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Comparative analysis of Extractive Distillation and Pressure Swing Distillation for different azeotropic mixtures

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Donar les gràcies als meus pares per animar-me en els moments més difícils, motivar-me i estar en totes les etapes de la meva vida. També als amics que m’han acompanyat durant aquesta etapa.

Agrair als meus tutors la seva ajuda durant el desenvolupament d’aquest treball.

CONTENTS

SUMMARY

One of the most used and important unit operation to separate mixtures in the chemical industry is distillation. Actually approximately 95% of all the separations are carried out by distillation processes, and indeed, a heuristic indicate that whenever possible distillation must be the first option to separate mixtures. There is situations where is not possible the separation by this operation as a result of closely boiling points (below 50ºC), low relative volatilities or the presence of azeotropes. In the first two cases, a high number of trays would be required for the column. In the case of azeotropes, the separation is impossible due to the composition of liquid and vapor is the same. For that reason, enhanced distillation techniques are necessary. In this work, a comparative analysis about these available techniques to break binary azeotropic mixtures is conducted to conclude which one is more convenient. In particular, it focus on the extractive distillation (ED) and the distillation by variation of the pressure known as pressure swing distillation (PSD).

ED is one of the most used and known techniques characteristically by the addition of an extractive agent (EA), with high boiling point and non-volatile, which modifies the relative volatilities thus allowing the recovery of one pure compound at extractive distillation column (EDC). To obtain the other compound and recovery the extractive agent, a second column is required: recovery distillation column (RDC). The disadvantages of this technique are the cost associated with the recovery of the EA and that always there will be traces of the added compound impurifying the products obtained. In the case of PSD, no additional components are added but is exploited the sensitive of the mixture by changes of the pressure. There are two columns one of which works at high pressure (HPC) and a second at low pressure (LPC), thus varying the azeotropic composition and obtaining the pure compounds. This second is the least used because it is necessary for the mixture to be sensitive to changes in the pressure. Actually, there is a general tendency to wonder that by working with pressure the process is more expensive or less feasible.

Therefore, one of the first questions in the early stages of conception of a process is the selection of which available techniques explained is the more feasible to break an azeotrope. Unfortunately, in my knowledge there is no works that focus on the comparison of both alternatives. The projects often focus on one of the techniques and there are some available articles which compares both for a specific mixture in basis economical terms.

To answer that question, an intense bibliographic research is carried out to select the different cases of binary mixtures which are sensitive to pressure changes. A list of 26 mixtures is selected and going to be studied out more thoroughly. The information available and necessary it is searched at one simulator, databases and one book thus reducing the list at 23 mixtures. The simulator selected is Aspen Plus V10. Then, based on the corresponding material balances and applying a simplified mathematical model (infinite/infinite analysis), the different energy efficiencies are obtained. For this calculus it is necessary to know the compositions and boiling-points. The variation of the azeotropic composition with the pressure and the sensitive is also being studied. Consecutively, the efficiencies achieved in the two alternatives are compared distinguishing azeotropes of minimum and maximum boiling point. Finally, to find the reason of the results obtained a critical comparison is conducted to establish useful general indications on the selection during the first stages of the design process.

Keywords: Enhanced distillation techniques, energy efficiencies, infinite/infinite analysis, general indications

RESUM

Una de les operacions unitàries més utilitzades i importants per a la separació de mescles en la indústria química és la destil·lació. Actualment, el 95% de les separacions es duen a terme per processos de destil·lació. De fet, un heurístic ens indica que sempre que sigui possible la primera opció per a separar mescles és la destil·lació. Hi ha situacions en la que no és possible la separació per mitjà d'aquesta operació com a conseqüència de la poca diferència entre els punts d'ebullició dels components (inferior de 50ºC), les baixes volatilitats relatives o la presència d'azeòtrops. En els dos primers casos, es requeririen un número de plats per a la columna tan elevat que la destil·lació deixaria de ser una opció viable. En el cas de la presència d'azeòtrops, és impossible la separació per mitjà d'aquesta opció ja que la composició del líquid i el vapor és la mateixa. Per això, són necessàries les tècniques de destil·lació avançada. En aquest treball es presentarà un anàlisis comparatiu sobre quina d'aquestes tècniques disponibles per al trencament de mescles azeotròpiques binàries és la més adient. En concret, ens centrem en la destil·lació extractiva (ED) i la destil·lació per variació de pressió, coneguda al anglès com la pressure-swing distillation (PSD).

La ED és una de les tècniques més utilitzades i conegudes que es caracteritza per l'addició d'un agent extractor, d'elevat punt d'ebullició i no volàtil, que modifica les volatilitats relatives permetent així la recuperació d'un dels components pur en la columna extractiva. Per a l'obtenció del segon component i la recuperació de l'agent extractor és necessària una segona columna. Els inconvenients que presenta aquesta tècnica són el cost associat a la recuperació del agent extractor i que sempre quedaran traces del compost afegit impurificant els productes. En el cas de la destil·lació per variació de la pressió, no s'afegeix cap component addicional sinó que s'aprofita el fet de que la mescla sigui sensible als canvis de pressió. Hi ha dues columnes una de les quals treballa a elevada pressió (HPC) i una segona a baixa (LPC) variant així la composició azeotròpica i permetent l'obtenció dels components purs. Aquesta segona és la menys emprada perquè és necessari que la mescla sigui sensible als canvis de pressió. A més, hi ha la tendència en general a pensar que pel fet d'estar treballant a pressió el procés ja ha ser més car o menys factible. Per això, una de les preguntes que ens podem fer durant les primeres etapes de concepció d'un procés és quina de les dues tècniques disponibles seria la més factible per a trencar l'azeòtrop. Malauradament, al meu coneixement no hi ha cap treball que es centri en la comparació d'ambdues alternatives ja que es solen centrar específicament en una de les tècniques. Es pot trobar algun article disponible que compari ambdues per alguna certa mescla i la majoria prenen decisions en base termes econòmics. Per respondre aquestes preguntes es durà a terme una intensa cerca bibliogràfica per seleccionar els diferents casos de mescles binàries sensibles als canvis de pressió. Es partirà d'una llista amb un total de 26 mescles les quals seran estudiades amb més profunditat. D'aquestes es buscarà la diferent informació disponible tant a pressió atmosfèrica com a sobrepressió en un simulador, base de dades i un llibre reduint així el número de mescles a 23. El simulador escollit és Aspen Plus V10. Seguidament, a partir dels corresponents balanços de matèria i aplicant un model matemàtic simplificat (anàlisis infinit/infinit) es calcularan les eficiències energètiques. Pel càlcul d'aquestes és necessari conèixer les composicions i temperatures. A més a més, també s'estudiarà com varia la composició d'azeòtrop amb la pressió i si és prou sensible. Amb aquests valors, es compararà l'eficiència assolida en els dos processos fent diferenciació entre els azeòtrops de màxim i mínim punt d'ebullició. Per últim, es realitzarà una comparació crítica entre ambdues alternatives per les diferents mescles amb l'objectiu de poder trobar una resposta als resultats obtinguts i establir unes indicacions generals útils en la tria durant les primeres etapes de concepció del procés de separació.

Paraules clau: Tècniques de destil·lació avançada, eficiències energètiques, anàlisis infinit/infinit, indicacions generals

1. INTRODUCTION

Separation processes achieve to separate the molecular species by creating two or more zones that coexist and that have differences in temperature, pressure, composition and/or phase. The separation occurs because each specie reacts in a different way to the different conditions present in those zones. When the system moves towards equilibrium, each specie will present a different concentration in each zone originating the separation between them (Perry, 2007).

One of these separation processes is distillation where a liquid and vapor phase coexist. The objective of this operation is to separate the components of the mixture introduced as feed in the column. The column is formed by the different trays where an intimate counter-current contact between the two phases takes place (Figure 1). The feed is introduced by one or several points in the column. The liquid flows downwards from tray to tray while the vapors ascends. Consequently, the vapor phase becomes enriched in the more light components while the opposite occurs in the liquid phase. When the liquid reaches the bottom, is partially vaporized in a reboiler where boil-up is formed and returned to the column. The remaining liquid is the bottom product. The vapor that reaches the top, enters to a condenser where it is cooled forming liquid. Part of this liquid is returned to the column as reflux to assure a liquid flow. The rest, is the distillate product.

The degree of separation depends on the relative volatilities of the components, the number of contacting trays in the column and the relation of the ratio between the liquid-phase reflux flow rate and vapor-phase. The relative volatility (Eq. 1) it is a parameter that indicate the ease of separation by distillation and it changes with temperature, pressure and composition.

$$\alpha_{ij} = \frac{y_i \cdot (1-x_i)}{x_i \cdot (1-y_i)} = \frac{y_i \cdot x_j}{x_i \cdot y_j} = \frac{\gamma_i \cdot P_i^{sat}}{\gamma_j \cdot P_j^{sat}} \qquad (1)$$

The larger the value is from 1, the easier it is to separate the component i from component j. For values below of 1.2, distillation is relatively difficult. For values higher to 2, the separation is relatively easy and less minimum reflux ratio and number of theoretical plates are needed. It is impossible to separate with distillation when alpha has a value of 1 because the liquid-and vapor-phase compositions are equal (Kirk-Othmer, 2004).

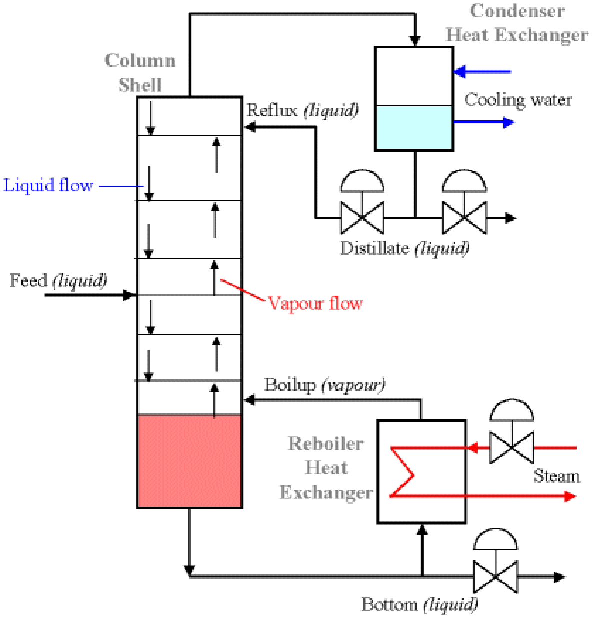


Figure 1. Schematic diagram for a simple continuous distillation column.

(Basics of Distillation Column Piping, 24/04/2019 via Piping Guide)

The equilibrium vapor-liquid (VLE) describes the distribution of the species in the two phases. At equilibrium state, coexisting phases have the same temperature T, the same total pressure p_t but different concentrations in the vapor y_i and in the liquid phase x_i.

The partial pressure in the vapor phase is determined by Dalton's law (Eq. 2) and in the liquid phase by Raoult's law (Eq. 3).

$$p_i = \gamma_i \cdot y_i \cdot P_t \qquad (2)$$

$$p_i = \gamma_i \cdot x_i \cdot p_i^* \qquad (3)$$

Activity coefficient γ_i is a measure of the liquid-phase nonideality mixture and depends of the temperature and composition. For ideal mixtures γ_i is unity. For non-ideal mixtures, the deviation from Raoult's law can be negative (lower than 1) or positive (larger than 1). 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. In the case of negative deviations, there are preferential attractive between the molecules of the different species that do now occur in the absence of the other species (Kirk-Othmer, 2004).

1.1. AZEOTROPE

Very large deviations from ideality lead to a special class of mixtures known as azeotropes. There is a point of intersection (Eq. 4) on the y-x diagram where vapor and liquid have the same composition.

$$y_i = x_i \quad for\ i = 1, \dots, n \qquad (4)$$

As a result, the mixture boils at constant temperature and the dew-point (vapor) and bubble-point (liquid) curves are tangent with zero slope. These conditions define an azeotrope that can be categorized in three different types:

1) Number of components: binary or ternary. Two liquids can form a binary azeotrope and when there are three liquids then is a ternary azeotrope. It is possible to have more constituents. This project focus on binary azeotropes.

2) Number of phases: homogeneous and heterogeneous. When the constituents are completely miscible then homogeneous azeotropes are formed. The opposite occurs with the heterogeneous.

3) Boiling temperature: positive and negative deviations. A positive or minimum boiling point azeotrope is formed when the boiling point of the mixture is lower than the boiling points of the constituents. As said before (Introduction), it is consequence of positive deviation from Raoult's law because there is no preferential interaction between species. A negative or maximum boiling point azeotrope is formed when the boiling point of the mixture is higher than the boiling points of the constituents. In this case, deviation from Raoult's law are negative and there are preferential interactions. Figure 2 shows a minimum boiling point azeotrope.

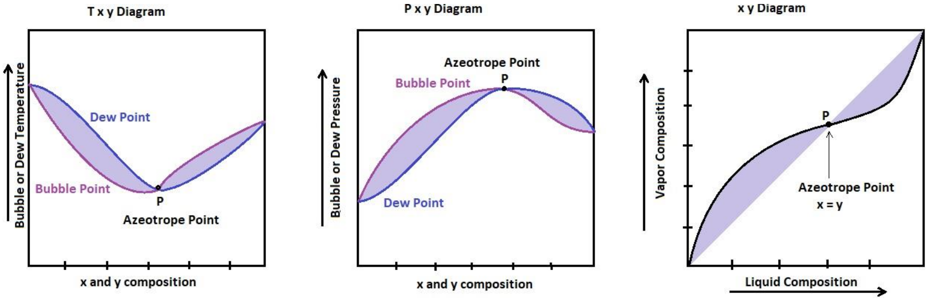


Figure 2. T-xy, P-xy and x-y diagrams for a minimum-boiling point azeotrope.

(Azeotropes, 09/05/2019 via The Gate Matrix)

1.2. AZEOTROPIC DISTILLATION

Azeotropic mixtures are impossible to separate by ordinary distillation and other techniques are necessary. There are five separation methods low relative volatilities or close boiling points and/or azeotropic mixtures:

1) Extractive distillation

2) Heterogeneous azeotropic distillation

3) Salt-effect distillation

4) Pressure swing distillation

5) Reactive distillation

All of these methods are based in some mechanism which modifies the behavior liquid-vapor of the principal compounds. Only ED and PSD are going to be studied.

1.2.1. Extractive distillation

ED is the distillation with the presence of a liquid separating agent, commonly called the solvent, which is miscible, not too much volatile and has a higher boiling point. The election of the solvent is the most important in this process because is chosen to interact differently with the components of the original mixture modifying their relative volatilities without generating an additional azeotrope.

The configuration of the extractive distillation is formed by two columns (Figure 3): EDC and SRDC. The solvent is introduced in the EDC trays up respect to the feed to maintain an appreciable concentration in the liquid phase on all the trays below. The compound with higher volatility in the presence of the solvent (A) is obtained pure at the distillate stream (D1). The other compound, with lower volatility (B), has more chemical affinity with the solvent so both are obtained as bottom product (B1). Then B1 is introduced as feed in the SRDC where the solvent is recovered at the bottom (B2) and recycled back to the EDC and B is also obtained pure as distillate stream (D2).

