the minimum cost, is the optimum pressure.



## REFERENCES

- Abu-Eishah, S.I., Luyben, W.L., Design and control of a two-column azeotropic distillation system. *Ind. Eng. Chem. Process Des. Dev.* 1985, 24, 132–140
- Arifeen, N., Wang, R., Kookos, I., Webb, C., Koutinas, A., Process Design and Optimization of Novel Wheat-Based Continuous Bioethanol Production System. *Biotechnol. Prog.* 2007, 23, 1394-1403
- Atkins, P.W.; Jones, Loretta. *Principios de química: los caminos del descubrimiento*. 3ª ed. Buenos Aires: Médica Panamericana, 2006
- Bonet, J., Thery, R., Meyer, X.-M., Meyer, M., Reneaume, J.-M., Galan, M.-I., Costa, J., Infinite/infinite analysis as a tool for an early oriented synthesis of a reactive pressure swing distillation. *Comput. Chem. Eng.* 2007, 31, 487–495
- Cao, Y., Li, M., Wang, Y., Zhao, T., Li, X., Zhu, Z., Wang, Y., Effect of feed temperature on economics and controllability of pressure-swing distillation for separating binary azeotrope. *Chem. Eng. Process.* 2016, <http://dx.doi.org/10.1016/j.cep.2016.10.011>
- Frank, T.C., Break azeotropes with pressure-sensitive distillation. *Chem. Eng. Prog.* 1997, 93, 52–63
- Fulgueras, A.M., Poudel, J., Kim, D.S., Cho, J., Optimization study of pressure-swing distillation for the separation process of a maximum-boiling azeotropic system of water-ethylenediamine. *Korean J. Chem. Eng.* 2015, 33, 46–56
- Fulgueras, A.M., Kim, D.S., Cho, J., Modeling and optimization study of pressure-swing distillation for the separation process of acetone–methanol mixture with vapor–liquid equilibrium analysis. *J. Chem. Eng. Jpn.* 2016, 49, 84–96
- Ghughe, P., Mali, N., Joshi S.S., Comparative analysis of extractive and pressure swing distillation for separation of THF–water separation. *Comp. Chem. Eng.* 2017, 103, 188-200
- Hamad, A., Dunn, R.F., Energy optimization of pressure-swing azeotropic distillation systems. *Ind. Eng. Chem. Res.* 2002, 41, 6082–6093
- Hosgor, E., Kucuk, T., Oksal, I.N., Kaymak, D.B., Design and control of distillation processes for methanol–chloroform separation. *Comput. Chem. Eng.* 2014, 67, 166–177
- Huang, K., Shan, L., Zhu, Q., Qian, J., Adding rectifying/stripping section type heat integration to a pressure-swing distillation (PSD) process. *Appl. Therm. Eng.* 2008, 28, 923–932
- Kiran, B., Jana, A.K., A hybrid heat integration scheme for bioethanol separation through pressure-swing distillation route. *Sep. Purif. Technol.* 2015b, 142, 307–315
- Kirk-Othmer's encyclopedia of chemical technology. 5th ed. Hoboken: Wiley-Interscience. cop. 2004-2007. vol. 8
- Knapp, Jeffrey P; Exploiting pressure effects in the distillation of homogeneous azeotropic mixtures, Ph. D. dissertation, University of Massachusetts, Amherst, 1991
- Lee, J., Cho, J., Kim, D.M., Park, S., Separation of tetrahydrofuran and water using pressure swing distillation: modeling and optimization. *Korean J. Chem. Eng.* 2011, 3q28, 591–596
- Li, R., Ye, Q., Suo, X., Dai, X., Yu, H., Heat-integrated pressure-swing distillation process for separation of a maximum-boiling azeotrope ethylenediamine/water. *Chem. Eng. Res. Des.* 2016, 105, 1–15
- Liang, S., Cao, Y., Liu, X., Li, X., Zhao, Y., Wang, Y., Wang, Y., Insight into pressure-swing distillation from azeotropic phenomenon to dynamic control. *Chem. Eng. Res. and Desg.* 2017, 117, 318-335
- Lladosa, E., Montón, J.B., Burquet, M., Separation of di-*n*-propyl ether and *n*-propyl alcohol by extractive distillation and pressure-swing distillation: computer simulation and economic optimization. *Chem. Eng. Process.* 2011, 50, 1266–1274

