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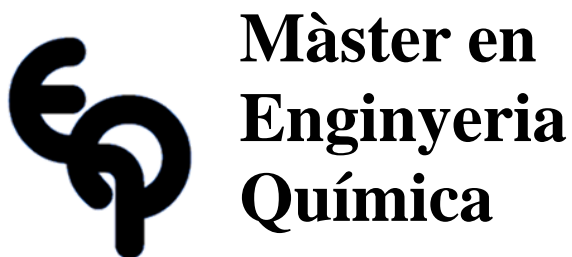
Treball Final de Màster

Contribution to the Study of Heat Integration of Pressure Swing Distillation

Contribució a l'estudi de la integració energètica de sistemes de rectificació per variació de pressió

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Agrair sobretot, als meus tutors Jordi i Victor per totes les hores invertides en ajudar-me en la realització d'aquest treball final de màster.

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REPORT

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<u>Contribution to the Study of Heat Integration of Pressure Swing Distillation</u>

1. SUMMARY

Separation processes of mixtures are one of the most important operations in the chemical industry due to the need of product purification or components recovery. Distillation is a widespread method of purification for liquid mixtures. The basis of this process is the selective boiling and condensation of the components. When it concerns an azeotropic mixture, the separation is limited to the azeotropic composition, so from this point it is impossible to continue with the purification and an alternative method must be used. Pressure swing distillation (PSD) process is an enhanced distillation method to break the azeotrope of azeotropic mixtures which are pressure sensitives. Heat integrated pressure swing distillation (HIPSD) is an improvement to overcome the high operating costs generated in the PSD process exchanging heat between hot and cold streams of the process in order to minimise the external energy requirements.

In this project, the mixture to be separated is composed of methyl acetate (MetAc) and methanol (MeOH). This mixture is obtained in the synthesis of polyvinyl alcohol (PVA), and the purification of the components is useful as MeOH is a raw material for the PVA process, and to sell / use MetAc as a solvent in production processes such as glue or paint production. The PSD process is designed according to heuristic rules for distillation, and using Aspen Plus as simulation software. The process consists of two columns. MeOH is obtained in the first one (operating at 1 atm) and MetAc is obtained in the second one (operating at 10 atm), both by bottoms and with a 99.45 % of purity.

Once the design is done, partial and full HIPSD are studied to achieve energy costs savings. This is done by means of Aspen Energy Analyzer complement, included in Aspen Plus. Since this is the first time using this tool in the department, the designs are also developed by a traditional method (Temperature-Interval) to compare the results and see how it works. For the partial HIPSD the feasible heat exchange between the first column reboiler and the second column condenser is performed, but the heat duties are not equal, hence an auxiliary reboiler is needed. The energy costs savings achieved are 37.47 %. For the full HIPSD, the PSD process is modified to equalise the heat duties, so that an auxiliary reboiler is not needed, and to minimise the second column reboiler heat requirements. The energy costs savings for this case are 46.27 %.

2. INTRODUCTION

In this chapter, some explanation about the separation methods in the industry is done, going in depth in the distillation. When the mixture to be separated is an azeotropic mixture, the distillation has limitations that can be overcome using enhanced distillation methods. Some of these methods are also explained in this chapter. PSD is one of them, and the method used in this work, so, it is described more in detail. One of the main disadvantages of PSD is the high energy consumption, some information about how energy consumption can be reduced is given too. Heat integration is one technique to do this, and the main methods to find the minimum heating and cooling utilities of the process are described below. Finally, some information about the mixture to be separated in this work is given, and finally some literature related to the topic is summarised in the last part of this chapter.

2.1. Separation Methods in the Chemical Industry

Separation methods are widely used in the chemical industry for example to increment the concentration of one of the components in a mixture, to recover one component present in a residual mixture or to purify a component. Although there are chemical and physical separation methods, in this section, only physical methods are treated.

Generally, the separation is achieved using one or more of the following techniques:

- Create a new phase by heat transfer or pressure reduction: the separation is reached by an energy separating agent (ESA) and because of differences in volatility.

- Introduce another fluid phase to the system: this fluid is considered a mass separating agent (MSA) and acts as a solvent that dissolves selectively some of the components in the mixture.

- Add a solid phase: the solid particles act as a MSA and they adsorb selectively some species.

- Place a selective membrane or barrier: the barrier allows the permeation of some of the components. This method involves an ESA.

In general terms, methods using ESA need less equipment than the ones using MSA because MSA methods involve the addition of an external agent, and this usually implies an extra piece of equipment to recover it.

Table 1 summarises the most common industrial separation methods.

Table 1 Common Industrial Separation Methods (D. Seider et al., 2016)

Separation method	Phase Condition of Feed	Separating Agent(s)	Developed or Added Phase	Separation Property
Flash	L and/or V	Pressure reduction or heat transfer ESA	V or L	Volatility
Distillation (ordinary)	L and/or V	Heat transfer or shaft work ESA	V or L	Volatility
Gas absorption	V	Liquid absorbent MSA	L	Volatility
Stripping	L	Vapor stripping agent MSA	V or L	Volatility
Extractive distillation	L and/or V	Liquid solvent and heat transfer MSA	L and V	Volatility
Azeotropic distillation	L and/or V	Liquid entrainer and heat transfer MSA	L and V	Volatility
Liquid-liquid extraction	L	Liquid solvent MSA	Second L	Solubility
Crystallization	L	Heat transfer ESA	S	Solubility or melting point
Gas adsorption	V	Solid adsorbent MSA	S	Adsorbability
Liquid adsorption	L	Solid adsorbent MSA	S	Adsorbability
Membrane	L or V	Membrane ESA	Membrane	Permeability and/or solubility
Supercritical extraction	L or V	Supercritical solvent MSA	Supercritical fluid	Solubility
Leaching	S	Liquid solvent MSA	L	Solubility
Drying	S and L	Heat transfer ESA	V	Volatility
Desublimation	V	Heat transfer ESA	S	Volatility

From the methods mentioned in Table 1, one of the most important is the distillation, extensively described below:

2.1.1. Distillation

Distillation is one of the oldest and, by far, the most used technique to separate liquid mixtures in the industry (Patil et al., 2009). In general terms, distillation consists of separating the components of a mixture by partial evaporation of its components. The mixture is fed into a column and inside of it, and because of the heat provided by a reboiler, a vapor phase is generated. Due to the difference of volatilities of the compounds, the composition of the vapor and liquid phases are not the same: the vapor phase becomes rich in the most volatile compound/s whereas the liquid phase in the less volatile compound/s.