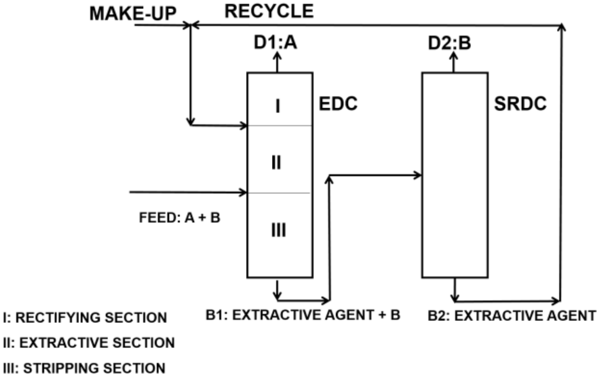


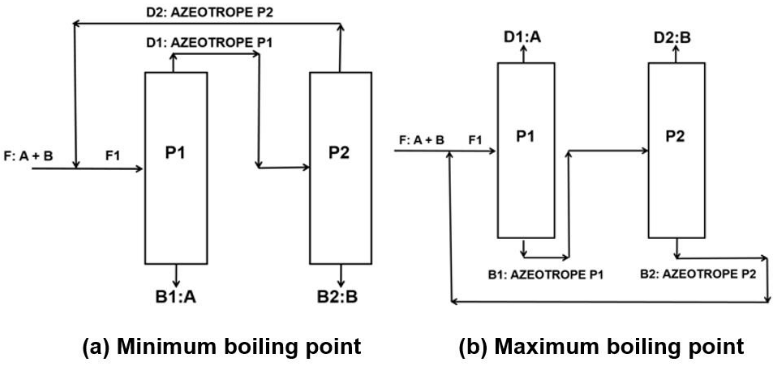
Figure 3. Sequence for ED: EDC and SRDC.

The section located between the two feed points is the extractive section where the concentration of the solvent remains high. It is necessary to maintain a high concentration because the solvent has to modify the relative volatilities. The rectifying section located upper respect the solvent feed point is where the solvent is separated from the "light" components to avoid the contamination of D1. Finally, the stripping section located under respect the feed point is to strip out the "light" components to complete the separation of the key components begun in the extractive section (Kirk-Othmer, 2004).

1.2.2. Pressure Swing Distillation

PSD is applied to systems where the concentration azeotropic composition must vary at least 5 percent over a pressure range not higher than 10 atm (Perry, R.H., Green, D.W.,1997). The bigger is the shift in azeotropic composition the more economical the process is. The intention is to take advantage of the sensitivity of the mixtures using two distillation columns operating at different pressures. In addition, it is important that the components must not decompose with the increase of the pressure. The difference between this operation and ED is the fact that not a third component is necessary to achieve the separation between the compounds.

What happens in PSD is shown in the Figure 4. In the case of minimum boiling point azeotrope, the fresh feed, F, is mixed with the recycled stream, B2, from the column operating at P2, to form the feed stream F1. At some point, this recycled stream changes the pressure from P2 to P1. F1 enters to the column which operates at P1. Being a minimum boiling point implicates that A is recovered as a bottom product, B1. A is recovered first because F1 lies to the right of the azeotropic composition at pressure P1. The distillate product, D1, is the azeotrope formed at P1. D1, which changes the pressure from P1 to P2, is the feed at the second column which operates at this pressure, P2. Now because the feed, D1, lies to the left of the azeotropic composition at pressure P2, the other pure component can be recovered, B, in the bottom too, B2. In the case of maximum boiling point azeotropes, pure compounds are obtained as distillate products while the azeotropic mixtures as bottom products.



(a) Minimum boiling point **(b) Maximum boiling point**

Figure 4. PSD sequence for (a) minimum boiling point and a (b) maximum boiling point.

Figure 5 is an example of T-xy diagram for a minimum-boiling point formed by acetone and methanol. The diagram is generated at different pressures and it can be seen that the azeotrope is richer in acetone at atmospheric pressure. Increasing pressure causes the decrease of the molar fraction of acetone (A) being now the azeotrope is richer in methanol (B). This implies that acetone is obtained as pure component in the HPC while methanol in the LPC.

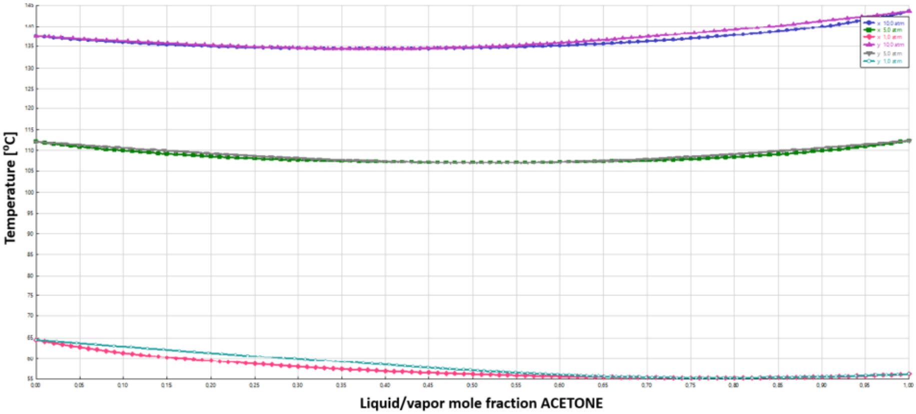


Figure 5. T-xy diagram for acetone-methanol system at 1, 5 and 10 atm made by Aspen Plus V10.

2. OBJECTIVES

The aim of this work is to define a shortcut method that help us to decide in the early stages of design which enhance distillation is the best option to break azeotropic binary mixtures. Specifically, it is going to be differentiated between the maximum and minimum boiling point azeotropes. Also there are several methods to break that mixtures but this project focus on ED and PSD. For this reason, the following tasks will be carried out:

1. Conduction of an exhaustive bibliographic research to select the mixtures that are going to be studied.

2. Calculus of the different efficiencies for the two types of azeotropes by the application of a mathematical simplified model that is to quantify, choose and conclude when ED or PSD is more advantageous.

3. Study of the different variables that affects the calculus of the efficiencies.

4. Verify the thermodynamic model selected in the simulator.

3. LITERATURE REVIEW

As explained before (1.3.2), to be feasible the technology of PSD the mixtures must be sensitive to pressure changes. A heuristic says that to be practical, the azeotropic composition must vary at least 5 percent over a pressure range not higher than 10 atm. This fact restricts the selection of the mixtures that are going to be studied.

Heydenreich developed a TFG (2018) with the aiming to find the optimal pressure for PSD. For this reason, Heydenreich carried out a research to select different mixtures appropriate for the study and generated a list. The research has been made in 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”)). The limitations are: only binary-non-reactive systems, operation on continuous, because most distillations commercially operate continuously, and without secondary entrainers. The list has a total of 26 mixtures. To compare both technologies the mixtures must be sensitive and then this list (Table 1) it is useful to generate the final list.

Table 1. List of mixtures made by Júlia Heydenreich.

	MIXTURE	**Type**	**Reference**
1	Acetic acid + dimethylacetamide (DMAC)	Max	Luyben (2012)
2	Acetone + chloroform	Max	Luyben (2013a)
3	Acetone + methanol	Min	Modla and Lang (2012) Luyben (2012) Luyben (2008a) Fulgueras et al. (2016) Wang et al. (2016a)
4	Acetonitrile + water	Min	Repke et al. (2005) Huang et al. (2008) Repke et al. (2004)
5	Chloroform + water	Min	Hosgor et al. (2014) Wang et al. (2016a)

6	Cyclohexanone + phenol	Max	Li et al. (2013)
7	Diisopropyl ether + isopropyl alcohol	Min	Luo et al. (2014) Xia et al. (2017) Luyben (2018)
8	Di-n-propyl ether + n-propyl alcohol	Min	Lladosa et al. (2011)
9	Ethanol + toluene	Min	Zhu et al. (2015)
10	Ethanol + water	Min	Kiran and Jana (2015b) Mulia-Soto and Flores-Tlacuahuac (2011) Arifeen et al. (2007)
11	Ethyl acetate + ethanol	Min	Zhang et al. (2017)
12	Isobutyl alcohol + isobutyl acetate	Min	Muñoz et al. (2006) Luo et al. (2016)
13	Isopentane + methanol	Min	Luyben (2005)
14	Methanol + dimethyl carbonate	Min	Wei et al. (2013) Zhang et al. (2017)
15	Methanol + tetrahydrofuran (THF)	Min	Want et al. (2015b) Wang et al. (2014)
16	Methanol + trimethoxysilane	Max	Luyben (2014a) Luyben (2014b)
17	Methyl acetate + methanol	Min	Bonet et al. (2007) Zhang et al. (2016) Cao et al. (2016)
18	Methylal + methanol	Min	Yu et al. (2012)
19	Methyl isobutyl ketone + butanol	Min	Li et al. (2016b)
20	Mesityl oxide + butanol	Min	Aspen database
21	N-Heptane + acetone	Min	Aspen database
22	N-Pentane + acetone	Min	Modla (2010)
23	THF + ethanol	Min	Wang et al. (2015a) Wang et al. (2015c)
24	THF + water	Min	Abu-Eishah and Luyben (1985) Frank (1997) Luyben (2008b)

			Lee et al. (2011) Ghuge et al. (2017) Hamad and Dunn (2002)
25	Toluene + 1-butanol	Min	Qasim et al. (2015)
26	Water + ethylenediamine	Max	Li et al. (2016) Fulgueras et al. (2015) Modla (2010) Modla and Lang (2007)

Not all the mixtures are studied in the same way. There are some mixtures more studied and then a lot of information is available in the different resources. That is why an intensive research is made to all the mixtures exposed at Table 1 in order to analyze the information on hand. The platforms selected to obtain all the data base are three: SpringerMaterials, NIST and Aspen Plus V10. In addition, “Azeotropic Data II” which is a book is also consulted. SpringerMaterials and NIST are both database. SpringerMaterials covers data from materials science, physics, physical and inorganic chemistry, engineering and other related fields. NIST is incorporated at Aspen Plus V10 and provides chemical and physical property data of a lot of compounds. Aspen Plus V10 is a software designed to build a process model and simulate. Also allows to determinate properties at atmospheric pressure and overpressure.

It can be seen that a lot of information at atmospheric pressure is available but it is difficult to have data at high overpressures. Aspen Plus let to determinate data at overpressure by the regression what makes from the database which has built-in. For this reason, if there is no information about the mixtures in Aspen Plus they are discarded. The data at overpressure selected to work with it is the provided by Aspen and will be compared with the values of the others database. If there is information, that mixtures are selected to be studied. The problem that Aspen Plus has is that data at atmospheric pressure that proportionate it is one value selected by default not taking into account all the data available. That is why the data at atmospheric pressure of the mixtures will be taking into account all the values obtained in the data base aforementioned (mode).

To search at SpringerMaterials at SEARCH the name of the mixture it is written. Then at DATA SOURCE “Thermophysical Properties” is selected and at “Properties” the option is “azeotropes”. To search at NIST the name of the mixtures it is written and then binary properties or directly azeotrope data is available. The final list of 23 mixtures to be studied is the one shown in Table 2 (maximum boiling point) and Table 3 (minimum boiling point).

Table 2. Azeotropes of maximum boiling point.

MIXTURE	COMPONENT A	COMPONENT B
1	Acetic acid	DMAC
2	Acetone	Chloroform
3	Phenol	Cyclohexanone
4	Water	Ethylenediamine

Table 3. Azeotropes of minimum boiling point.

MIXTURE	COMPONENT A	COMPONENT B
1	Acetone	Methanol
2	Acetonitrile	Water
3	Chloroform	Water
4	Diisopropyl ether	Isopropyl alcohol
5	Ethanol	Toluene
6	Ethanol	Water
7	Ethyl acetate	Ethanol
8	Isobutyl alcohol	Isobutyl acetate
9	Isopentane	Methanol
10	Methanol	Dimethyl carbonate
11	Methanol	THF
12	Methyl acetate	Methanol
13	Methylal	Methanol
14	Methyl isobutyl ketone	Butanol
15	Mesityl oxide	Butanol
16	N-Heptane	Isobutanol
17	THF	Ethanol
18	THF	Water
19	Toluene	1-Butanol

It can be seen that maximum-boiling point azeotropes are less common than minimum boiling point.

3.1. SELECTION OF THE PRESSURES

Most of authors to choice the pressure values to work with take into account the extended heuristic of 1-10 atm without considering if the reboiler and the condenser are obtaining the energy by the services available. This decision helps to know if the PSD should be considered as an option but not to decide the pressures (Risco et al., 2019).

The low pressure (LP) can be reduced to the point where it is complicated to use refrigeration water achieving vacuum pressures. Working below the limit involves the use of alternative cooling agents that are more expensive than water. Fixing the low pressure at 1 atmosphere is the most common for the next reasons:

1. Is a low-pressure value very extended as a suitable value.
2. Cooling water can be used as refrigerant.
3. The operating conditions are easier at atmospheric pressure than working at vacuum although operating at vacuum provides more separation.

For the reasons exposed the LPC will be working at atmospheric pressure.

On the other hand, the high pressure (HP) must be adequate to heat from the available hot services. It is important to consider the existent relation between this pressure and the quality of the steam used. As the pressure increases, the quality necessary increases too (low, medium and high pressure steam). For this reason, the decision is based on this direct relation.

High pressure steam (HPS) is the steam with higher quality and the selected one. The equivalent temperature for this quality is approximately 240ºC so to find the value of the HP to fix at the column, the temperature of the bottom product fixed can’t be higher of this value. It is fixed at 220ºC to provide a margin to ensure a sufficient heat transference.

The majority of the authors selects 10 atmospheres because this existent heuristic. It is going to be verified if this value it is the optimal to work with.

4. METODOLOGY

In this section the methodology developed to obtain the results is commented with the aim that any person who reads this will be able to understand and replicate them.

4.1. DESTILLATION SEQUENCE EFFICIENCY

Distillation Sequence Efficiency (DSE) is a useful parameter to quantify and choose the most efficient processes in early stages of design. As said before, the aim of this work is to define an heuristic which help us to decide the best technique of advanced distillation (ED or PSD) to break azeotropic mixtures in the first steps of designs so, DSE is a good basis to quantify that not being necessary doing rigorous simulations. For that reason, the decision will be taken in terms of efficiency not economical like the vast majority of literature available.

The analysis infinite/infinite is a simplified mathematical model that allow us to calculate DSE and assumes two important things:

1) The number of stages in the columns is infinite.

2) In case of ED, the reflux flow rate equivalent to extractive agent flow rate is infinite. This implies that the stream which leaves the column from the bottom will have the same temperature as the extractive agent (boiling point).

At the same time, this statements imply:

1) The column and investment costs are infinite.

2) The energy requirements and operational costs are infinite.