- Luo, H., Liang, K., Li, W., Li, Y., Xia, M., Xu, C., Comparison of pressure-swing distillation and extractive distillation methods for isopropyl alcohol/diisopropyl ether separation. *Ind. Eng. Chem. Res.* 2014, 53, 15167–15182
- Luo, B., Feng, H., Sun, D., Zhong, X., Control of fully heat-integrated pressure swing distillation for separating isobutyl alcohol and isobutyl acetate. *Chem. Eng. Process.* 2016, 110,9–20
- Luyben, W.L., Comparison of extractive distillation and pressure-swing distillation for acetone-methanol separation. *Ind. Eng. Chem. Res.* 2008a, 47, 2696–2707
- Luyben, W.L., Design and control of a fully heat-integrated pressure-swing azeotropic distillation system. *Ind. Eng. Chem. Res.* 2008b, 47, 2681–2695
- Luyben, W.L., Pressure-swing distillation for minimum- and maximum-boiling homogeneous azeotropes. *Ind. Eng. Chem. Res.* 2012, 51, 10881–10886
- Luyben, W.L., Comparison of extractive distillation and pressure-swing distillation for acetone/chloroform separation. *Comput. Chem. Eng.* 2013a, 50, 1–7
- Luyben, W.L., Control of a heat-integrated pressure-swing distillation process for the separation of a maximum-boiling azeotrope. *Ind. Eng. Chem. Res.* 2014a, 53, 18042–18053
- Luyben, W.L., Methanol/trimethoxysilane azeotrope separation using pressure-swing distillation. *Ind. Eng. Chem. Res.* 2014b, 53, 5590–5597
- Luyben W.L., Design and Control Comparison of Alternative Separation Methods for *n*-Heptane/Isobutanol. *Chem. Eng. Technol.* 2017, 40. No.10, 1895-1906
- Luyben W.L., Design and control of a pressure-swing distillation process with vapor recompression. *Chem. Eng. Proc.* 2018, 123, 174-184
- Modla, G., Lang, P., New column configurations for pressure swing batch distillation II. Rigorous simulation calculations. *IFAC Proceedings* 2007, 40, 361–366
- Modla, G., Pressure swing batch distillation by double column systems in closed mode. *Comput. Chem. Eng.* 2010, 34, 1640–1654
- Modla, G., Lang, P., Removal and recovery of organic solvents from aqueous waste mixtures by extractive and pressure swing distillation. *Ind. Eng. Chem. Res.* 2012, 51,11473–11481
- Muñoz, R., Montón, J.B., Burguet, M.C., de la Torre, J., Separation of isobutyl alcohol and isobutyl acetate by extractive distillation and pressure-swing distillation: simulation and optimization. *Sep. Purif. Technol.* 2006, 50, 175–183.
- Neutrium. Unit Operations: Distillation Fundamentals. <https://neutrium.net/unit-operations/distillation-fundamentals/> (accessed 13/04/2018)
- Mulia-Soto, J.F., Flores-Tlacuahuac, A., Modeling, simulation and control of an internally heat integrated pressure-swing distillation process for bioethanol separation. *Comput. Chem. Eng.* 2011, 35, 1532–1546
- Perry's chemical engineers handbook. 8th ed. New York: McGraw- Hill, 2008
- Qasim, F., Shin, J.S., Cho, S.J., Park, S.J., Optimizations and heat integrations on the separation of toluene and 1-butanol azeotropic mixture by pressure swing distillation. *Separ. Sci. Technol.* 2015, 51, 316–326
- Qasim, F., Shin, J.S., Park, S.J., A simulation study on selection of optimized process for azeotropic separation of methanol and benzene: Internal heat integration and economic analysis. *Korean J. Chem. Eng.* 2018, 35(5), 1185-1194
- Repke, J.-U., Klein, A., Forner, F., Wozny, G., Pressure swing distillation for separation of homogeneous azeotropic mixtures in a mass-and heat-integrated column system: operation performance. *Intelligent control and automation. WCICA 2004 Fifth World Congress on. IEEE*, 2004, 3543–3546
- Repke, J.U., Forner, F., Klein, A., Separation of homogeneous azeotropic mixtures by pressure swing distillation—analysis of the operation performance. *Chem. Eng. Technol.* 2005, 28,1151–1157
- Rojas, O., Salazar, A., Gil, I., Rodríguez, G., Effect of Pressure on the Azeotrope of the Mixture Isoamyl Acetate-Isoamyl Alcohol at 50.00, 101.32, 250.00, and 350.00 kPa. *J. Chem. Eng. Data* 2016, 61, 3109-3115