A typical distillation column is represented in Figure 1, and the main components are explained below.

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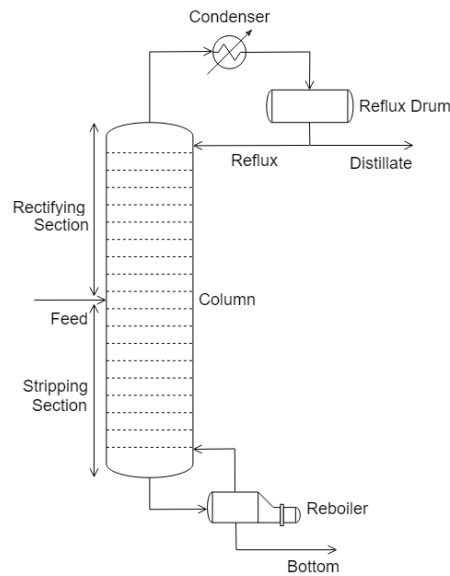

Figure 1 Distillation Column (Patil et al., 2009)

- Vertical shell: inside of this component the separation is performed.
- Column internals: trays are typically used as internals. Trays divide the column into stages. On each stage, liquid is retained to improve the contact between liquid and vapor, and liquid-vapor equilibrium is reached.
- Reboiler: it provides heat to enable the vaporization.
- Condenser: it cools and condenses the vapor of the top of the column.
- Reflux drum: it is a tank where the condensate is stored.

As seen in Figure 1, the feed is introduced into the column by the feed tray. The area of trays above the feed tray is called rectifying section and it is where the vapor phase becomes rich in the most volatile component. The area of trays below the feed tray is called stripping section and, in this section, the liquid phase becomes rich in the less volatile component. Distillation is based on liquid-vapor equilibrium in multiple stages, so in each tray of the column, the equilibrium between the vapor and liquid phases is reached. The liquid phase goes down through the column, and at the bottom, it is partially vaporised by the heat provided by the reboiler. The liquid that has not been vaporised is removed from the column enriched in the less volatile component, and the vapor is reintroduced into the column. The vapor phase ascends through the column, and it is condensate at the head by the condenser. The condensate, enriched in the most volatile component, is collected in the reflux drum, and partially

recirculated into the column, and partially removed as the distillate. Due to the huge amount of heat provided to the reboiler and the heat removed from the condenser the thermodynamic efficiency of the distillation process is poor.

Distillation is used, for instance, to produce distillate drinks with high alcohol content, to obtain perfumes, and in the petroleum industry to transform crude oil into fuels and other chemicals. Some cases to be considered are when the mixture is high in solids and when the mixture forms an azeotrope. In the first case, if the mixture contains solids that can plug the column when it operates in continuous, a possible alternative is to perform a batch separation. If the mixture forms an azeotrope, the distillation has limitations that can be overcome by using advanced distillation methods as for example, extractive distillation, azeotropic distillation or pressure swing distillation. These methods are explained below.

2.1.2.   Separation Methods for Azeotropic Mixtures

Some mixtures at certain conditions of pressure and temperature have the same composition at liquid and vapor phases (azeotropic point). When it happens, the mixture acts as if there is only one component and boils at constant temperature. In consequence, this prevents the separation of the pure compounds through conventional distillation. If this temperature is higher than the boiling point of any of the components forming the mixture, the azeotrope is called maximum boiling point or negative azeotrope. On the other hand, if the boiling point of the mixture is lower than the boiling point of any of the components, the azeotrope is known as minimum boiling point or positive azeotrope. As shown in Figure 2, the presence of an azeotrope involves a deviation of Raoult Law from a mixture with an ideal behaviour. Maximum boiling point azeotropes represent a negative deviation, and minimum boiling azeotropes represent a positive deviation.
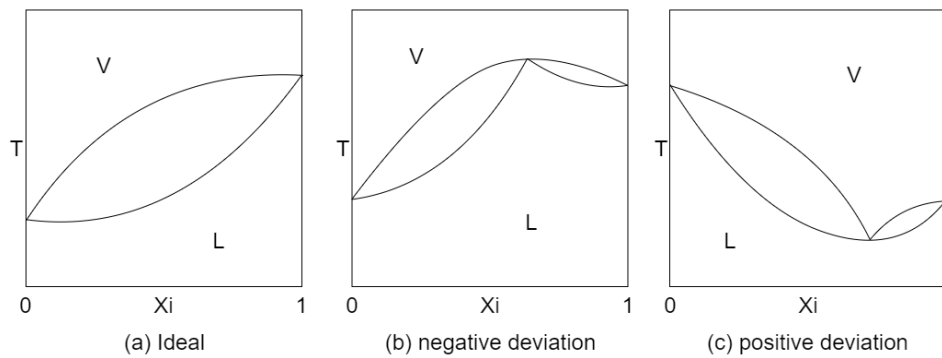
Figure 2 Txy Phase Diagram (a) Ideal Mixture (b) Negative Deviation (c) Positive Deviation

The formation of an azeotrope might have a positive impact, for example, when manipulating and transporting mixtures of a flammable component with a non-flammable component, avoiding the natural evaporation of the flammable substance.