The simplifying assumptions prevent any cost assessment but allow the calculation of Coefficient of Ease of Separation (CES) by Nadir and Liu (1983):

$$CES = \frac{D}{B} \cdot (T_B - T_D) \qquad (5)$$

Where D refers to distillate and B to the bottom product.

This parameter gives us an idea of the facility of the separation when the heuristics are contradictory but not permits quantifying that fact. The problem of the CES it is that not suitable for the overall process that is why necessary to define the DSE proposed by Plesu et al. (2015).

Plesu et al. assumes the distillation columns as Carnot engines that produces the separation where the reboiler is the hot source and the condenser the cold source. If now in the Eq. 5 B is replaced by F and divided by the temperature of the bottom (T_B) Carnot efficiencies appears (Eq. 6).

$$\frac{D}{F}\cdot\frac{(T_B-T_D)}{T_B} \rightarrow \frac{B}{F}+\frac{D}{F}\cdot\eta \rightarrow DSE = \sum_i \frac{W_i}{F_C}\cdot\prod_C \eta_{iC} \qquad (6)$$

Eq. 6 allows us to calculate DSE being only necessary knowing the streams flow rates, compositions and the temperatures in the system to find the efficiencies. Figure 6 it is a schematic diagram which resumes this lastly equation.

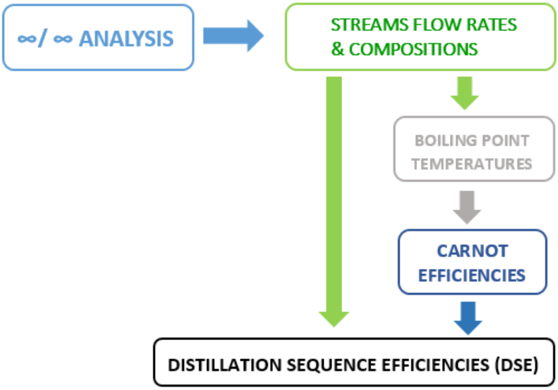


Figure 6. Schematic diagram to calculate DSE by the application of ∞/∞ analysis.

Carnot efficiencies appears when is a stream of distillate and is calculated by the quotient of the difference between temperatures of the distillate and bottom and the temperature of the bottom. The streams from the bottom advance with an efficiency of 1. In case of recirculating a stream, we are mixing again the stream separated being necessary to subtract a valor of 1 from the factor of efficiencies. That is the reason why efficiencies can have a negative valor. Figure 7 it is an instructive example to calculate DSE.

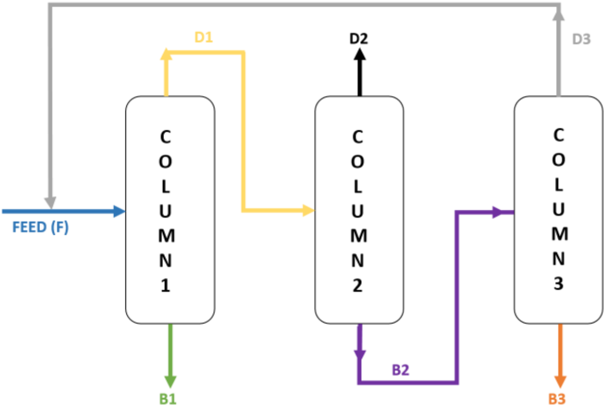


Figure 7. Instructive example to calculate DSE from three-column sequence.

$$DSE_{\infty} = \frac{B1}{F} + \frac{D2}{F} \cdot (\eta_1 \cdot \eta_2) + \frac{B3}{F} \cdot \eta_1 + \frac{D3}{F} \cdot (\eta_1 \cdot \eta_3 - 1)$$

4.1.1. Extractive distillation

The schematic diagram for ED is shown in Figure 8. T_A and T_B are the boiling points of the pure compounds at atmospheric pressure. T_E it is the boiling point of the extractive agent.

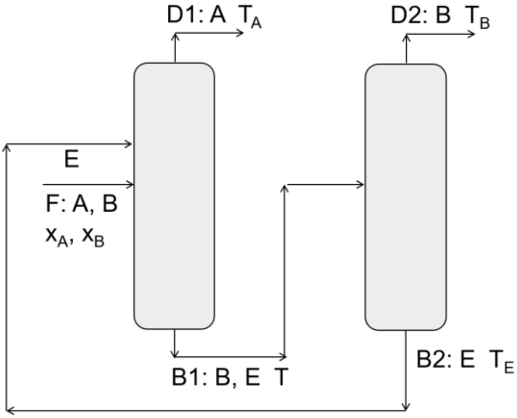


Figure 8. Schematic diagram for ED.

The F and the EA are introduced in the EDC. The streams D_i make reference to distillate streams which contains pure compounds. A is the compound with most chemical affinity with the

EA that not must to be the one with lowest boiling point because the relative volatilities are modified. This one is obtained at EDC. The opposite occurs with B which is obtained at RDC. On the other hand, the streams B_i make reference to bottom streams. Applying the Eq. 6:

$$DSE = \frac{A}{F} \cdot \eta_1 + \frac{B}{F} \cdot \eta_2 = x_{A,F} \cdot \frac{T - T_A}{T} + (1 - x_{A,F}) \cdot \frac{T_E - T_B}{T_E}$$

Assuming an infinite flow rate of extractive agent as limit condition, then both column bottoms temperatures are the same as the boiling point of pure extractive agent:

$$T = T_E$$

This assumption provides the maximum DSE:

$$DSE_\infty = x_{A,F} \cdot \frac{T_E - T_A}{T_E} + (1 - x_{A,F}) \cdot \frac{T_E - T_B}{T_E} \qquad (7)$$

Where x_i refers to molar fractions of compounds at the crude feed and T_i to the boiling points in Kelvin.

Del Castillo developed a TFG (2017) to propose an extractive agent flow rate (Eq. 8) and found that DSE of extractive distillation is the 78% of DSE working with an infinite flow rate of extractive agent.

$$DSE = 0.78 \cdot DSE_\infty \qquad (8)$$

4.1.2. Pressure Swing Distillation

For PSD, the nature of the azeotrope (minimum or maximum boiling point) affect on the calculation of DSE. In the case of having an azeotrope of minimum boiling point, the pure components are obtained at the bottom of the column and the azeotropic mixtures at the top. On the other hand, with azeotropes of maximum boiling point, the pure components are obtained at the top of the column. The compound A or B depends on which band the azeotrope feed composition is located.

4.1.2.1 Azeotropes of minimum boiling point

Figure 9 represents the sequence for azeotropes of minimum boiling point. F, which has the azeotropic composition and the temperature corresponding at LP fixed at LPC, is introduced. Pure compounds are obtained from the bottom (A, B) consequently of being a minimum-boiling point azeotrope. T_{az1} it is the boiling point of the azeotrope at HP and T_{az2} at LP. T_A is the boiling point of the compound A at HP and T_B of the compounds B at LP. The molar fraction at LP is $x_{A,az1=LP}$ and the one at HP is $x_{A,az1=HP}$.

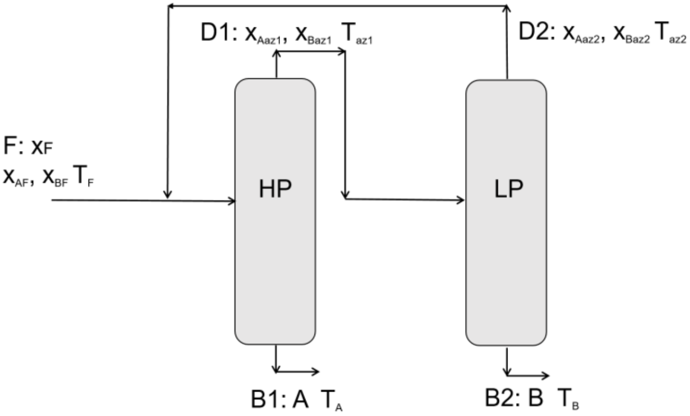


Figure 9. Schematic diagram for PSD in case of minimum-boiling point.

Global balance at column 2: $D1 = D2 + B2$

Component balance at column 2: $D1 \cdot x_{A,az1=HP} = D2 \cdot x_{A,az2=LP} + 0$

Application of the equation (6):

$$DSE = \frac{B1}{F} + \frac{B2}{F} \cdot \eta_1 + \frac{D2}{F} \cdot (\eta_1 \cdot \eta_2 - 1)$$

The unique unknown it is the quotient between the distillate of the second column and the feed flow rate. That is why global and component balance it is useful and then the Eq. 9 is obtained.

$$D2 \cdot x_{A,az1=HP} + B2 \cdot x_{A,az1=HP} = D2 \cdot x_{A,az2=LP}$$

$$D2 \cdot \left(x_{A,az1=HP} - x_{A,az2=LP}\right) = -B2 \cdot x_{A,az1=HP}$$

$$\frac{D2}{F} = \frac{-B2 \cdot x_{A,az1=HP}}{F \cdot \left(x_{A,az1=HP} - x_{A,az2=LP}\right)} \rightarrow \frac{D2}{F} = \frac{x_{B,F} \cdot x_{A,az1=HP}}{\left(x_{A,az2=LP} - x_{A,az1=HP}\right)}$$

$$DSE = \frac{B1}{F} + \frac{B2}{F} \cdot \eta_1 + (\frac{x_{B,F} \cdot x_{A,az1=HP}}{x_{A,az2=LP} - x_{A,az1=HP}}) \cdot (\eta_1 \cdot \eta_2 - 1)$$

$$DSE = x_{A,F} + (1 - x_{A,F}) \cdot \frac{TB1 - TD1}{TB1} + \left(\frac{(1 - x_{A,F}) \cdot x_{A,az1=HP}}{x_{A,az2=LP} - x_{A,az1=HP}}\right) \cdot \left(\frac{TB1 - TD1}{TB1} \cdot \frac{TB2 - TD2}{TB2} - 1\right)$$

$$DSE = x_{A,F} + (1 - x_{A,F}) \cdot \frac{T_A - T_{az1}}{T_A} + \left(\frac{(1 - x_{A,F}) \cdot x_{A,az1=HP}}{x_{A,az2=LP} - x_{A,az1=HP}}\right) \cdot \left(\frac{T_A - T_{az1}}{T_A} \cdot \frac{T_B - T_{az2}}{T_B} - 1\right) \quad (9)$$

4.1.2.2 Azeotropes of maximum boiling point

Figure 10 represents the sequence for azeotropes of maximum boiling point and consequently pure compounds are obtained as distillate. The nomenclature is the same explained as the minimum boiling point azeotropes.

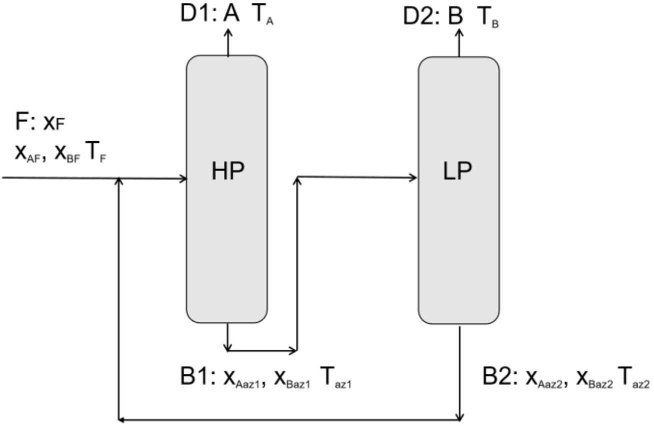


Figure 10. Schematic diagram for PSD in the case of maximum-boiling point.

Global balance at column 2: $B1 = B2 + D2$

Component balance at column 2: $B1 \cdot x_{A,az1=HP} = B2 \cdot x_{A,az2=LP} + 0$

Application of the equation (2):

$$DSE = \frac{B1}{F} \cdot \eta_1 + \frac{B2}{F} \cdot \eta_2 + \frac{B2}{F} \cdot (1 - 1)$$

In this case, the quotient between the distillate and feed flow rate don't have influence in the calculation of DSE and then the Eq. 10 is obtained.

$$DSE = x_{A,F} \cdot \frac{TB1 - TD1}{TB1} + \left(1 - x_{A,F}\right) \cdot \frac{TB2 - TD2}{TB2}$$

$$DSE = x_{A,F} \cdot \frac{T_{az1} - T_A}{T_{az1}} + \left(1 - x_{A,F}\right) \cdot \frac{T_{az2} - T_B}{T_{az2}} \quad (10)$$

4.1.3. Extractive distillation vs Pressure swing distillation

To observe the effect of the different variables which are involved in the equations of the DSE the ratio (Eq. 11) between the efficiencies of both alternatives is calculated.

$$Ratio = \frac{DSE_{PSD}}{DSE_{ED}} \qquad (11)$$

When the ratio is greater than 1 the PSD is more favorable than ED because the denominator is lower than the numerator. The opposite occurs when is lower than unity being ED more benefited consequently of increasing the denominator. As explained before, the DSE expressions for maximum or minimum boiling point are different for PSD so it is necessary to calculate the relation for every case.

Pressure Swing distillation DSE:

$$DSE_{PSD,min} = x_{A,F} + (1 - x_{A,F}) \cdot \frac{T_A - T_{az1}}{T_A} + \left(\frac{(1 - x_{A,F}) \cdot x_{A,az1=HP}}{x_{A,az2=LP} - x_{A,az1=HP}}\right) \cdot \left(\frac{T_A - T_{az1}}{T_A} \cdot \frac{T_B - T_{az2}}{T_B} - 1\right)$$

$$DSE_{PSD,max} = x_{A,F} \cdot \frac{T_{az1} - T_A}{T_{az1}} + \left(1 - x_{A,F}\right) \cdot \frac{T_{az2} - T_B}{T_{az2}}$$

Extractive distillation DSE:

$$DSE_{ED} = 0.78 \cdot (x_{A,F} \cdot \frac{T_E - T_A}{T_E} + (1 - x_{A,F}) \cdot \frac{T_E - T_B}{T_E})$$

For minimum boiling point, it is important to take into account that fixing the temperature of the bottom as the temperature of the EA means that T_A it is equal to T_E. For maximum-boiling point, the T_{az1} it is also fixed as the value of T_E.