- Ullmann's encyclopedia of industrial chemistry. 7th completely rev. ed. Weinheim: Wiley-VCH, cop. 2011. Vol. 11
- Wang, Y., Cui, P., Zhang, Z., Heat-integrated pressure-swing-distillation process for separation of tetrahydrofuran/methanol with different feed compositions. *Ind. Eng. Chem. Res.* 2014, 53, 7186–7194
- Wang, Y., Cui, P., Ma, Y., Zhang, Z., Extractive distillation and pressure-swing distillation for THF/ethanol separation. *J. Chem. Technol. Biotechnol.* 2015a, 90, 1463–1472
- Wang, Y., Zhang, Z., Zhang, H., Zhang, Q., Control of heat integrated pressure-swing-distillation process for separating azeotropic mixture of tetrahydrofuran and methanol. *Ind. Eng. Chem. Res.* 2015b, 54, 1646–1655
- Wang, Y., Zhang, Z., Zhao, Y., Liang, S., Bu, G., Control of extractive distillation and partially heat-integrated pressure-swing distillation for separating azeotropic mixture of ethanol and tetrahydrofuran. *Ind. Eng. Chem. Res.* 2015c, 54, 8533–8545.
- Wang, Y., Bu, G., Wang, Y., Zhao, T., Zhang, Z., Zhu, Z., Application of a simulated annealing algorithm to design and optimize a pressure-swing distillation process. *Comput. Chem. Eng.* 2016a, 95, 97–107
- Wang, Y., Zhang, Z., Xu, D., Liu, W., Zhu, Z., Design and control of pressure-swing distillation for azeotropes with different types of boiling behaviour at different pressures. *J. Process Control* 2016b, 42, 59–76
- Wei, H.-M., Wang, F., Zhang, J.-L., Liao, B., Zhao, N., Xiao, F.-k., Wei, W., Sun, Y.-H., Design and control of dimethyl carbonate–methanol separation via pressure-swing distillation. *Ind. Eng. Chem. Res.* 2013, 52, 11463–11478
- Xia, H., Ye, Q., Feng, S., Li, R., Suo, X., A novel energy-saving pressure swing distillation process based on self-heat recuperation technology. *Energy*, 2017, 141, 770-781
- Yu, B., Wang, Q., Xu, C., Design and control of distillation system for methylal/methanol separation. Part 2: pressure swing distillation with full heat integration. *Ind. Eng. Chem. Res.* 2012, 51, 1293–1310.
- Zhang, Z., Zhang, Q., Li, G., Liu, M., Gao, J., Design and control of methyl acetate-methanol separation via heat-integrated pressure-swing distillation. *Chin. J. Chem. Eng.*, 2016, <http://dx.doi.org/10.1016/j.cjche.2016.06.013>
- Zhang, Q., Peng, J., Zhang, K., Separation of an azeotropic mixture of dimethyl carbonate and methanol via partial heat integration pressure swing distillation. *Asia-Pac. J. Chem. Eng.* 2017, 12, 50-64
- Zhang, Q., Liu, M., Li, C., Zeng, A., Heat-integrated pressure-swing distillation process for separating the minimum-boiling azeotrope ethyl-acetate and ethanol. *Sep. and Pur. Tech.* 2017, 189, 310-334
- Zhu, Z., Wang, L., Ma, Y., Wang, W., Wang, Y., Separating an azeotropic mixture of toluene and ethanol via heat integration pressure swing distillation. *Comput. Chem. Eng.* 2015, 76, 137–1