However, the fact that mixtures in the azeotrope act as a single component, constrains the distillation since it is not possible to continue the separation once the azeotropic point has been reached. This limitation can be seen in in Figure 3, where a representation of the simple distillation process over a Txy phase diagram of an azeotropic mixture is shown (F represents the feed stream, B the bottom rate and D the distillate).
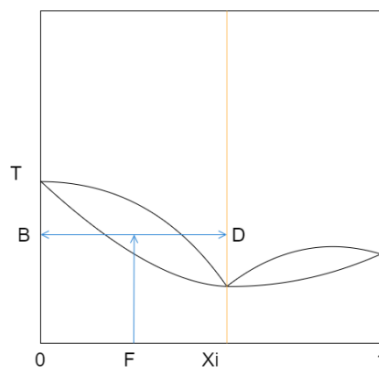
Figure 3 Txy Phase Diagram of a Binary Azeotropic Mixture with Distillation Process

Having into account that there are a lot of azeotropic mixtures in the industry, many techniques have been developed to overcome this limitation, known as "break the azeotrope". Some of the most popular enhanced distillations are:

- Extractive distillation:

This method implies the addition of an extra component to the mixture with the purpose of varying the relative volatility of the original mixture. The relative volatility

measures how easy the separation of two components is. The higher the relative volatility is, the easier is the separation. When the mixture is on its azeotropic point, the volatility equals 1. Hence, making this value different to 1, the separation can be performed by distillation. The solvent used usually has low volatility, high boiling point and it has to be miscible with the mixture. It is also important that this solvent does not form a new azeotrope with the mixture. Talking about a binary azeotropic mixture, the component with the highest volatility is obtained in heads of the column, while in bottoms, the product obtained is a mixture of the less volatile component and the solvent. Since the solvent does not form an azeotropic mixture with any of the components, this mixture obtained can be separated by conventional distillation in another column. One of the most important points of this method is the selection of a suitable solvent. Some factors to be considered when choosing a solvent are for example, the range of variation of the relative volatilities and the ease of its recovery. In Figure 4, the extractive distillation process for a binary mixture is schematically represented, where A is the most volatile component, B is the less volatile, and S is the solvent. In the first column, pure A is obtained in heads, while a mixture of B and S is obtained in bottoms. This stream is conducted to a second column where B is obtained in heads, and S is recovered (and then recycled) in bottoms.
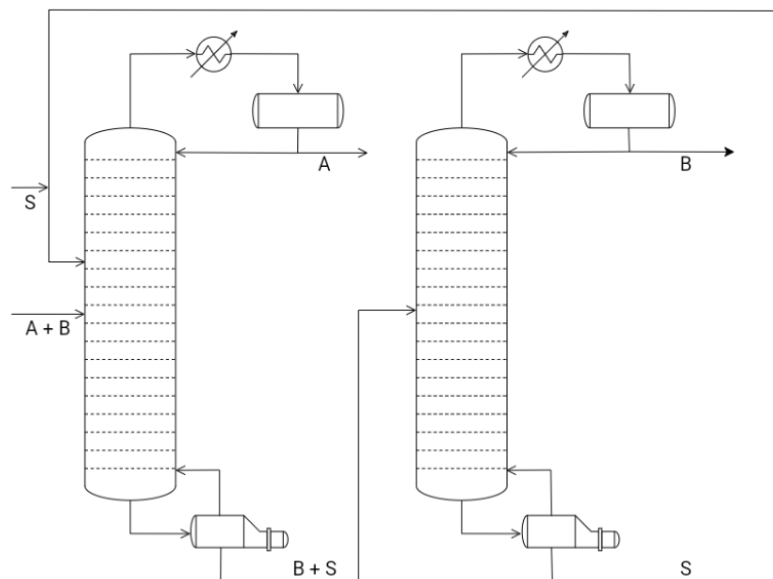

Figure 4 Extractive Distillation Process

- Azeotropic heterogeneous distillation:

This method consists of adding an extra component called the entrainer, which forms a ternary heterogeneous minimum azeotrope. As the new azeotrope has lower boiling point than the pure components of the mixture, the new heterogeneous azeotropic mixture, containing all of one of the components (B), is obtained by the top of the column whereas the other component (A) is obtained by the bottom of the column. The vapor phase obtained by the top of the column is condensate and decanted. The organic phase, rich in the entrainer is recirculated into the column again. The aqueous phase (rich in product B) is introduced into a second column, where B is obtained in bottoms and the stream containing the three components in heads. This mixture is recirculated into the first column. An example of application is in the dehydration of many components such as acetic acid, ethanol, or higher alcohols so component B is usually water. In Figure 5 a schematic representation of this technique is shown. This technology is more difficult than extractive distillation and may present many drawbacks during the design and performance.
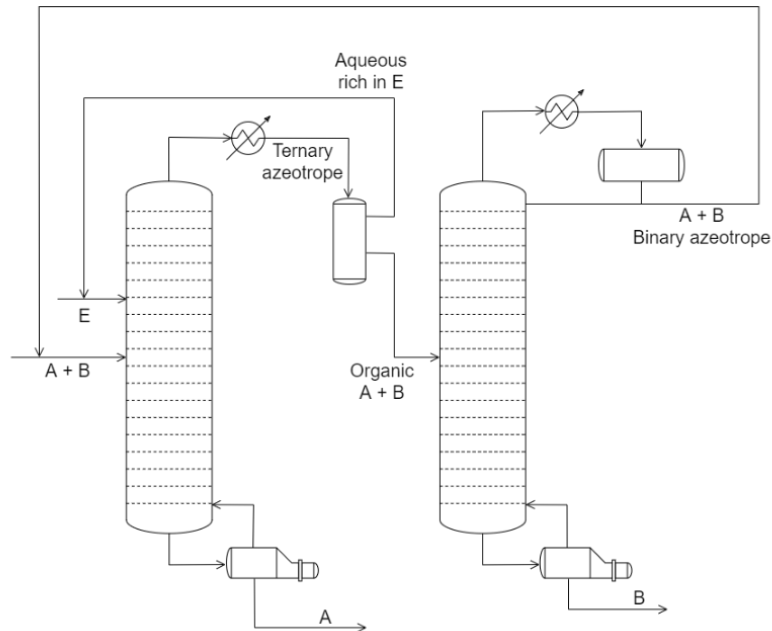