Resulting:

A) Minimum boiling point

$$\frac{x_{A,F} + (1 - x_{A,F}) \cdot \frac{T_E - T_{az1}}{T_E} + \left(\frac{(1 - x_{A,F}) \cdot x_{A,az1=HP}}{x_{A,az2=LP} - x_{A,az1=HP}}\right) \cdot \left(\frac{T_E - T_{az1}}{T_E} \cdot \frac{T_B - T_{az2}}{T_B} - 1\right)}{0.78 \cdot (x_{A,F} \cdot \frac{T_E - T_A}{T_E} + (1 - x_{A,F}) \cdot \frac{T_E - T_B}{T_E})}$$

B) Maximum boiling point

$$\frac{x_{A,F} \cdot \frac{T_E - T_A}{T_E} + \left(1 - x_{A,F}\right) \cdot \frac{T_{az2} - T_B}{T_{az2}}}{0.78 \cdot (x_{A,F} \cdot \frac{T_E - T_A}{T_E} + (1 - x_{A,F}) \cdot \frac{T_E - T_B}{T_E})}$$

Simplifying:

A) Minimum boiling point

$$\frac{T_B\cdot T_{az2}\cdot\left(x_{A,az2=LP}-x_{A,az1=HP}\right)+\left(x_{A,F}-1\right)\cdot\left(T_B\cdot T_{az1}\cdot x_{A,az2=LP}+T_{az2}\cdot x_{A,az1=HP}\cdot\left(\cdot T_E-T_{az1}\right)\right)}{0.78\cdot TB\cdot\left(T_A\cdot x_{A,F}-T_B\right)\cdot\left(x_{A,az1=HP}-x_{A,az2=LP}\right)-0{,}78\cdot\left(\cdot T_E-T_B\cdot x_{A,F}\right)\cdot\left(x_{A,az1=HP}+x_{A,az2=LP}\right)} \quad (12)$$

The expression simplified for minimum boiling point is the expressed by Eq. 12. The azeotropic composition of the compound A is important: $x_{A,az1=LP}$ it is higher than $x_{A,az1=HP}$ so A is obtained pure in the HPC. For that reason, the term $(x_{A,az1=HP}-x_{A,az1=LP})$ is always negative. Focusing in the denominator it can be seen that the first term depends of the value of azeotropic composition in the feed: if it is located on one band or another respect from the azeotropic composition at HP being T_B higher than T_A or not. Normally, T_B is higher so the first term is positive. In the second term, the difference between the compositions is positive. The other part forming the second term is the difference between the boiling points T_E and T_B. If the term is negative because the product between $T_B\cdot x_{A,F}$ is higher than T_E then the second term becomes positive. So is interesting having a higher T_B for both terms of the denominator but respect $x_{A,F}$ is not clear what more beneficiary is. Focusing in the first term of the numerator now it can be seen that $(x_{A,az1=LP}-x_{A,az1=HP})$ is always a positive value so having higher T_B and T_{az2} makes the term more higher. For the second term $(x_{A,F}-1)$ is a negative value because $x_{A,F}$ is lower than the unity. The rest of the term can be discomposed in two:

$(T_B\cdot T_{az1}\cdot x_{A,az2=LP})$: this term is always positive. Is more positive when the variables are higher.

$(T_{az2}\cdot x_{A,az1=HP})\cdot(T_E-T_{az1})$: consequently of having $(x_{A,F}-1)$ negative is interesting making that term positive but T_{az1} is lower than T_E. being the term positive. The term is more positive when T_{az2} and T_B increase.

Both terms combined make the sign positive and then multiplied by $(x_{A,F}-1)$ becomes negative. Is difficult to know when the numerator is higher because most of the variables are contradictory in the first and second term. More difficult is to know without numbers when ED is better than PSD because the same variables affect the numerator and denominator and in the same way.

B) Maximum boiling point

$$\frac{(x_{A,F}-1)\cdot T_E\cdot T_B-x_{A,F}\cdot T_{az2}\cdot T_A+T_E\cdot T_{az2}}{0.78\cdot T_{az2}\cdot\left(T_E-x_{A,F}\cdot T_A+\left(x_{A,F}-1\right)\cdot T_B\right)} \quad (13)$$

The expression simplified for maximum boiling point is the Eq. 13 where T_E is fixed. The variables that can favour the denominator, that is to say, extractive distillation, are the different boiling points of the pure compounds (T_A, T_B), T_{az2} and $x_{A,F}$. When the boiling points of both compounds are higher, the two terms of the denominator are more negative subtracting a higher quantity from T_E. This implies that the value multiplying the factor 0.78·TB2 is smaller. The factor gets an even smaller when TB2 is lower. Respect the composition, when $x_{A,F}$ gets lower the value subtracting T_E is higher and the denominator is not benefited. This implies that the value multiplying the factor 0.78·TB2 is smaller. The factor gets an even smaller when TB2 is lower. Consequently, the ratio is greater than 1 being PSD more efficient. On the other hand, the same variables affect the numerator: $T_{A,}$ T_B, T_{az2} and $x_{A,F}$. The first two terms of the numerator are also negative so higher boiling points are unfavorable for PSD. It have been explained that the same occurs for the denominator so it is impossible to say when is PSD or ED better until the variables are substituted by numeric values. This is consequently of having the same variables and affecting in the same way in the numerator and the denominator.

4.2. HYPOTHESIS

HPS used at HPC is the one selected for two reasons:

- There is an existent direct relation between the pressure and the quality as explained in 3.1. With PSD there is the possibility of working with high-pressures so high quality will be needed.
- Maximum boiling point azeotropes are going to be studied. In the case of separating mixtures with ED, it is necessary to select an extractive agent with high-boiling point. The equivalent temperature of high-steam it is approximately 220ºC so the extractive agent selected will have a boiling point with this value.

The selection of this steam fixes the temperature of the solvent. This decisions in calculus is reflected in both processes. For ED, the boiling point of the solvent is defined and is reflected on DSE. Solvent leaves the EDC with the compound of higher chemical affinity from the bottom. To be available compare both processes it is necessary to fix the bottom temperature of this column at 220ºC in the case of PSD. For ED, is not influential the nature of azeotropes but the opposite occurs with PSD. As mentioned before (4.1.2), there are different formulas for maximum or minimum boiling point azeotropes. In the first case, azeotropes are obtained as bottom products so to find the HP to operate with is necessary to search pressure whom the azeotrope has a temperature of 220ºC. With minimum boiling point, the compounds are obtained pure from the bottom. It is necessary to study how varies the composition of the azeotrope with the pressure to find which of the compounds is obtained in the first column (A) because is not necessarily the component with the highest boiling point. When the compound is found, the equation of Antoine is solved to find at which pressure the boiling point is 220ºC. The data necessary is how varies the vapor pressure with temperature and it is provided by Aspen Plus V10.

Another important question is the sequence of the columns in PSD. The feed stream is introduced in the column where the composition is more different of azeotropic composition at the correspondent pressure, minimizing distillate flux. It has been decided to feed with azeotropic composition at atmospheric pressure. That is why the sequence selected is HPC-LPC.

4.3. OBTENTION OF AZEOTROPIC DATA

As explained in Literature Review, the information of azeotropic has been searched in two database (SpringerMaterials and NIST), in a book (Azeotropic Data II) and in the simulator Aspen Plus V10. As a result of the multitude of data available at atmospheric pressure and considering that Aspen only proportionate a value of all the data incorporated, it has been decided that the atmospheric values will be a mode of all the available data obtained in all the sources searched. In the case of overpressure data, it have been determined from only Aspen Plus which it makes a regression from the atmospheric data incorporated. The thermodynamic model selected is Non-Random Two-Liquid (NRTL) and it is recommended for highly non-ideal chemical systems. Concretely the thermodynamic model selected is NRTL-Hayden O'Connell (NRTL-HOC).

With the compounds and the thermodynamic model selected, there is an option of "Binary" that allow to generate T-xy and P-xy diagrams. In the case of selecting T-xy, different values of pressures can be selected. In the section "Results" binary information is available. In the point where the vapor has the same composition of the liquid, there is an azeotrope. Another option is to find the minimum or maximum temperature depending on the nature of the azeotrope.

In addition, to calculate DSE is also necessary to have the boiling points of the different components that form the mixture at different pressures. That is why these are calculated by the extended equation of Antoine (Eq. 14) proportionated by Aspen Plus.

$$\ln(p_i) = C_{1i} + \frac{C_{2i}}{C_{3i}+T} + C_{4i} \cdot T + C_{5i} \cdot \ln(T) + C_{6i} \cdot T^{C_{7i}} \qquad (14)$$

The coefficients C_{xi} (x=1,...,7) are characteristic of every component and also proportionated by the simulator. From these values and fixing the pressure in bars the temperature in Kelvin is determined by a Solver. There is a tendency to think that the values provided by the program are not correct because it is not the same as obtaining them experimentally. It is going to be checked with Antoine's equation (Eq. 15), where the coefficients are obtained from a database (Poling, B., et al., 2011) if the difference is very large. The total pressure is in mmHg and the temperature in Celsius.

$$\ln(p_t) = A_{Ant} + \frac{B_{Ant}}{T+C_{Ant}} \qquad (15)$$

5. RESULTS AND DISCUSSION

In this chapter the results obtained are discussed. First for azeotropes of maximum boiling point and then for the minimum.

5.1. AZEOTROPES OF MAXIMUM BOILING POINT

Only 4 of the 23 mixtures selected are azeotropes of maximum boiling point because these are the less common. The results of the DSE calculated by Eq. 6 shows that for these type of azeotropes ED is more favorable (Table 4). The objective of this section is to find out the reason of this behavior.

Table 4. Ordinated mixtures of higher to lowest DSE for ED.

MIXTURE	COMPONENT A	COMPONENT B	DSE ED	PRESSURE OF PSD [atm]	DSE PSD	DSE PSD AT 10 ATM
1	Acetone	Chloroform	0.2556	30	0.0169	0.0153
2	Water	Ethylenediamine	0.1792	12.3	0.0301	0.0229
3	Acetic acid	DMAC	0.1399	3.4	0.0374	0.0389
4	Phenol	Cyclohexanone	0.0904	1.2	0.0626	0.1302

To see the results more clearly the Figure 11 is a representation of the three different efficiencies for every mixture: DSE for ED, PSD fixing HP with the criteria exposed (3.1.) and PSD with HP fixed at 10 atmospheres.

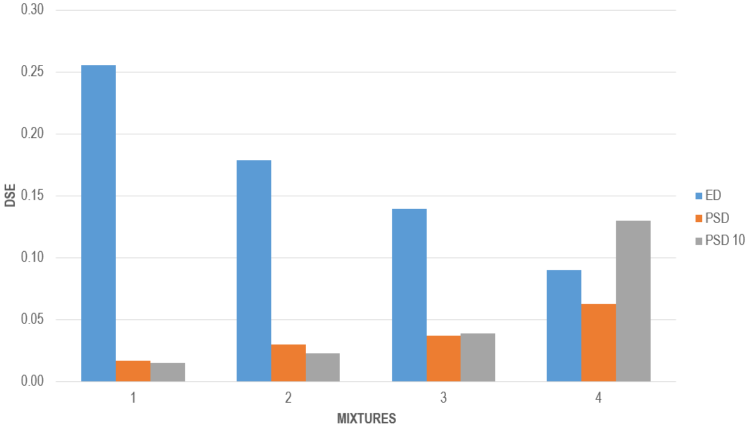


Figure 11. Representation of the different results for maximum-boiling point azeotropes.

At first glance, it can be observed that DSE for ED decreases while the one for PSD increases and simultaneously the pressure fixed at HPC decreases. There is a heuristic which affirms that PSD to be practical the azeotropic composition must vary at least 5 percent over a pressure range not higher than 10 atmospheres so, first of all the shift obtained is calculated to verify this heuristic (Table 5).

Table 5. The shift obtained on the azeotropic composition for a range of 10 atmospheres.

MIXTURE	SHIFT OBTAINED [%]
1	34.8
2	31.3
3	14.4
4	14.0

Mixture 1 is the one with the biggest shift but the better to separate by ED so, having a shift in the azeotropic composition higher than a 5 percent in a range of 10 atmospheres is not enough. In fact, the shift obtained decreases when the PSD is more favorable. The tendency of these azeotropes is that the efficiency with PSD fixing HP at the pressure calculated provides lower efficiencies and therefore, ED is a better option.

To justify that fact is important take into account Eq. 13 which expresses the ratio between DSE of PSD and ED. It is necessary to know the boiling points of the pure compounds (A, B).

Figure 12 shows the variation between the boiling points for the two compounds forming every mixture and simultaneously the values of DSE for both alternatives.

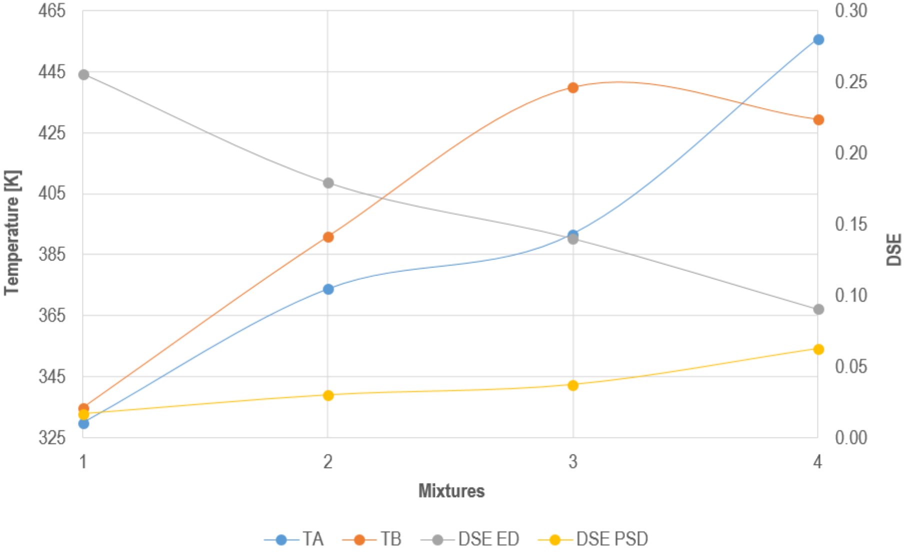


Figure 12. Representation of the variation of boiling points and the DSE with the different mixtures

Mixture 1 formed by acetone and methanol has the highest DSE with ED consequently of having the lowest boiling points for both compounds. To be available to separate by PSD, is necessary to work with high pressures. In this case, the HP necessary is 30 atmospheres. For mixture 2, the boiling points are higher and then DSE of ED is lowest respect from mixture 1 while the value of PSD increases and the pressure necessary to work with at HPC decreases. The same occurs with mixtures 3 and 4. It can be concluded that ED is benefited with lower boiling points of the pure components (A, B) because the denominator is more favorite consequently that the subtracting at the EA boiling point is lower and also, the product with the factor 0.78. Higher boiling points of the azeotrope at atmospheric pressure benefits ED too. Making the factor of ED higher means having a ratio lower than 1 and this is verified and exposed at Table 6. The factor increases when PSD is more advantageous.

Table 6. Ratio between the DSE of both alternatives.

MIXTURE	RATIO DSE PSD/ DSE ED
1	0.066
2	0.168
3	0.267
4	0.692

Figure 13 shows the intersection between the lines of the boiling points previously of arriving at mixture 4 formed by phenol and cyclohexanone. It depends on the composition of the feed and the fact that the azeotrope at higher pressures gets richer in the compound with lowest boiling point (cyclohexanone). In all of the other cases, the compound in excess at the feed is the one with the lowest boiling point so it is the obtained as a pure component from the bottom of the HPC. The opposite occurs with this mixture: phenol, with highest boiling point, is obtained pure in the HPC and cyclohexanone at the LPC.