## ACRONYMS

$y_i$	mole fraction of component $i$ in the vapor phase
$P$	total system pressure
$x_i$	mole fraction of component $i$ in the liquid phase
$\gamma_i$	liquid-phase activity coefficient of component $i$
$P_i^{sat}$	vapor pressure of component $i$
$\alpha_{ij}$	relative volatility
$\eta_i$	efficiency of column $i$
$D_i$	distillate flow of column $i$
$F$	feed flow
$TM$	maximum temperature in accord with the hot services (remember de shit of 10 to 20 °C that must be between the hot services and the column temperature)
$Tm$	minimum temperature in accord with the cooling water steam
$T_{i,pj}$	boiling temperature of component $i$ at pressure $j$
$T_{az,pj}$	boiling temperature of azeotrope at pressure $j$
$x_{az,pj}$	azeotropic composition at pressure $j$
$T_i$	boiling temperature of component $i$ at 1 atm
PSD	Pressure Swing Distillation
HPC	High Pressure Column
LPC	Low Pressure Column
TAC	Total Annual Costs
VLE	Vapor-Liquid Equilibrium
HIPSD	Heat Integration Pressure-Swing Distillation

LPS	Low Pressure Steam
MPS	Medium Pressure Steam
HPS	High Pressure Steam
DSE	distillation sequence efficiency
$NT_i$	Stages of column i
$P_i$	pressure of the column i
$RR_i$	reflux ratio of column i
$z_F$	feed composition



# APPENDICES



# APPENDIX 1: SIMULATIONS

## 0.5 – 4 atm SIMULATION

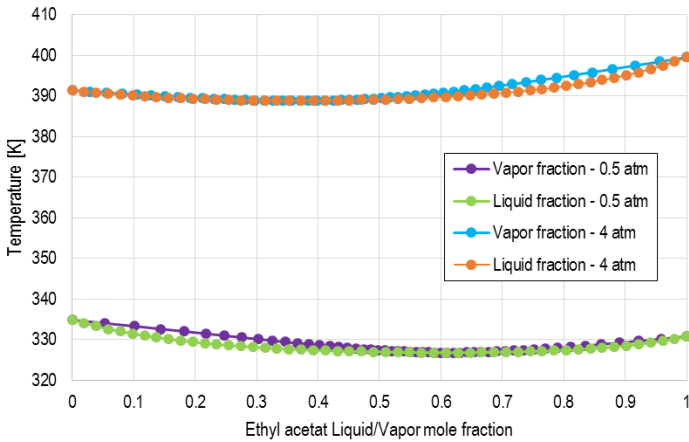


Figure 18. Azeotrope ethyl acetate/ethanol at 0.5 and 4 atm

Table 15. Characteristics of the streams at 0.5 – 4 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	388.9	399.3	326.8	334.7
<b>Pressure [atm]</b>	49.3	4	4	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	123.4	50.0	73.4	50.0
<b>Ethanol</b>	50	78.2	0.2	28.5	50
<b>Ethyl acetate</b>	50	45.2	49.8	45.0	0.2
<b>Mole Fractions</b>					
<b>Ethanol</b>	0.500	0.634	0.004	0.388	0.996
<b>Ethyl acetate</b>	0.500	0.366	0.996	0.612	0.004