Figure 5 Azeotropic Heterogeneous Distillation Process

- Pressure swing distillation:

In general terms, for a binary mixture PSD consists of adding a second distillation column which operates at a different pressure. The azeotropic mixture must be

sensitive to pressure, which means that the azeotropic composition varies with the pressure. The main advantage of the PSD over the other methods mentioned is that it uses an ESA instead of MSAs, so the use of a entrainer is avoided. This method is explained extensively in the next point.

2.2.   Pressure Swing Distillation

As said above, PSD is a method that allows the separation of certain azeotropic mixtures, both maximum and minimum. It is based on the fact that for some mixtures, the azeotropic composition "changes" when the pressure changes. As mentioned before, these mixtures are called azeotropic mixtures sensitive to pressure. The variation in the composition has to be at least of 5 % (K. Wang et al., 2019) to enable the separation through PSD. In Figure 6 the Txy phase diagram at two different pressures (red and green lines) of a minimum boiling azeotropic mixture which is sensitive to pressure is represented. The variation of the azeotropic point can be seen in this figure.
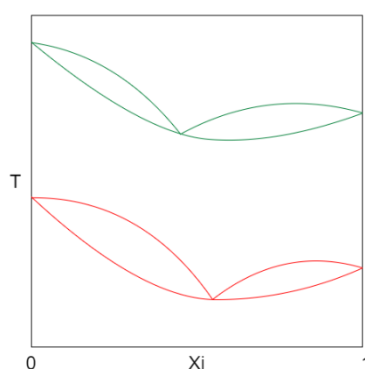
Figure 6 Txy Phase Diagram of a Binary Azeotropic Mixture for Two Different Pressures

PSD involves performing different distillations at different pressures to "move" the azeotropic point and thus break the azeotrope. A PSD process for a binary mixture generally involves two columns, one operating at low pressure, known as low pressure column (LPC), and another operating at a higher pressure, called high pressure column (HPC). LPC usually operates at atmospheric pressure (in order to avoid operating at vacuum conditions), and HPC usually operates between 7 and 12 atm. Depending on the mixture to be separated, the order of the columns can be different, feeding the mixture to the LPC or to the HPC.

Figure 7 shows a PSD process for a binary minimum boiling point azeotrope mixture (A + B). The feed (F_1) is introduced into the first column (C_1), operating at P_1, where the purification of the first component is carried. This first component is obtained in bottoms (B_1), and the distillate (D_1) leaves the column with the azeotropic composition at P_1. The distillate (D_1) is feed to a second column (C_2) operating at P_2. By the bottom of this column (C_2) the second component is obtained (B_2), and the distillate (D_2) is obtained at the azeotropic composition for P_2, and recirculated (F_D) into the first column.
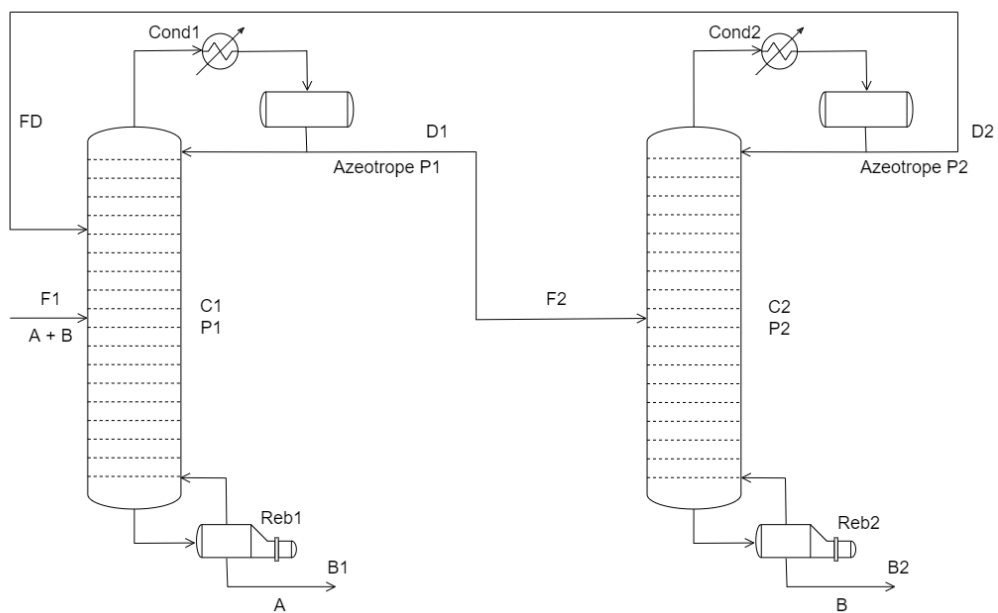

Figure 7 PSD Process

In Figure 8 the PSD process is represented over the Txy phase diagram represented in Figure 6. As explained before, by changing the operation pressure, the azeotropic composition can be overpassed, and the two components can be purified (B_1 and B_2).
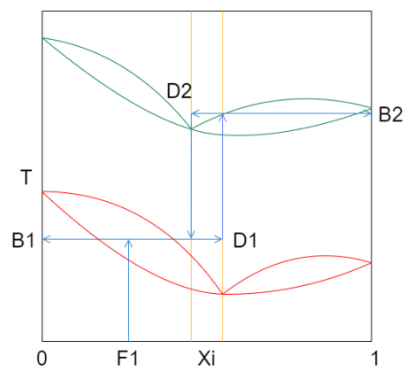

Figure 8 Txy Phase Diagram for Two Pressures with PSD Process

In this case, the first column is the LPC and when the distillate, near to the azeotropic composition at P_1, is fed to the HPC, it is "at the other side" of the azeotrope at P_2, and so, the azeotrope is broken, and the second component can be purified.