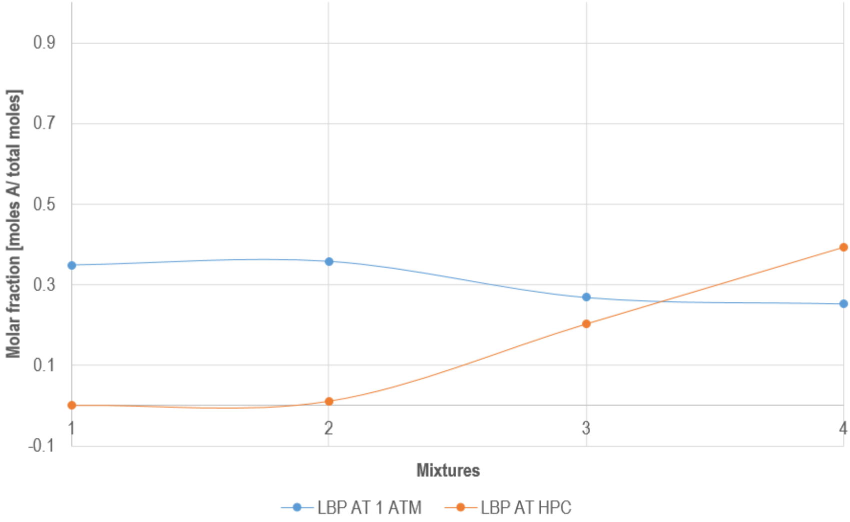


Figure 13. Representation of the variation of molar fraction for the compound with lowest boiling point.

Eq. 13 is also influenced by the boiling point of the azeotropes at atmospheric pressure and they are collectively represented on Figure 14 with the boiling points of the pure compounds previously exposed. PSD gets more advantageous when the difference between the boiling points is higher and the boiling point of the azeotrope too. The boiling point of the azeotrope at HP don't influence because is a variable fixed at 220 ºC to calculate the pressure at HPC.

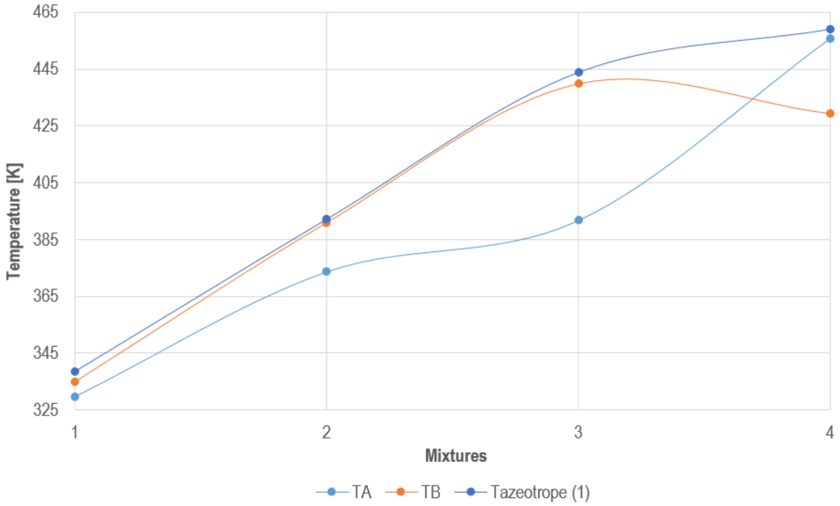


Figure 14. Representation of the variation of boiling points and azeotrope temperature.

If ED and PSD fixing at 10 atmospheres the pressure to work with at HPC are compared, the tendency remains the same. Mixture 4 is an exception with a higher DSE for PSD consequently of having the azeotrope with highest boiling point (668 K).

Lastly, if both DSE's for PSD are compared, it can be verified the strong relation of the efficiency with the pressure. In the case of fixing the pressure taking into account the quality of the steam and obtaining a value greater than 10 atmospheres then, the efficiency at HPC is higher. This is the situation for mixture 1 (30 atm) and mixture 2 (12.3 atm). The opposite occurs with mixture 3 (3.4 atm) and mixture 4 (1.2 atm), being the efficiencies lower than the provided by working at 10 atmospheres. The efficiency obtained at LPC is equal consequently of having the same boiling points at atmospheric pressure. It can be guaranteed that fixing the pressure at one value is a limitation in relation to the efficiency obtained, and it is important to study at the first steps of the design how varies the composition of the mixtures with the pressure.

The mixtures have been studied at different pressures to see at which point the azeotrope disappears and pure compounds are directly obtained. This pressure is compared with the one fixed at HPC (Table 7).

Table 7. Pressure for PSD and the one which disappear the azeotrope for every mixture in atmospheres.

MIXTURES	PSD	SINGLE COLUMN
1	30	10
2	12.3	13
3	3.4	15.5

For mixture 1 is not necessary to work at 30 atm when with a lower pressure, 10 atm, the pure compounds are directly obtained without adding a third component and being only necessary one column. In the case of mixture 2, the difference between the pressures is lower. For mixture 3, the compounds have high boiling points limiting the value of the pressure fixed (3.4 atm) because if the pressure increases, the boiling points would be too much high. The same happens with mixture 4 (1.2 atm), that is not exposed on the grounds because despite increasing the pressure the azeotrope don’t disappear: 30 atm is the limit where the molar fraction of phenol is maximum (0.60). On the other hand, it has no sense working with two columns at similar pressures but fixing the temperature of the bottom proportionate these values.

If the efficiencies are calculated in the case of having a single column working with the pressure exposed then, Table 8 is generated. For one column the DSE is calculated by the Eq. 16.

$$DSE_{ONE\ COLUMN} = \frac{D1}{F} \cdot \eta_1 + \frac{B1}{F} = x_{A,F} \cdot \frac{T_B - T_A}{T_B} + x_{B,F} \qquad (16)$$

Table 8. Efficiencies working with one or two columns.

MIXTURE	DSE PSD	DSE WITH 1 COLUMN
1	0.0169	0.6603
2	0.0301	0.6447
3	0.0374	0.7641
4	0.0626	0.2671

Effectively, working with one column is an option to considerate when the pressure at which the azeotrope disappear is lower to not have excessive temperatures at the column. For all the cases, the efficiency provided is higher than working with two columns. For mixture 4 the efficiency is the lower because the azeotrope don't disappear so it would be necessary an additional operation.

It can be a surprise the value at HPC for the mixture: 30 atm. The first though it is that too much large and unfeasible to work with. There is an equipment known as FISCHER (Figure 15) that allow us to determinate liquid-vapor equilibrium of binary and multi-component with a charge of 50 mL mixtures from vacuum (1 to 1.013 mbar) to overpressures (1 to 50 bar). The temperature limit is 453 K. There is one at the University of Bucharest. Despite this, it also depends on the thickness and the security conditions implemented.

Figure 15. FISCHER apparatus to determinate liquid-vapor equilibrium.

(Vapour-Liquid-Equilibrium Determination from vacuum (1 mbar) up to overpressure (50 bar), 09/05/2019 via ILUDEST)

It can be conclude that for maximum-boiling points azeotropes studied, there is a global tendency of being more efficient ED than PSD despite having a significant shift on the azeotropic composition with the pressure. ED is more favored when the boiling points of the compounds forming the mixture are lower as well as higher pressures are needed in the case of working with PSD. PSD is more benefited when the boiling points are higher and the difference between them too. Fixing the pressure at HPC with a value of 10 atmospheres directly limits the efficiency being important to study the influence of the pressure on the azeotrope. It is clear that when the pressure calculated taking into account the quality of the steam is higher than 10 atm, the efficiency obtained is better. It also have been studied and verified that working with one column would be a better option to separate directly the mixture because the efficiencies provided are higher than working with PSD.

5.2. AZEOTROPES OF MINIMUM BOILING POINT

19 of the 23 mixtures selected are azeotrope of minimum-boiling point: the study shows a 21% of those have a higher efficiency with ED and 79% with PSD (Figure 16).

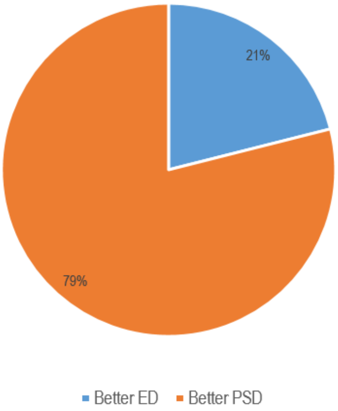


Figure 16. Representation of the percentage favorable for every technique.

The results of the mixtures with better efficiency for ED are shown in Table 9 ordinated from higher to lower. Also the pressure fixed at HPC in the case of PSD is exposed. It can be seen that the efficiency of PSD and also the pressure decreases. Table 10 represents the same for the group which have better DSE for PSD and the efficiencies are also ordinated from higher to lower value respect from PSD. It can be seen that there is not a clearly tendency like the other case: an increment of the efficiency for PSD not implicate a decrease for the DSE of ED and the pressure fixed at the HPC.

Table 9. Results of the mixtures with higher DSE's for ED with pressures at atmospheres.

MIXTURE	COMPONENT A	COMPONENT B	DSE ED	PRESSURE OF PSD	DSE PSD	DSE PSD AT 10 ATM
1	Methanol	Isopentane	0.7155	57.6	0.6606	0.7696
2	Acetonitrile	Water	0.1973	21.3	0.0782	0.0065
3	Toluene	Ethanol	0.1837	10.4	0.0662	0.0654
4	Mesityl oxide	Butanol	0.1471	7.4	0.1228	0.2461

Table 10. Results of the mixtures with higher DSE's for PSD with pressures at atmospheres.

MIXTURE	COMPONENT A	COMPONENT B	DSE PSD	DSE ED	PRESSURE OF PSD [atm]	DSE PSD AT 10 ATM
5	THF	Ethanol	0.9146	0.2251	26.8	0.9009
6	Methylal	Methanol	0.7778	0.2494	47.2	0.5838
7	Acetone	Methanol	0.7552	0.2481	37.4	0.5662
8	N-Heptane	Isobutanol	0.7127	0.1812	13.5	0.7100
9	Toluene	1-Butanol	0.6585	0.1756	10.4	0.6423
10	Diisopropyl ether	Isopropyl alcohol	0.6046	0.221	25.7	0.4141
11	Methyl isobutyl ketone	Butanol	0.5907	0.1618	9.3	0.6027
12	Chloroform	Water	0.5839	0.4195	30	0.1924

13	Ethyl acetate	Ethanol	0.5740	0.2186	24.1	0.3115
14	Methanol	THF	0.5536	0.2440	26.8	0.3343
15	Methyl acetate	Methanol	0.4588	0.2491	37.8	-0.0215
16	THF	Water	0.4238	0.1986	26.8	0.1896
17	Dimethyl carbonate	Methanol	0.2478	0.2105	19	-0.2313
18	Ethanol	Water	0.2410	0.1925	42.5	0.0423
19	Isobutyl alcohol	Isobutyl acetate	0.1802	0.1647	10.7	0.1794

The shift achieved in the azeotropic composition for a range of 10 atmospheres is shown in Table 11 and Table 12. Table 11 is for the mixtures with better efficiency with ED and Table 12 for PSD.

Table 11. Shift in the azeotropic composition in the case of better efficiency with ED.

Mixture	$x_{A,LP}$	$x_{A,HP}$	Shift obtained [%]
1	0.8507	0.3279	52.3
2	0.7109	0.5070	20.4
3	0.2301	0.06	17.0
4	0.2687	0.0249	24.4

For all the mixtures the shift is higher than 5% meaning that PSD is a feasible option. Despite this, ED is a better option.

Table 12. Shift in the azeotropic composition in the case of better efficiency with PSD.

MIXTURE	$x_{A,LP}$	$x_{A,HP}$	Shift obtained [%]
5	0.9099	0.0995	81.0
6	0.8807	0.6300	25.1
7	0.7772	0.3831	39.4
8	0.7023	0.0000	70.2
9	0.7156	0.1393	57.6
10	0.7807	0.4925	28.8
11	0.6251	0.0597	56.5
12	0.8344	0.6654	16.9
13	0.5469	0.2040	34.3
14	0.5146	0.1542	36.0
15	0.6638	0.4478	21.6
16	0.8210	0.6418	17.9
17	0.1499	0.0536	9.6
18	0.8972	0.8010	9.6
19	0.1320	0.0000	13.2

Also the shift obtained for all the mixtures is higher than 5%. The values in general are higher than the obtained for ED so, when the shift is higher PSD becomes more benefited because the mixture is more sensitive to changes of pressure. Despite that fact, having a bigger shift not means having a better efficiency like the mixtures 11, 13, 14, etc. The minimum value is 9.6 for the mixtures 17 and 18 being one of the latest with lower efficiency and not having a bad efficiency with ED. Also is verified the Eq. 12 by the calculus of the ratio between the DSE of PSD and ED is higher or lower than the unity for every group (Table 13 and Table 14).

Table 13. Ratio between the DSE of both alternatives for the mixtures with better DSE for ED.

MIXTURE	RATIO DSE PSD/ DSE ED
1	0.923
2	0.396
3	0.361
4	0.835

Table 14. Ratio between the DSE of both alternatives for the mixtures with better DSE for PSD.

MIXTURE	RATIO DSE PSD/ DSE ED
5	4.063
6	3.667
7	3.044
8	3.935
9	3.749
10	2.722
11	3.652
12	1.392
13	2.625
14	2.269
15	1.842
16	2.135
17	1.177
18	1.252
19	1.094

For the mixtures with higher DSE for ED the ratio must be lower than unity. Despite all the mixtures comply this, mixture 1 with higher efficiency has the ratio with a higher value proximal to one being different than the expected. In the case of the mixtures with higher DSE for PSD, the ratio must be higher than the unity. In this case, mixture 5 with a better efficiency have the greater ratio being the expected but the tendency not remain for all the mixtures. To find the reason why mixtures 1 to 4 have a better efficiency with ED and not with PSD the different boiling points of the pure compounds at atmospheric pressure, overpressure and the boiling points of the azeotropes are compared. There is not a clear tendency like the maximum to explain why one technique is better but there are some outstanding facts to take into account.

For the mixtures with better DSE for ED the boiling points of pure compounds (T_A, T_B) at atmospheric pressure decreases while DSE for PSD decreases too not being clearly how affects. The mixtures 5, 6 and 7, which better efficiency with PSD than ED, have the lower T_A. At the same time, the difference of the boiling points between T_A and the $T_{az2,LP}$ is lower like 0.82, 0.87 and 3.54. In the case of the mixture 1, 2, 3 and 4 the differences values are 40.48, 14.14, 44.10 and 14.12 respectively. The tendency between the difference of T_B and $T_{az2,LP}$ it is not clearly. Respect the difference between T_A, T_B nothing can be conclude because both groups of mixtures have higher and lower values.

On the other hand, the tendency respect $T_{az2,LP}$ it is also not clear: mixture 1 with better DSE for ED has the lowest $T_{az2,LP}$ but also the mixtures 5, 6 and 7, with better DSE for PSD, have lower boiling points. Mixture 4 with a DSE for ED of 0.1471 and for PSD of 0.1228 have one of the highest $T_{az2,LP}$ (389.2 K) but mixture 15 with values of DSE of 0.1802 and 0.1647 respectively, have a higher boiling point too (380.6 K).