## 0.5 – 5 atm SIMULATION

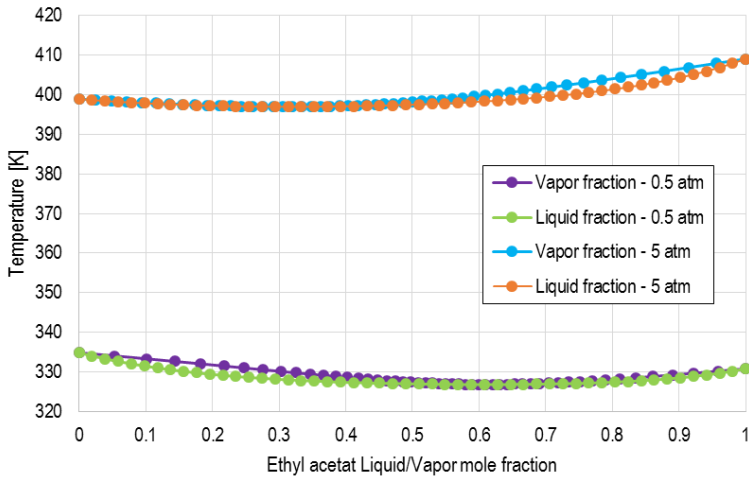


Figure 19. Azeotrope ethyl acetate/ethanol at 0.5 and 5 atm

Table 16. Characteristics of the streams at 0.5 – 5 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	397.0	408.8	326.8	334.7
<b>Pressure [atm]</b>	49.3	5	5	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	104.6	50.0	54.6	50.0
<b>Ethanol</b>	50	71.0	0.2	21.2	50
<b>Ethyl acetate</b>	50	33.6	49.8	33.4	0.2
<b>Mole Fractions</b>					
<b>Ethanol</b>	0.500	0.678	0.004	0.388	0.996
<b>Ethyl acetate</b>	0.500	0.322	0.996	0.612	0.004

### 0.5 – 6 atm SIMULATION

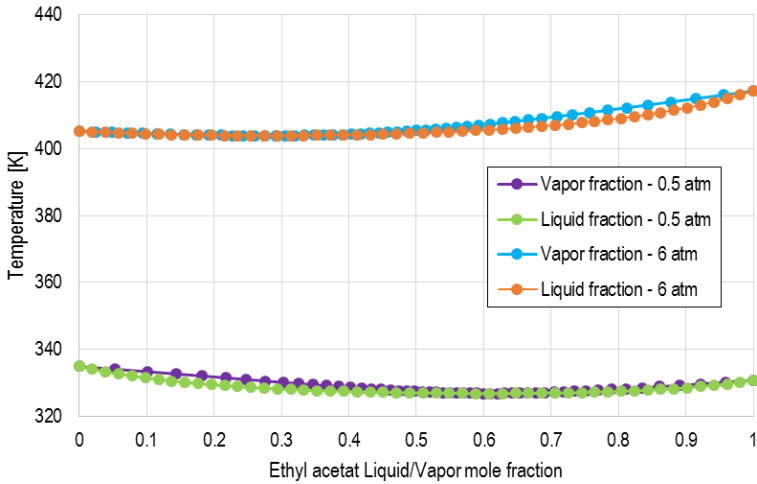


Figure 20. Azeotrope ethyl acetate/ethanol at 0.5 and 6 atm

Table 17. Characteristics of the streams at 0.5 – 6 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	403.9	417.0	326.8	334.7
<b>Pressure [atm]</b>	49.3	6	6	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	91.8	50.0	41.8	50.0
Ethanol	50	66.0	0.2	16.2	50
Ethyl acetate	50	25.8	49.8	25.6	0.2
<b>Mole Fractions</b>					
Ethanol	0.500	0.719	0.004	0.388	0.996
Ethyl acetate	0.500	0.281	0.996	0.612	0.004