As stated before, one of the main advantages of this method is that it does not use a MSA, which involves no dealings with availability and suitability of the extra component. Also, the recovery of the MSA is not needed.

On the other hand, the main disadvantages of this technology are that the control structure needed is complex, accurate equilibrium and azeotropic data of the mixture is important to design the process and the high energy requirements. Also, not every azeotropic mixture is suitable to be separated through PSD, as it has been stated before, the azeotrope must be enough sensitive to pressure.

In order to improve the PSD process, one of the most studied aspects is the energy requirements reduction in order to decrease the operating costs. Some methods are treated in the next section.

2.3. Energy Consumption Reduction Methods

As mentioned before, distillation has a low thermodynamic efficiency since a lot of heat is required by the reboiler and a similar amount is removed from the condenser. These high energy requirements mean that a distillation process can represent more than the 50 % of a plant operating costs (Kiss, 2013). This fact encourages to develop techniques to reduce energy costs. Several proposals are being studied, and the ones with a higher importance are the application of heat integration using heat pump technologies and exchanging heat between process streams.

Heat integration consists of optimising the heat exchanges between heat sources and sinks to reduce the external heating and cooling services required by the process. In the case of distillation, it is a promising way of reducing energy costs due to the big amount of both heating and cooling requirements of the process.

A heat pump is a machine that moves heat from low temperature heat source to a higher temperature heat sink. Heat pump technology is one of the most applied methods to achieve a reduction of the energy requirements in the distillation process,

and it can also be combined with the enhanced distillation technologies mentioned above. In the case of PSD, the heat pump technology can be applied to use the LPC vapor to heat the HPC liquid after being compressed. This exchange is not spontaneously since the HPC liquid is at a higher temperature than the LPC vapor.

Heat integration between the hot and cold streams of the process is also a proposal widely used to decrease the energy requirement of the process. How to apply this technique is explained in the next section.

2.4. Heat Integration

Heat integration lies on using the energy of hot stream that need to be cooled/condensed to heat cold streams that need to be heated/vaporised. The principal aim for heat integration is to find the minimum energy requirement (MER) in order to design a heat exchanger network (HEN), considering the minimum approach temperature (ΔT_{min}) chosen, in a way that the loss of energy is optimised. ΔT_{min} is defined as the minimum allowable temperature difference between the heat source and sink when they are exchanging heat. A small ΔT_{min} involves better heat recovery (lower operating costs), but also may result in higher capital costs since the heat transfer area increases. Hence, the optimal value of ΔT_{min} should be found for each process to obtain the best economic results. The typical values for the ΔT_{min} are between 5 and 30 ºC.

To perform the MER targeting, there are two main methods available: Composite Curve method and Temperature-Interval method, both described below.

- Composite Curve method:

It is a graphical method based on the temperature – enthalpy diagram. To develop this method, the hot and cold composite curves are generated. The composite curve is a temperature – enthalpy graphic in which the enthalpy availability of the hot and cold streams as a function of the temperature are represented. Once both composite curves are generated, the composite curves must be displaced horizontally in order to accomplish with the ΔT_{min} requirement. The ΔT_{min} requirement is achieved when the temperature difference between hot and cold streams at any point is equal or higher than the ΔT_{min}. The point at which both composite curves are coincident is called pinch

point. The MER are determined by this resulting graphic. The enthalpy difference between the hot side of the composite curves determines the minimum hot utilities required, and the enthalpy differences at the cold side of the composite curves is the minimum cold utilities required. In Figure 9, a representation of the composite curve method process for a $\Delta T_{min} = 10\ ^\circ C$ is displayed, where it can be seen that the minimum heating and cooling utilities are 48 kW and 6 kW respectively.
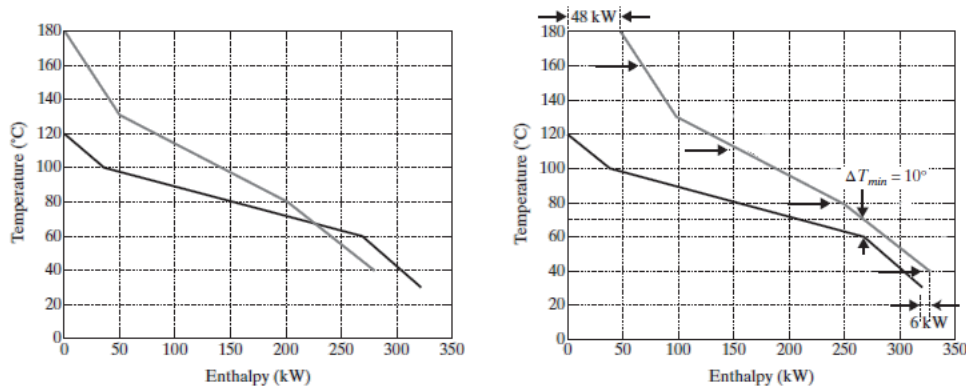
Figure 9 Example of a Composite Curve Method (D. Seider et al., 2016)

- Temperature – Interval method

For the Temperature – Interval method, the first step is to adjust the hot / cold streams temperatures taking into account the ΔT_{min} chosen. This can be done summing ΔT_{min} to the cold streams temperatures or subtracting it from the hot streams. To determine the intervals, all the temperatures are ordered from the higher to the lower without the repeated temperatures, and these are considered the initial temperature of the interval. The interval final temperature is the initial temperature of the following interval. Then, interval enthalpy difference is calculated for each interval using Equation 1.