T_A at HP is fixed at 493.15 K. T_B at HP is not fixed and higher values of the boiling point implies a better efficiency with ED: mixture 1 has the higher efficiency for ED but also a higher T_B (501.4 K). Mixtures with higher DSE for PSD have lower T_B, in fact, the mixtures of this group with lower efficiencies with PSD but higher DSE for ED respect the others have higher T_B. Mixture 8, formed by chloroform and water, have a DSE for PSD and ED of 0.5839 and 0.4195 respectively with a T_B of 508.9 K. The same happens for mixture 12 and 14 with a boiling point of 502.7 K and 529.1 K. At the same time, it seems like when the difference between $T_{az1,HP}$ and T_B is lower the efficiency for PSD increases having the mixtures 1 and 2 a difference of 32.3 and 25.5 but the mixtures 5, 6 and 7 a difference of 1.1, 10.2 and 1.5. Despite that fact, this tendency is not clear because mixture 19 with lowest DSE for PSD has a difference of 0.95.

As shown in Eq. 12, not only the temperatures affect the calculus of the efficiencies. The change in the azeotropic composition achieved is important too: Table 15 is for the mixtures with better DSE for ED and Table 16 for PSD.

Table 15. Change in the azeotropic composition expressed as molar fractions for mixtures with better DSE for ED.

MIXTURE	$x_{A,LP}$	$x_{A,HP}$	$x_{A,LP} - x_{A,HP}$
1	0.8507	0.4848	0.3659
2	0.7109	0.4928	0.2181
3	0.2301	0.0600	0.1701
4	0.2687	0.0563	0.2123

Table 16. Change in the azeotropic composition expressed as molar fractions for mixtures with better DSE for PSD.

MIXTURE	$x_{A,LP}$	$x_{A,HP}$	$x_{A,LP} - x_{A,HP}$
5	0.9099	0.0012	0.9088
6	0.8807	0.4200	0.4607
7	0.7772	0.1013	0.6759
8	0.7023	0.0000	0.7023
9	0.7156	0.1174	0.5982
10	0.7807	0.3607	0.4200
11	0.6251	0.0752	0.5499
12	0.8344	0.5096	0.3248
13	0.5469	0.0000	0.5469
14	0.5146	0.0018	0.5128
15	0.6638	0.2650	0.3988
16	0.8210	0.5721	0.2489
17	0.1499	0.0000	0.1499
18	0.8972	0.7761	0.1211
19	0.1320	0.0000	0.1320

When the difference between the molar fractions is lower, ED becomes more favorable because there is not a substantial change in the azeotropic composition. The efficiency of PSD increases when this difference becomes higher because the shift achieved is more substantial and means that the mixture is more sensitive to the pressure. Lastly, respect the pressure fixed it can be conclude that an increase of the pressure not imply an increase of the efficiency: mixture 18 with a pressure fixed at 42.5 atm is the penultimate of the group with higher efficiency for PSD. Mixture 1 with higher DSE for ED needs a HP consequently of the lowest point of the compound B being ED more efficient. For the four mixtures with a better DSE for ED, working with a pressure higher than 10 atm at HPC don't imply obtaining better efficiencies. For mixture 1, working at 57.6 atm provides a lower efficiency than working with 10 atmospheres. The opposite occurs with mixture 2 and 3: working at higher pressures than 10 atm provides better efficiencies. For mixture 4, working at 7.4 atm provides lower efficiency than 10 atmospheres. For the mixtures with a better DSE for PSD, the tendency is the same as the minimum boiling point azeotropes: working with higher pressures than 10 atm provides always a better efficiency. It can be seen negative values for PSD consequently of having higher flow rate of the recirculation. The recirculations are mixed again with the feed making the efficiency negative. Like the maximum boiling point azeotropes, is also studied the effect of working with one column in spite of two. The study has been made for the mixtures where the azeotrope disappears at one pressure (Table 17). There is some mixtures which despite increasing the pressure the azeotrope never disappears being discarded working with one column.

Table 17. Pressure for PSD and the one which disappear the azeotrope for every mixture in atmospheres.

MIXTURE	PSD	SINGLE COLUMN
7	37.4	58
3	10.4	42.5
13	24.1	24
19	10.7	5
14	26.8	27
11	9.3	15
4	7.4	14
8	13.5	8
5	26.8	27
9	10.4	14.5

Some of the pressures obtained are excessive and not feasible to work with being the case for the mixture 7 and 3. For mixture 13, is not necessary to work with two columns when the pressures obtained are the same. The pressure obtained to work with in one column can be lower than the fixed at PSD (mixtures 19 and 8). For this cases, is more feasible working with one column consequently of obtaining a lower pressure. For the remaining mixtures, the pressure obtained is higher than the pressure fixed at PSD but not excessive being necessary to considerate if working with one column provides more benefits than PSD.

Figure 17 represents the efficiency for PSD and working with one column by the application of Eq. 16. The efficiency provided by working with one column is higher for mixture 7 and 3 consequently of working with higher pressures. For mixture 11, 4 and 9 where the pressure is higher than working with PSD, the efficiency provided is higher too. There are some mixtures where the difference between both efficiencies is lower: 13, 19, 14 and 8. For mixtures 8 and 19, the single column works at lower pressures respect HPC and provides the same efficiency so, it is clear the benefits of working with one column. Lastly, there is only one mixture, mixture 5, with the efficiency for PSD is higher than working with one column despite the fact both works at similar pressures.

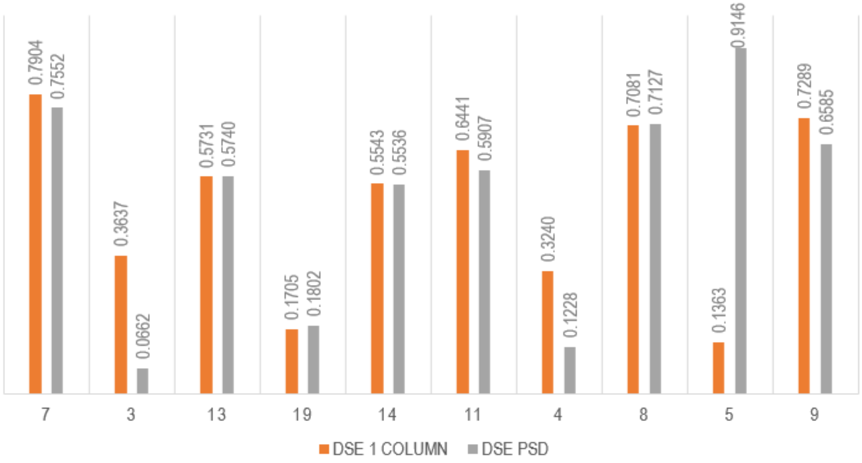


Figure 17. DSE for PSD and working with one column.

It have been verified the fact that minimum boiling point azeotropes are so much difficult to treat than the maximum. PSD is benefited when the mixtures have a lower T_A and the difference between this boiling point and T_{az1} is higher. For T_B, $T_{az1,LP}$ and the difference between them, there is not a clear trend. Increasing T_B at HP benefits ED, in fact, the first mixtures with higher DSE for PSD have a low T_B and the mixture of this group with highest DSE for ED has a higher T_B. PSD is also benefited when the difference of T_B and $T_{az2,HP}$ is smaller. Respect the change in azeotropic composition achieved, PSD is more benefited when this value is higher.

For the mixtures with a higher DSE for ED, an increase of the pressure don't imply having higher efficiencies and also fixing the HPC at 10 atm not imply a limitation on the efficiency achieved. There is an example of a mixture working at 52.6 atm and providing a lower efficiency respect than 10 atm. On the other hand, the mixtures with a higher DSE for PSD the tendency is the same as the maximum boiling point azeotropes: fixing the HP at 10 atm is a limitation and working at higher pressures provides more efficiency.

Working with one column can provide excessive and no feasible pressures but, there are cases where the pressure is lower or similar at the one fixed at HPC for PSD and provide an equal or higher efficiency. Also, higher pressures but not excessive are obtained and the idea of working with only one column must be considerated.

5.3. VALIDATION OF THE USED THERMODYNAMIC MODEL

This section is dedicated to validate the thermodynamic model used to obtain all the data necessary to calculate the efficiencies. First, is going to be verified if the boiling points obtained by using the extended equation of Antoine proportionated by Aspen Plus (Eq. 14). Secondly, is checked the difference between the overpressure data available with the one provided by the simulator.

5.3.1. *Equation of Antoine*

The different boiling points are calculated by the extended equation of Antoine (Eq. 14) where the coefficients necessary (C_i) are obtained by Aspen Plus. To check these values, the boiling points are also obtained by the application of the equation of Antoine (Eq. 15) where the coefficients (A, B and C) are recollected from a database (Polling, B., 2001) being experimental values. For some components, it has not been possible to find the correspondent coefficients being discarded, that is to say, that this is verified in some and not all components. The boiling points obtained by Aspen Plus and the database are represented in the Figure 18 for different compounds.

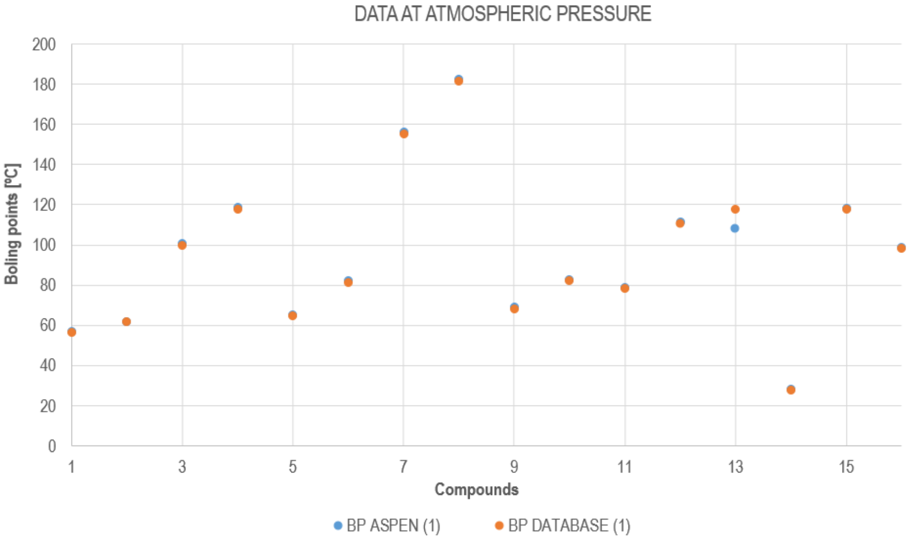


Figure 18. Representation of the boiling points obtained by Aspen Plus and from a database for the different compounds.

It can be seen that almost all the points overlap for the compounds because the difference between them is very lower. This means that both boiling points have similar values being correct to work with. The compound 13 is the one with the higher difference.

Figure 19 represents the same for the boiling points at 10 atm. The tendency is the same: most of the points overlap both boiling points. At first glance, there are more compounds (6, 10, 13 and 15) with higher difference from the previous representation.

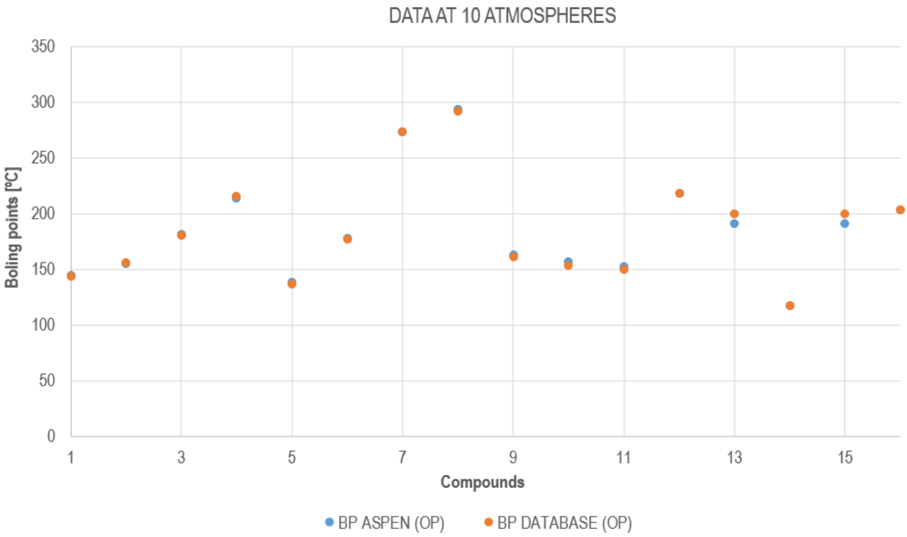


Figure 19. Representation of the boiling points obtained by Aspen Plus and from a database for the different compounds at overpressure values.

The difference between the boiling points and the nomenclature used in the Figures for every compound is shown in Table 18. At 1 and 10 atmospheres, the compound 13 is the one with higher difference corresponding to isobutyl alcohol. At overpressure, the difference between both boiling points is higher than at atmospheric pressure. This is the case for the compounds 1, 2, 4, 5, 8, 9, 10, 11 and 15. There are compounds with high difference superior than 2 as 10, 11, 13 and 15. For others, the difference is lower than the unity as 1, 2, 3, 7, 12, 13 and 16. In the case of working at atmospheric pressure, the difference in general are lower than unity. Generally, the difference is slightly but more appreciable for some components at higher pressures.

Table 18. Difference between both boiling points for the compounds.

		DIFFERENCE 1 ATM	DIFFERENCE 10 ATM
1	Acetone	0.400	0.625
2	Chloroform	0.058	0.977
3	Water	0.705	0.690
4	Acetic acid	0.730	1.698
5	Methanol	0.510	1.185
6	Acetonitrile	1.165	1.155
7	Cyclohexanone	0.730	0.384
8	Phenol	0.776	1.783
9	Diisopropyl ether	0.781	1.800
10	Isopropyl alcohol	0.287	3.022
11	Ethanol	0.460	2.297
12	Toluene	0.716	0.523
13	Isobutyl alcohol	9.507	8.797
14	Isopentane	0.525	0.353
15	Butanol	0.581	8.797
16	N-heptane	0.609	0.220

5.3.2. Overpressure azeotropic data

There is some information available at overpressure, not too much, for some of the binary mixtures studied. It is going to be verified if the experimental values of azeotropic data are far from the corresponding obtained by Aspen Plus.

For acetic acid and DMAC, only three values slightly higher than 1 atmosphere (1.1, 1.3 and 1.6) are available (Figure 20). The difference for the molar fraction of acetic acid between the database and the proportionated by Aspen Plus is 0.006, 0.002 and 0.008 respectively and it can be considered negligible.