## 0.5 – 7 atm SIMULATION

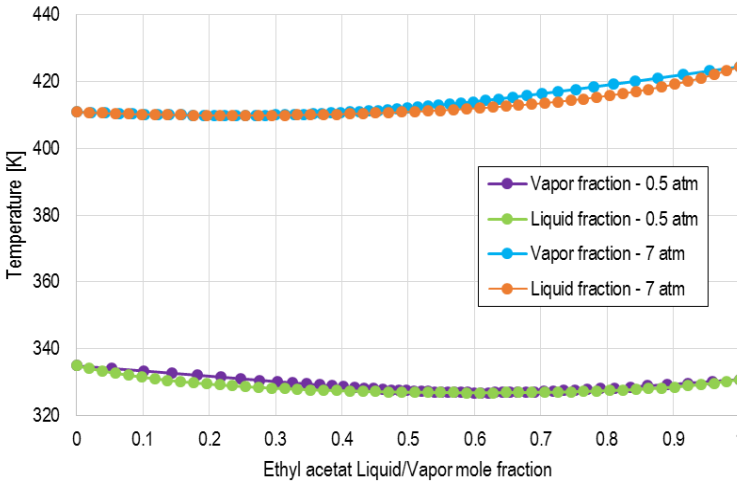


Figure 21. Azeotrope ethyl acetate/ethanol at 0.5 and 7 atm

Table 18. Characteristics of the streams at 0.5 – 7 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	409.9	424.2	326.8	334.7
<b>Pressure [atm]</b>	49.3	7	7	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	82.4	50.0	32.5	50.0
Ethanol	50	62.4	0.2	12.6	50
Ethyl acetate	50	20.1	49.8	19.9	0.2
<b>Mole Fractions</b>					
Ethanol	0.500	0.757	0.004	0.388	0.996
Ethyl acetate	0.500	0.243	0.996	0.612	0.004

### 0.5 – 9 atm SIMULATION

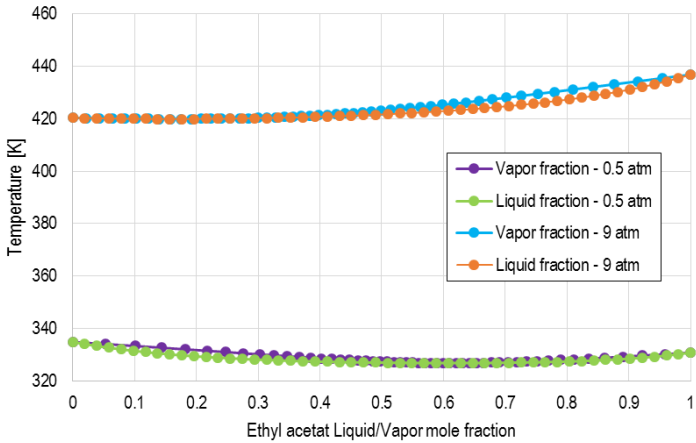


Figure 22. Azeotrope ethyl acetate/ethanol at 0.5 and 9 atm

Table 19. Characteristics of the streams at 0.5 – 9 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	420.0	436.6	326.8	334.7
<b>Pressure [atm]</b>	49.3	9	9	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	69.9	50.0	19.9	50.0
<b>Ethanol</b>	50	57.5	0.2	7.7	50
<b>Ethyl acetate</b>	50	12.4	49.8	12.2	0.2
<b>Mole Fractions</b>					
<b>Ethanol</b>	0.500	0.823	0.004	0.388	0.996
<b>Ethyl acetate</b>	0.500	0.177	0.996	0.612	0.004

## 0.5 – 10 atm SIMULATION

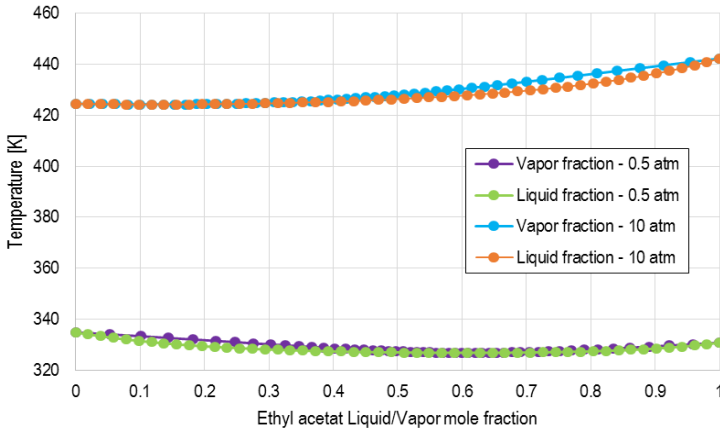


Figure 23. Azeotrope ethyl acetate/ethanol at 0.5 and 10 atm

Table 20. Characteristics of the streams at 0.5 – 10 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	424.3	442.0	326.8	334.7
<b>Pressure [atm]</b>	49.3	10	10	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	65.5	50.0	15.6	50.0
<b>Ethanol</b>	50	55.8	0.2	6.0	50
<b>Ethyl acetate</b>	50	9.7	49.8	9.5	0.2
<b>Mole Fractions</b>					
<b>Ethanol</b>	0.500	0.852	0.004	0.388	0.996
<b>Ethyl acetate</b>	0.500	0.148	0.996	0.612	0.004