Equation 1 Interval Enthalpy Difference (D. Seider et al., 2016)

$$\Delta H_i[kW] = \left(\sum C_H[kW/^\circ C] - C_C[kW/^\circ C]\right)_i (T_0[^\circ C] - T_1[^\circ C])$$

ΔH_i = Interval enthalpy difference

C_H = Total flowing heat capacity of hot streams that passes through the interval

C_C = Total flowing heat capacity of cold streams that passes through the interval

T_0 = Initial temperature of the interval

T_1 = Final temperature of the interval

To calculate the enthalpy cascade, starting with an ΔH = 0, the ΔH of each interval is added to the previous ΔH. Then the cascade is repeated, taking the minimum value of ΔH obtained in the first cascade as the initial value of ΔH. The pinch temperatures are the minimum temperatures of the intervals with an ΔH = 0 in this last cascade. The minimum heating utilities required are the initial ΔH of this cascade, and the minimum cooling requirements are the ΔH of the last interval.

Once the MER targeting is done, the HEN can be designed. There are some important points that must be followed in order to design a feasible HEN: only streams at the same side of the pinch can exchange heat, and in countercurrent heat exchangers, the differences of temperatures between hot and cold streams in each end of the heat exchanger has to be equal or higher than the imposed ΔT_{min}. When the optimal HEN is designed, the heat exchanges between hot and cold streams make the energy requirements equal to the MER target.

Regarding the PSD, there are two possibilities to design a HIPSD: with rectifying-stripping section heat integration and with condenser-reboiler heat integration. The first one consists of exchanging heat between the rectifying section of the HPC and the stripping section of the LPC. The second is the most widely studied and the one used in this work. It is based on providing the heat removed from the HPC condenser to the reboiler of the LPC. It is possible to talk about partial and full HIPSD. In partial heat integration, the heat removed from the HPC condenser is not equal to the heat needed in the LPC reboiler, so the residual heat must be provided by an auxiliary reboiler / condenser. In the full heat integration, both heat duties are equal, therefore there is no need to use the auxiliary reboiler / condenser.

Once the PSD process and the heat integration methods have been introduced, in the next section, information about the selected mixture is given.

2.5. Methanol – Methyl Acetate Mixture

As mentioned before, not every azeotropic mixture is suitable to be separated through PSD, it must be sensitive to pressure. In this work, the selected mixture, that fulfil this requirement, is the mixture formed by MetAc and MeOH, obtained in the

synthesis of the PVA. PVA is a synthetic water-soluble polymer used worldwide. It has excellent properties such as low toxicity, odourless, harmless, low tendency for protein adhesion, high flexibility, and it acts as a barrier for oxygen and scents. These properties make it suitable for a broad range of applications as for example producing end products such as lacquers, resins, packaging materials and surgical threads in industrial, medical and food sectors. It is considered the most commercially important water-soluble plastic in use (Nagarkar & Patel, 2019).

PVA is synthetised by hydrolysis of radical polymerization of polyvinyl acetate in an alcohol, commonly MeOH, and treating it with an alkaline catalyst as sodium hydroxide. MetAc is obtained as a by-product with a proportion of 1.68 tons of MetAc per ton of PVA (Xu et al., 2009).

MetAc is commonly used as a low toxicity volatile solvent for adhesive, glues, paints, and nail polish removers production, so it is considered a bulk commodity (Zheng et al., 2015). It is obtained as a residual mixture in the PVA production. This mixture contains MetAc and MeOH in a large amount, in addition to light organic impurities, polymer solids and water in low proportions. If the products of this mixture are purified, MeOH can be used again in the production of PVA. MetAc can be used in other production processes, some of them mentioned above. Therefore, it is interesting to purify them.

MetAc and MeOH forms a minimum boiling point azeotrope and the azeotropic composition at 1 atm is about 66.5 %mol MetAc (using the UNIQUAC-RK thermodynamical model). As stated before, this mixture is sensitive to pressure: the azeotropic composition varies considerably by changing the pressure as seen in Figure 10. Hence, PSD can be used to perform this purification.
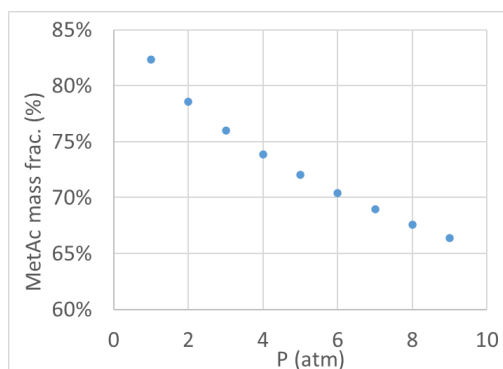

Figure 10 Variation of Azeotropic Composition (K. Wang et al., 2019)

In this chapter some general research about the topic, including separation methods and enhanced distillation methods, going depth in the PSD process and the point of reducing its energy costs by heat integration has been done. Information about the studied mixture in this work is also described above, and in the next section some research about the state of the art concerning PSD and HIPSD is done.

2.6.   Related Literature

In this section, some papers about condenser-reboiler HIPSD process are summarised, and tables with the main results are presented. In these tables, some abbreviations have been used: number of trays (N_T), feed stage (N_F), recirculated feed tray (N_{FD}), reflux ratio (RR), reboiler and condenser heat duty (Q_R and Q_C), the exchanged heat duty between the condenser and reboiler (Q_{exch}) and the distillate and bottom temperatures (T_D and T_B). The capital costs are shown per year, taking into account the PP used in each paper.