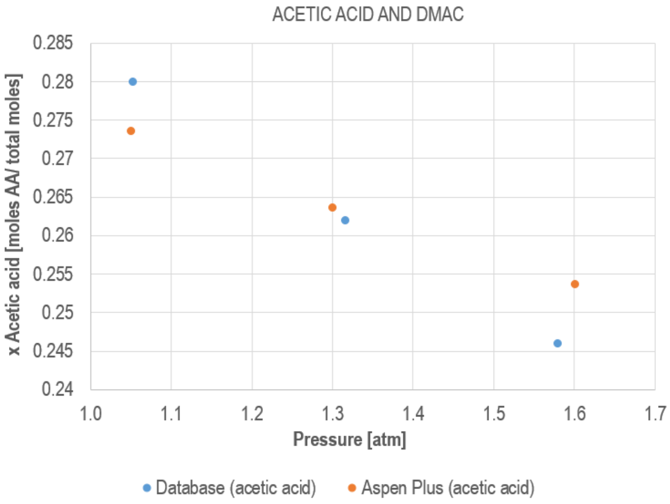


Figure 20. Representation of the values of the database and Aspen Plus for acetic acid and DMAC.

For acetone and methanol, there is more information at overpressure values reaching 14.1 atmospheres (Figure 21). It can be seen that the difference between two points at the same pressure is not too much having the higher at 14.1 atmospheres with a difference of 0.089.

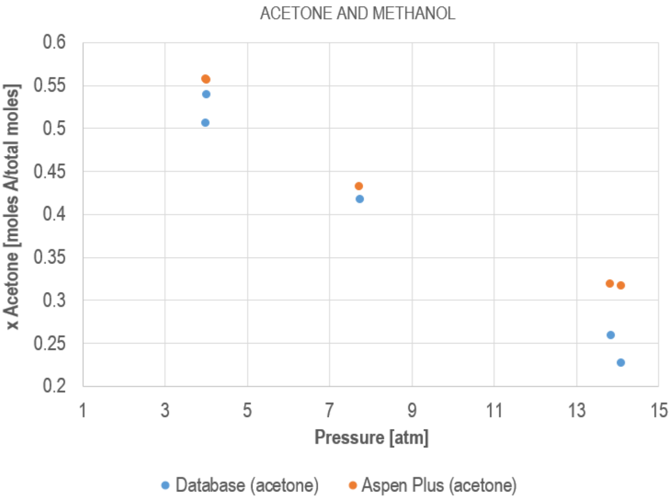


Figure 21. Representation of the values of the database and Aspen Plus for acetone and methanol.

Acetonitrile and water is one of the mixtures with more data available (Figure 22). The maximum pressure that someone experimented is 6.8 atmospheres. There is some difference for all the pressures without having any overlap but remains low being the maximum 0.038.

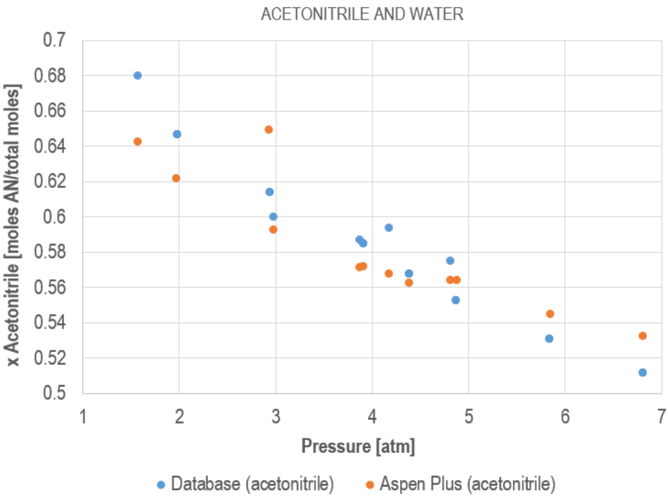


Figure 22. Representation of the values of the database and Aspen Plus for acetonitrile and water.

For the binary mixture formed by ethanol and toluene there is only one experimental value availabe at 1.2 atm. The difference is the one exposed at Table 19.

Table 19. Information of the binary mixture formed by ethanol and toluene.

Source	$x_{ethanol}$	**Difference** $x_{ethanol}$
Database	0.815	0.013
Aspen Plus	0.802	

Ethanol and water is another mixture very studied for the authors having more data available reaching the 20.4 atmospheres (Figure 23). When the pressure increase, the difference between the values also increase. The higher difference is at 19.46 atmospheres with a value of 0.109 and the lower at 1.18 atmospheres with a value of 0.004. For ethyl acetate and methanol (Figure 24), the tendency remains the same: an increase of pressure implies a higher difference. In this case, the maximum pressure data is at 8.99 atm with the maximum difference having a value of 0.568. The differences are higher than the other cases but can be considered suitable for a preliminary decision.

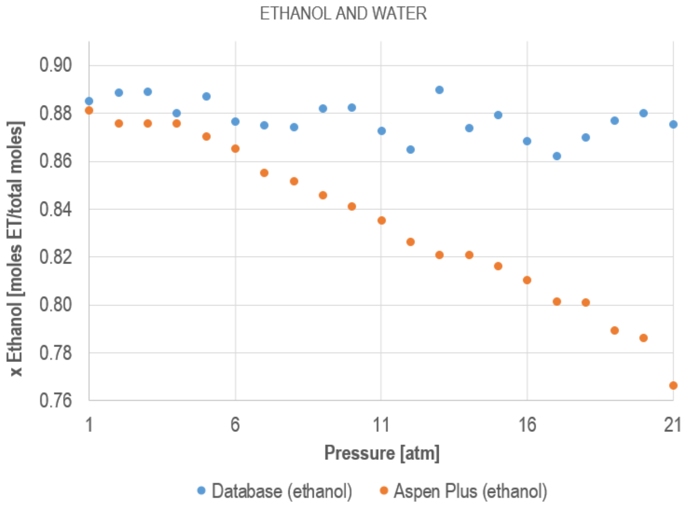


Figure 23. Representation of the values of the database and Aspen Plus for ethanol and water.

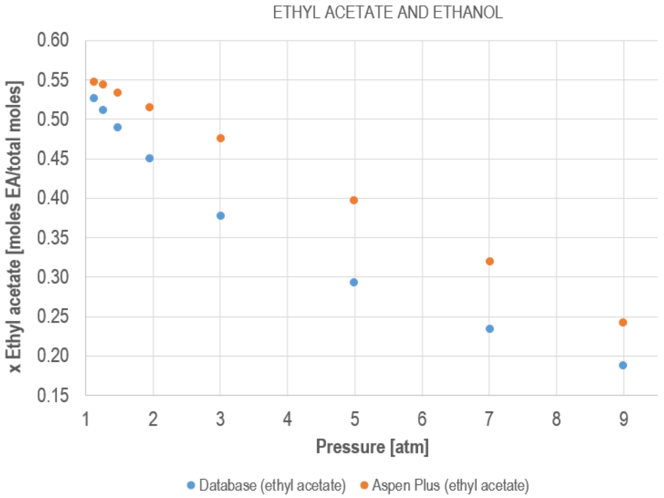


Figure 24. Representation of the values of the database and Aspen Plus for ethyl acetate and ethanol.

For the mixture formed by ethanol and THF, there is only two experimental values availabe at 1.23 and 1.48 atmospheres (Table 20). If ethanol is substituied for water (Figure 25), the maximum pressure is 13.6 atmospheres. The differences remains lower for both cases being the higher 0.011 and 0.042 respectively.

Table 20. Information of the binary mixture formed by ethanol and THF.

Source	**Pressure**	$x_{ethanol}$	**Difference** $x_{ethanol}$
Database	1.23	0.129	0.008
Aspen Plus		0.121	
Database	1.48	0.156	0.011
Aspen Plus		0.145	

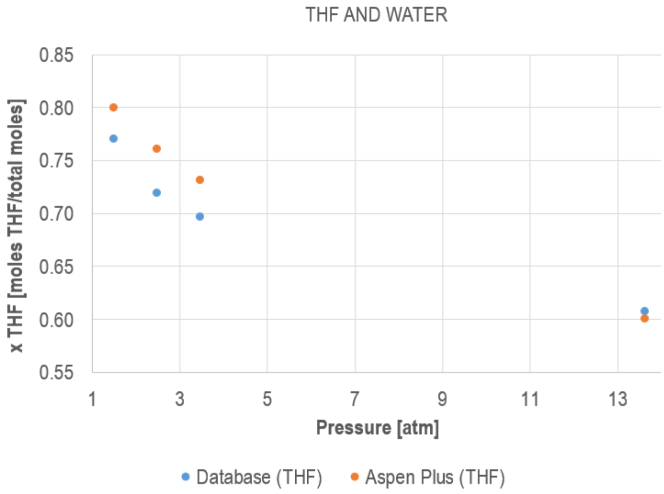


Figure 25. Representation of the values of the database and Aspen Plus for tetrahydrofuran and water.

Lastly, for 1-butanol and toluene (Figure 26) shows that the maximum experimental pressure worked with is 9 atmospheres. The differences are lower like all the other mixtures having the more higher a value of 0.131.

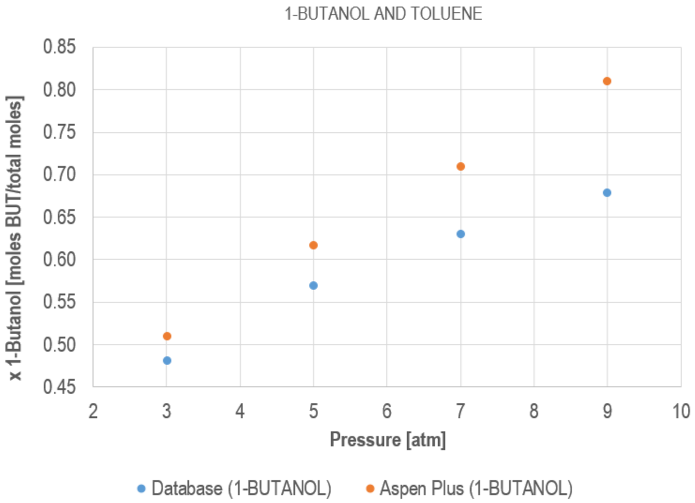


Figure 26. Representation of the values of the database and Aspen Plus for 1-butanol and toluene.

It can be conclude that the data available is limitated and the range of the pressure worked with too. The maximum value of pressure found is the 24.1 atm corresponding to the mixture formed by ethanol and water. The difference between the molar fractions is low with a maximum value of 0.568. The values proportionaded by Aspen Plus using the corresponding thermodynamic model are very similar of the obtained experimentally, being the data used correct.

6. CONCLUSIONS

The DSE gives a good first approximation to help at the selection of which is the most adequate distillation technique by the values of the efficiencies obtained. It is only necessary to know the azeotropic data at the corresponding pressures and the boiling points of the pure compounds. There is a lot of available sources to obtain this information but, it is true that overpressure data is limited in comparison with atmospheric pressure data. For this reason, the simulators are good for, in fact, it has been proven that the information obtained by Aspen Plus is not far off the one obtained by the other sources.

Respect PSD, the values of the pressures selected to work with are decisive respect the efficiency obtained. It is important to take into account where the energy necessary provides from. The HP has been fixed taking into account the quality of the steam used and the LP at atmospheric pressure for simplicity. Consequently, the boiling point of the extractive agent is limited to be available to compare both efficiencies.

For maximum boiling point azeotropes, ED is better than PSD for all the mixtures. This follows from the lower boiling points of both compounds forming the binary mixture. Increasing them, implicate a diminution of the efficiency of ED but an increase respect from PSD. At the same time, the pressure necessary at the HPC decreases.

For minimum boiling point azeotropes the trend is not the same. The mixtures with better DSE for ED are lower respect the ones with better DSE for PSD. PSD is benefited by lower T_A and higher differences between T_A and $T_{az1,LP}$ at atmospheric pressure. Respect data at overpressure, is benefited with lower T_B and small differences between T_B and $T_{az2,HP}$. Higher changes in the azeotropic composition achieved also benefited PSD. Fixing the pressure at HPC can be or not a limitation.

It is important to study the pressure necessary to make azeotrope disappear and if this value provides a better efficiency or not. Working with one column implicate not adding a third compound and not having a second column.

REFERENCES AND NOTES

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 WheatBased Continuous Bioethanol Production System. *Biotechnol. Prog.* **2007**, *23*, 1394-1403.

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**, *110*, 160-171.

Frank, T.C. Break azeotropes with pressure-sensitive distillation. *Chem. Eng. Prog.* **1997**, *93*, 52–63.

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.

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.

Ghuge, 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.

Iludest. Distillation tailor-made: Phase Equilibrium Apparatuses.
https://www.iludest.de/en/products/distillation-systems/phase-equilibrium-apparatuses (accessed May 9, 2019)

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.

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**, *28*, 591–596.

Li, C., Song, Y., Fang, J., Liu, Y., Su, W., Hu, Y. Separation process of butanol-butyl-acetate-methyl isobutyl ketone system by the analysis to residual curve and the double effect pressure-swing distillation. *Chinese J. Chem. Eng.* **2017**, *25*, 274-277.

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.

Li, W., Shi, L., Yu, B., Xia, M., Luo, J., Shi, H., Xu, C. New pressure-swing distillation for separating pressure-insensitive maximum boiling point azeotrope via introducing a heavy entrainer: design and control. *Ind. Eng. Chem. Res.* **2013**, *52*, 7836-7853.

Lladosa, E., Montón, J.B., Burguet, 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, 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.

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.

Luyben W.L. Design and control of a pressure-swing distillation process with vapor recompression. *Chem. Eng. Proc.* **2018**, *123*, 174-184.

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. Comparison of extractive distillation and pressure-swing distillation for acetone/chloroform separation. *Comput. Chem. Eng.* **2013a**, *50*, 1–7.

Luyben, W.L. Comparison of pressure-swing and extractive-distillation methods for methanol-recovery systems in the TAME reactive-distillation process. *Ind. Eng. Chem. Res.* **2005**, *15*, 5717-5725.

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. Design and control of a fully heat-integrated pressure-swing azeotropic distillation system. *Ind. Eng. Chem. Res.* **2008b**, *47*, 2681–2695.

Luyben, W.L. Methanol/trimethoxysilane azeotrope separation using pressure-swing distillation. *Ind. Eng. Chem. Res*. **2014b**, *53*, 5590–5597.

Luyben, W.L. Pressure-swing distillation for minimum- and maximum-boiling homogeneous azeotropes. *Ind. Eng. Chem. Res.* **2012**, *51*, 10881–10886.

Luyben, W.L. Pressure-swing distillation for minimum-and maximum-boiling homogeneous azeotropes. *Ind. Eng. Chem. Res.* **2012**, *51*, 10881-10886.

Modla, G. Pressure swing batch distillation by double column systems in closed mode. *Comput. Chem. Eng*. **2010**, *34*, 1640–1654.

Modla, G., Lang, P. New column configurations for pressure swing batch distillation II. Rigorous simulation calculations. *IFAC Proceedings.* **2007**, *40*, 361–366.

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*, 1473–11481.

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.

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.

Perry, R.H., Green, D.W. Perry's Chemical Engineers' Handbook, 7th ed.; McGraw-Hill, 1997.

Perry's chemical engineers handbook, 8th ed.; New York: McGraw- Hill, 2008.