### 0.5 – 11 atm SIMULATION

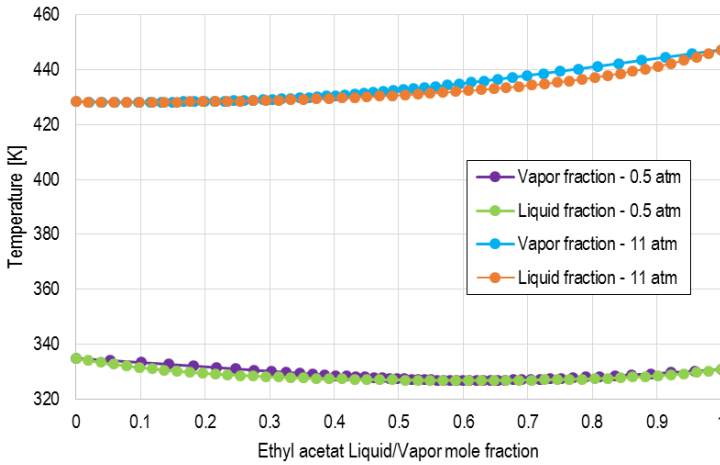


Figure 24. Azeotrope ethyl acetate/ethanol at 0.5 and 11 atm

Table 21. Characteristics of the streams at 0.5 – 11 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	428.3	447.0	326.8	334.7
<b>Pressure [atm]</b>	49.3	11	11	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	62.1	50.0	12.2	50.0
<b>Ethanol</b>	50	54.5	0.2	4.7	50
<b>Ethyl acetate</b>	50	7.6	49.8	7.4	0.2
<b>Mole Fractions</b>					
<b>Ethanol</b>	0.500	0.877	0.004	0.388	0.996
<b>Ethyl acetate</b>	0.500	0.123	0.996	0.612	0.004

## 0.5 – 12 atm SIMULATION

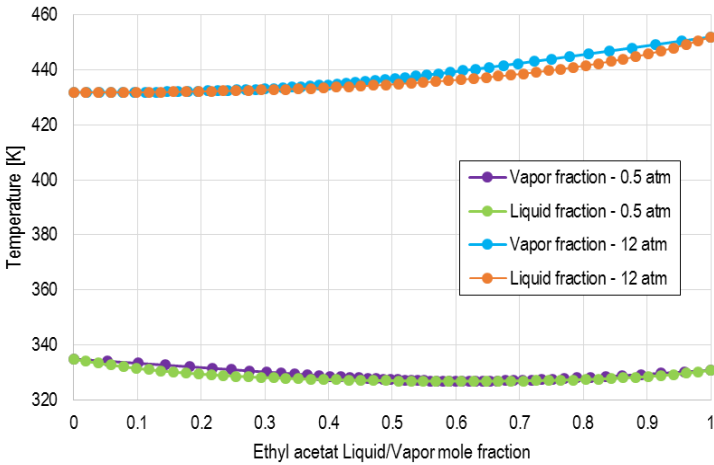


Figure 25. Azeotrope ethyl acetate/ethanol at 0.5 and 12 atm

Table 22. Characteristics of the streams at 0.5 – 12 atm

	FC	HPD	HPB	LPD	LPB
<b>Temperature [K]</b>	320.0	431.9	451.7	326.8	334.7
<b>Pressure [atm]</b>	49.3	12	12	0.5	0.5
<b>Mole Flows [kmol/hr]</b>	100.0	59.5	50.0	9.5	50.0
<b>Ethanol</b>	50	53.5	0.2	3.7	50
<b>Ethyl acetate</b>	50	6.0	49.8	5.8	0.2
<b>Mole Fractions</b>					
<b>Ethanol</b>	0.500	0.899	0.004	0.388	0.996
<b>Ethyl acetate</b>	0.500	0.101	0.996	0.612	0.004