Apart from the literature mentioned below, other papers have been checked. Some of them are about different HIPSD processes as for example rectifying-stripping section HIPSD to separate acetonitrile and water (Huang et al., 2008), an hybrid HIPSD for the dehydration of bioethanol (Kiran & Jana, 2015), and HIPSD process with an intermediate connection to separate a mixture of ethylenediamine and water (Y. Wang et al., 2018). Also, a paper talking about the influence of the feed temperature in a PSD process for separation of MeOH – MetAc (Cao et al., 2016) has been checked.

2.6.1. PSD with Heat Integration for MeOH – MetAc Separation

The following papers are about HIPSD for the separation of a mixture of MeOH – MetAc. Although in some paper other aspects are treated, only the process followed for the design and the results obtained in each paper for the PSD and HIPSD processes are compiled in this section.

<u>Paper 1: Design and control of methyl acetate – methanol separation via heat-integrated pressure-swing distillation</u> (Zhang et al., 2016)

In this paper, the feed mixture is 100 kmol/h of a mixture of MeOH and MetAc with a composition of 50 %mol. The LPC (first column) operates at atmospheric pressure

(0.99 atm), and the bottom purities are obtained using Design Spec. Tool, varying the bottom flowrates to achieve a product purity of 99.5 %mol. The optimum tray numbers and the operating pressure of the HPC (10.85 atm) are chosen to minimise the TAC, and the optimum feed stages and the optimum reflux ratios are determined to make the total reboiler heat duty (sum of reboiler heat duty of both columns) the minimum. The recirculated distillate of the HPC is fed to the LPC column at the stage with the most similar composition. The MeOH is obtained by the bottom of the first column, and MetAc by the bottom of the second.

For partial HIPSD, after checking the temperature difference between the HPC top vapor and the LPC bottom liquid to determine the feasibility to heat exchange, all the heat duty removed from the HPC condenser is given to the LPC reboiler, and the residual heating requirements of the LPC reboiler are provided by an auxiliar reboiler.

For full HIPSD, the heat duties of the LPC reboiler and the HPC condenser are made equal by varying the reflux ratio of the HPC column. The bottom flow rates of both columns are still used to achieve the product purities desired. The reflux ratio of the LPC is modified to achieve the minimum HPC reboiler heat duty.

The optimum design parameters and economic results for the three scenarios are shown in Table 2. The conclusions obtained in this paper are that the full heat integration is the best option if minimising the TAC is the objective, and both capital and energy costs are reduced. However, there is no information about how the costs have been calculated.

Table 2 Results Zhang et al. (2016)

	PSD		Partial HIPSD		Full HIPSD	
	LPC	HPC	LPC	HPC	LPC	HPC
N_T	25	37	25	37	25	37
N_F	11	26	11	26	11	26
N_{FD}	16	-	16	-	16	-
RR	0.80	1.30	0.80	1.30	0.60	1.44
Q_R (kW)	1,936	2,067	393	2,067	-	2,322
Q_C (kW)	2,246	1,543	2,246	-	2,108	-
$Q_{exch.}$ (kW)	-		1,543		1,774	
T_D (ºC)	53.8	135.3	53.8	135.3	53.8	135.3
T_B (ºC)	68.3	149.2	68.3	149.2	68.3	149.2
Capital Cost (1,000 USD/year)	728		627		601	
Capital Cost Reduction	-		13.87%		17.45%	
Energy Cost (1,000 USD/year)	1,024		681		665	
Energy Cost Reduction	-		33.50%		35.06%	
TAC (1,000 USD/year)	1,752		1,307		1,267	
TAC Reduction	-		25.40%		27.68%	

Paper 2: Pressure swing distillation for the separation of methyl acetate-methanol azeotrope (K. Wang et al., 2019)

In this paper, the PSD process is developed, studying the influence of feeding stages, reflux ratios and column stage numbers. Also, the full and partial HIPSD are designed. The three scenarios are evaluated for three different pressures of the HPC and the bests results are obtained for 9 atm. Therefore, it is the pressure chosen to summarise this paper. The MeOH is obtained by the bottom of the first column (LPC), and MetAc by the bottom of the second (HPC).

The LPC pressure is fixed at 1 atm due to convenience of operation. The HPC pressure is chosen at 9 atm because at that pressure, the HPC reboiler can use LPS to heat, reducing energy costs compared to if MPS or HPS is used. The feed mixture of the process designed consists of 1,000 kg/h with a composition 60 %wt of MeOH and 40 %wt MetAc, at a normal temperature. The product purity fixed for both columns is 99 %wt. In this process, the bottom flow rates are varied to meet the product purity specifications. The rest of variables (number of trays of each column, three feed stages, and the reflux ratios) are varied following an iterative sequence in order to

minimize the TAC. The iterative sequence consists of fix all the variable involved, and then vary the value of one to find the optimum (minimum TAC). Then repeat the process one by one, until all the variables are optimised.

To develop the partial HIPSD, the temperature difference between the HPC distillate and PLC bottom rate is suitable for heat exchange, so the LPC reboiler and HPC condenser can be partially integrated, needing an auxiliary reboiler to provide the missing heat required by the LPC reboiler.

For the full HIPSD, the LPC condenser duty and HPC reboiler duty are made equal by regulating the reflux ratio of the LPC, which at the time, regulates the HPC reflux ratio.

In Table 3, the results obtained are represented. The TAC without heat integration is the highest, and the minimum is found when full HIPSD is performed. Also, the capital and energy costs are reduced. Capital cost in this paper only takes into account the column, condenser and reboiler costs, and operating costs considers the utilities costs. The PP is taken as 3 years.