Pipping Guide. Basics of Distillation Column Piping.
http://www.pipingguide.net/2014/06/basics-of-distillation-column.html (accessed Apr 25, 2019)

Poling B., Prausnitz, J., John & O'Connell, J. The properties of gases and liquids, 5th ed.; McGraw-Hill, 2011.

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.

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.

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.

Risco, A., Plesu, V., Heydenreich, J.A., Bonet, J., Bonet-Ruiz, A.E., Calvet, A., Iancu, P., Llorens, J. Pressure selection for non-reactive and reactive pressure-swing distillation. *Chem. Eng. Process.* **2019**, *135*, 9-21.

Ullmann's Encyclopedia of Industrial Chemistry, 7th completely rev. ed.; Weinheim: Wiley-VCH, cop. 2011. Vol. 11.

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., 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., 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., 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.

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, 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.

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, 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**, *24*, 1584-1599.

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*, 13

ACRONYMS

ED	Extractive Distillation
PSD	Pressure Swing Distillation
EA	Extractive Agent
EDC	Extractive Distillation Column
RDC	Recovery Distillation Column
HPC	High Pressure Column
LPC	Low Pressure Column
α_{ij}	Relative volatility
y_i	Mole fraction of component i in the vapor phase
x_i	Mole fraction of component i in the liquid phase
P_i^{sat}	Vapor pressure of component i
γ_i	Liquid-phase activity coefficient of component i
VLE	Vapor-Liquid Equilibrium
p_i	Partial pressure of component i
P_t	Total system pressure
p_i^*	Partial vapor pressure of component i
A	Compound with highest chemical affinity with the extractive agent
	Compound which lies to the right of the azeotropic composition at high pressure
B	Compound with lowest chemical affinity with the extractive agent
	Compound which lies to the right of the azeotropic composition at low pressure
D_i	Distillate flow of column i
B_i	Bottom flow of column i
F	Fresh flow feed

F1	Total flow feed
P1	Pressure at HPC
P2	Pressure at LPC
LP	Low pressure
HP	High pressure
HPS	High pressure steam
DSE	Distillation Sequence Efficiency
CES	Coefficient of Ease of Separation
η_i	Carnot efficiency of column i
T_i	Temperature of the compound i (A, B, EA)
$x_{i,F}$	Molar fraction on the feed stream for the compound i
$x_{i,azc=Pj}$	Azeotropic composition for the compound i at pressure j at column c
DSE_{PSD}	Distillation Sequence Efficiency for Pressure Swing Distillation
DSE_{ED}	Distillation Sequence Efficiency for Extractive Distillation
NRTL	Non-Random Two-Liquid
NRTL-HOC	Non-Random Two-Liquid-Hayden O'Connell
C_{xi}	Coefficient of Antoine extended equation x for the compound i
T	Temperature
X_{Ant}	Coefficient of Antoine equation X (A, B or C)
DMAC	Dimethylacetamide
THF	Tetrahydrofuran

APPENDICES

APPENDIX 1: MAXIMUM BOILING POINT

INFORMATION OF THE AZEOTROPE AT LOW PRESSURE

Table 21. Azeotropic data at amospheric pressure.

FEED (LP=1 ATM)				
MIXTURES		$x_{A,az2}$	$x_{B,az2}$	T_{az2} **[K]**
Acid acetic	DMAC	0.2686	0.7314	443.87
Acetone	Chloroform	0.3484	0.6516	338.66
Phenol	Cyclohexanone	0.7470	0.2530	459.06
Water	Ethylenediamine	0.3573	0.6427	392.22

Table 22. Boiling points of the pure compounds at amospheric pressure.

BOILING POINTS [K]	
T_A	T_B
391.77	439.80
329.84	334.83
455.77	429.30
373.70	390.89

INFORMATION OF THE AZEOTROPE AT HIGH PRESSURE

Table 23. Azeotropic data at high pressure.

HPC DATA				
MIXTURES		$x_{A,az1}$	$x_{B,az1}$	T_{az1} **[K]**
Acid acetic	DMAC	0.2030	0.7970	493.27
Acetone	Chloroform	0.0000	1.0000	493.24
Phenol	Cyclohexanone	0.6060	0.3940	493.08
Water	Ethylenediamine	0.0104	0.9896	493.06

Table 24. Boiling points for pure compounds at high pressure.

BOILING POINTS HP [K]	
T_A	T_B
436.92	492.19
479.78	494.51
462.57	436.52
454.52	494.29

INFORMATION OF THE AZEOTROPE AT 10 ATMOSPHERES

Table 25. Azeotropic data at 10 atmospheres.

HPC AT 10 ATM				
MIXTURES		$x_{A,az1}$	$x_{B,az1}$	T_{az1} [K]
Acid acetic	DMAC	0.1244	0.8756	553.54
Acetone	Chloroform	0.0000	1.0000	427.39
Phenol	Cyclohexanone	0.6070	0.3930	668.09
Water	Ethylenediamine	0.0448	0.9552	482.55

Table 26. Boiling points for pure compounds at 10 atmospheres.

BOILING POINTS 10 ATM	
T_A	T_B
487.25	552.41
417.66	428.38
566.32	546.78
454.52	483.46

APPENDIX 2: MINIMUM BOILING POINT

INFORMATION OF THE AZEOTROPE AT LOW PRESSURE

Table 27. Azeotropic data at amospheric pressure.

MIXTURES		$x_{A,az2}$	$x_{B,az2}$	T_{az2} [K]
Acetone	Methanol	0.7772	0.2228	326.30
Acetonitrile	Water	0.7109	0.2891	341.27
Chloroform	Water	0.8344	0.1656	325.29
Diisopropyl ether	Isopropyl alcohol	0.7807	0.2193	339.38
Toluene	Ethanol	0.7699	0.2301	340.44
Ethanol	Water	0.8972	0.1028	343.31
Ethyl acetate	Ethanol	0.5469	0.4289	332.07
Isobutyl acetate	Isobutyl alcohol	0.8680	0.1320	380.61
Methanol	Isopentane	0.1493	0.8507	297.68
Dimethyl carbonate	Methanol	0.8502	0.1499	337.13
Tetrahydrofuran	Methanol	0.4854	0.5146	328.60
Methyl acetate	Methanol	0.6638	0.3362	326.85
Methylal	Methanol	0.8807	0.1193	314.75
Methyl isobutyl ketone	Butanol	0.6251	0.3749	386.21
Mesityl oxide	Butanol	0.7313	0.2687	389.22
N-heptane	Isobutanol	0.7023	0.2977	365.01
Tetrahydrofuran	Ethanol	0.9099	0.0901	338.88
Tetrahydrofuran	Water	0.8210	0.1790	336.50
Toluene	1-butanol	0.7156	0.3521	357.85

Table 28. Boiling points of the pure compounds at amospheric pressure.

BOILING POINTS 1 ATM [K]	
T_A	T_B
329.84	338.16
355.41	373.70
334.83	373.70
342.19	355.67
384.49	351.94
351.94	373.70
350.92	351.94
390.18	381.34
338.16	301.55
363.96	338.16
339.70	338.16
330.74	338.16
315.62	338.16
389.96	391.43
403.33	391.43
372.19	381.34
339.70	351.94
339.70	373.70
384.49	391.43

INFORMATION OF THE AZEOTROPE AT HIGH PRESSURE

Table 29. Azeotropic data at high pressure.

MIXTURES		$x_{A,az1}$	$x_{B,az1}$	T_{az1} [K]
Acetone	Methanol	0.1013	0.8987	469.32
Acetonitrile	Water	0.4928	0.5072	464.96
Chloroform	Water	0.5096	0.4904	471.34
Diisopropyl ether	Isopropyl alcohol	0.3607	0.6393	467.90
Toluene	Ethanol	0.9400	0.0600	425.82
Ethanol	Water	0.7761	0.2239	486.28
Ethyl acetate	Ethanol	0.0000	1.0000	463.33
Isobutyl acetate	Isobutyl alcohol	1.0000	0.0000	466.80
Methanol	Isopentane	0.5152	0.4848	469.05
Dimethyl carbonate	Methanol	1.0000	0.0000	437.36
Tetrahydrofuran	Methanol	0.9982	0.0018	453.15
Methyl acetate	Methanol	0.2650	0.7350	467.81
Methylal	Methanol	0.4200	0.5800	472.92
Methyl isobutyl ketone	Butanol	0.0752	0.9248	472.06
Mesityl oxide	Butanol	0.9437	0.0563	461.72
N-heptane	Isobutanol	0.0000	1.0000	476.88
Tetrahydrofuran	Ethanol	0.0012	0.9988	468.45
Tetrahydrofuran	Water	0.5721	0.4279	462.61
Toluene	1-butanol	0.1174	0.8826	477.43

Table 30. Boiling points for pure compounds at high pressure.

BOILING POINTS HP [K]	
T_A	**T_B**
494.39	470.85
494.17	490.48
494.51	508.87
494.39	473.91
494.09	426.86
494.28	529.11
494.48	464.26
494.22	467.75
494.18	501.38
494.28	438.20
494.55	454.21
494.33	471.40
495.36	483.16
494.21	473.34
494.21	462.76
494.26	479.46
494.55	469.55
494.55	502.65
494.09	478.75

INFORMATION OF THE AZEOTROPE AT 10 ATMOSPHERES

Table 31. Azeotropic data at 10 atmospheres.

MIXTURES		$x_{A,az1}$	$x_{B,az1}$	T_{az1} [K]
Acetone	Methanol	0.3831	0.6169	407.53
Acetonitrile	Water	0.5070	0.4930	432.39
Chloroform	Water	0.6654	0.3346	410.87
Diisopropyl ether	Isopropyl alcohol	0.4925	0.5075	420.91
Toluene	Ethanol	0.9400	0.0600	424.25
Ethanol	Water	0.8010	0.1990	423.65
Ethyl acetate	Ethanol	0.2040	0.7960	423.71
Isobutyl acetate	Isobutyl alcohol	1.0000	0.0000	463.59
Methanol	Isopentane	0.6721	0.3279	377.05
Dimethyl carbonate	Methanol	0.9193	0.0536	408.40
Tetrahydrofuran	Methanol	0.8458	0.1542	409.95
Methyl acetate	Methanol	0.4478	0.5522	404.29
Methylal	Methanol	0.6300	0.3700	393.90
Methyl isobutyl ketone	Butanol	0.0597	0.9403	475.83
Mesityl oxide	Butanol	0.9751	0.0249	475.90
N-heptane	Isobutanol	0.0000	1.0000	463.59
Tetrahydrofuran	Ethanol	0.0995	0.9005	424.51
Tetrahydrofuran	Water	0.6418	0.3582	417.35
Toluene	1-butanol	0.1393	0.8607	475.44

Table 32. Boiling points for pure compounds at 10 atmospheres.

BOILING POINTS 10 ATM [K]	
T_A	T_B
417.66	411.22
450.96	454.52
428.38	454.52
435.95	429.64
491.69	425.28
425.28	454.52
443.30	425.28
490.37	464.49
411.22	390.57
458.08	411.22
434.13	411.22
417.70	411.22
401.63	411.22
498.61	476.83
512.34	476.83
475.93	464.49
434.13	425.28
434.13	454.52
491.69	476.83

APPENDIX 3: COEFFICIENTS OF ANTOINE

Property units [bar]							
COMPOUND	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
DMAC	57.4881	7685.9	0	0	-6.6412	2.2755E-06	2
ACETONE	57.4931	5599.6	0	0	-7.0985	6.2237E-06	2
CHLOROFORM	134.917	7792.3	0	0	-20.614	0.024578	1
WATER	62.1361	7258.2	0	0	-7.3037	4.1653E-06	2
ACETIC ACID	41.7571	6304.5	0	0	-4.2985	8.8865E-18	6
METHANOL	71.2051	6904.5	0	0	-8.8622	7.4664E-06	2
ACETONITRILE	35.2221	5126.2	0	0	-3.5406	1.3995E-17	6
CYLOHEXANONE	73.9111	7944.4	0	0	-9.2862	4.9957E-06	2
PHENOL	83.9311	10113	0	0	-10.09	6.7603E-18	6
DIISOPROPYL ETHER	30.1181	4668.7	0	0	-2.8551	0.00063693	1
ISOPROPYL ALCOHOL	99.2071	-9040	0	0	-12.676	0.000005538	2
ETHANOL	61.7911	7122.3	0	0	-7.1424	2.8853E-06	2
TOLUENE	65.4321	6729.8	0	0	-8.179	5.3017E-06	2
ETHYL ACETATE	55.3111	6227.6	0	0	-6.41	1.7914E-17	6
ISOBUTYL ACETATE	60.7971	6944.3	0	0	-7.298	3.7892E-06	2
ISOBUTYL ALCOHOL	110.267	10504	0	0	-13.921	1.6898E-17	6
ISOPENTANE	59.7951	-4976	0	0	-7.7169	8.7271E-06	2
TETRAHYDROFURAN	43.3851	5305.4	0	0	-4.7627	1.4291E-17	6
METHYL ACETATE	49.7541	5618.6	0	0	-5.6473	2.108E-17	6
METHYLAL	80.1271	6279.1	0	0	-10.631	9.7948E-06	2

METHYL ISOBUTYL KETONE	68.9901	7421.8	0	0	-8.379	1.8114E-17	6
BUTANOL	94.7771	9866.4	0	0	-11.655	1.0832E-17	6
MESITYL OXIDE	51.1661	-6815	0	0	-5.7103	5.3452E-18	6
N-HEPTANE	76.3161	6996.4	0	0	-9.8802	7.2099E-06	2
TOLUENE	65.4321	6729.8	0	0	-8.179	5.3017E-06	2
ETHYLENEDIAMINE	61.9971	7572.7	0	0	-7.1435	1.2124E-17	6

PROPORTIONATED BY ASPEN PLUS

Table 33. Coefficients of Antoine proportionated by Aspen Plus V10.

PROPORTIONATED BY DATABASE

Table 34. Coefficients of Antoine proportionated by database.

	A	B	C
ACETONE	7.2316	1277.03	237.23
CHLOROFORM	6.9371	1171.2	227
WATER	8.14019	1810.94	244.485
ACETIC ACID	7.2996	1479.02	216.82
METHANOL	8.0724	1574.99	238.87
ACETONITRILE	7.0735	1279.2	224.01
CYLOHEXANONE	6.97851	1495.58	209.559
PHENOL	7.1345	1516.07	174.57
DIISOPROPYL ETHER	7.0971	1257.6	230.01
ISOPROPYL ALCOHOL	8.1182	1580.92	219.62
ETHANOL	8.2133	1652.05	231.48
TOLUENE	6.95464	1344.8	219.482
ETHYL ACETATE	7.0146	1211.9	216.01
ISOBUTYL ALCOHOL	7.4768	1362.39	178.73
ISOPENTANE	6.83315	1040.73	235.445
BUTANOL	7.4768	1362.39	178.73
N-HEPTANE	6.87632	1075.78	233.205
ISOBUTANOL	7.4768	1362.39	178.73