Table 3 Results Wang et al (2019)

	PSD		Partial HIPSD		Full HIPSD	
	LPC	HPC	LPC	HPC	LPC	HPC
N_T	34	27	34	27	34	27
N_F	23	16	23	16	23	16
N_{FD}	18	-	18	-	18	-
RR	1.1	1.2	1.1	1.2	1.0	2.4
Q_R (kW)	276.60	223.61	104.64	223.61	-	309.35
Q_C (kW)	292.34	171.96	292.34	-	273.52	-
$Q_{exch.}$ (kW)	-		171.96		258.89	
T_D (ºC)	53.62	126.78	53.62	126.78	53.62	126.77
T_B (ºC)	64.51	138.33	64.51	138.33	64.51	138.33
Capital Cost (1,000 USD/year)	105.441		91.148		88.957	
Capital Cost Reduction	-		13.56%		15.63%	
Energy Cost (1,000 USD/year)	171.315		110.827		104.210	
Energy Cost Reduction	-		35.31%		39.17%	
TAC (1,000 USD/year)	276.756		201.975		193.167	
TAC Reduction	-		27.02%		30.20%	

(Chen et al., 2018)

In this case, the feed mixture contains 75 %wt MetAc, 25 %wt MeOH and a small quantity acetaldehyde (0.05 %wt), in a flow of 3,000 kg/h, at the dew point temperature. MeOH is obtained from the bottom of the first column (LPS) and MetAc from the bottom of the second (HPC). Because of the boiling point of acetaldehyde, a side withdrawal is necessary. The distillate (small flow rate) is removed from the LPC, with a high proportion of acetaldehyde in it. The side withdrawal is introduced into the HPC. The LPC pressure is fixed at 1 atm and for the HPC, 6, 8 and 10 atm are tested to select the optimum based on the minimum TAC.

In this paper, to check the feasibility of the process, the values of number of trays of both columns, the LPC distillate rate and mass reflux rate, the side withdrawal tray location, the HPC pressure and the HPC reflux ratio are fixed at imposed values. The liquid side withdrawal rate of the LPC and the distillate rate of the HPC are manipulated to achieve the desired product purity specifications. With these conditions, almost all the acetaldehyde is in the distillate of the LPC, which is removed, so it is not accumulated in the system, and the temperatures and heat duties make possible the full HIPSD. In order to make equal the HPC condenser heat duty and the LPC reboiler heat duty, reflux rate of the LPC is adjusted. In order to calculate the TAC, only column, reboiler and condenser are considered. Although the PP is not given, by the economic results presented, it can be known as 3 years.

In Table 4, the results obtained for the HPC pressure of 10 atm are shown, owing to the best results are found at this pressure. Although operating at this pressure increases the capital costs (it affects the thickness of the vessel, for example), the recycle flow rates and reflux ratios decrease due to the difference in the azeotropic compositions is higher. Since this paper only designs in detail the full HIPSD, the results table only shows data for this design, and therefore savings cannot be calculated.

Table 4 Results Chen et al. (2018)

	Full HIPSD	
	LPC	HPC
N_T	32	30
N_F	18	16
N_{FD}	19	-
N_{sw}	8	-
RR	-	1.3
MASS-L (kg/h)	12,014	-
SWR (kg/h)	5,632	-
Q_R (kW)	-	1,416
Q_C (kW)	1,785	-
$Q_{exch.}$ (kW)	1,115	
T_D (ºC)	52.07	130.05
T_B (ºC)	69.50	144.60
Capital Cost (1,000 USD/year)	578.00	
Energy Cost (1,000 USD/year)	369.64	
TAC (1,000 USD/year)	947.64	

N_{sw}	side withdrawal tray
MASS-L	mass reflux rate
SWR	liquid side withdrawal rate

2.6.2. PSD with Heat Integration for Other Mixtures Separation

This section is about HIPSD processes to separate mixtures different from MeOH – MetAc. The mixtures studied also present minimum boiling point azeotrope, the same type that the mixture studied in this project.

<u>Paper 4: Separating an azeotropic mixture of toluene and ethanol via heat integration pressure swing distillation</u> (Zhu et al., 2015)

This paper designs a HIPSD to separate 3,500 kg/h of a mixture composed by 28 %wt toluene and 72 %wt ethanol at the normal temperature. The ethanol purity is fixed as 99.9 %wt and the ethanol impurities in HPC bottom rate (pure toluene) must be less than 0.2 %wt. Before starting with the PSD design, the influence of the pressure and the distillation sequence have been studied and found that the best option is to operate the first column at 0.5 atm (LPC) and the second at 11 atm (HPC). However, in the papers results for 10, 11 and 12 atm are shown.

To start with the design, the number of trays of both are fixed at 50, the three feed stages are near to the middle, with the recirculated feed some trays above the fresh feed, and the reflux ratios of both columns are 2. The distillate rates of LPC and HPC are manipulated to reach the products specifications. Then an iterative sequence is followed to find the optimum values of these variables in order to minimise the TAC. The sequence consists of vary the variables one by one, starting with the reflux ratio of the HPC, then of the LPC, the feed staged of HPC and LPC, and then the trays number of HPC and LPC.

The difference between the HPC condenser heat duty, and the LPC reboiler heat duty is enough, and the temperatures are suitable to partial integration.

For full HIPSD, the same iterative sequence is followed but without the LPC reflux ratio, that in this case, is manipulated to equalise the LPC reboiler and HPC condenser heat duties.

For the TAC calculation, the operating costs are considered the utilities costs, and the capital costs include the columns (with condensers and reboilers) costs. The PP is considered 5 years. In Table 5 the results are shown for a pressure of 11 atm for the HPC.

Table 5 Results Zhu et al. (2015)

	PSD		Partial HIPSD		Full HIPSD	
	LPC	HPC	LPC	HPC	LPC	HPC
N_T	35	22	35	22	37	21
N_F	6	16	6	16	5	16
N_{FD}	16	-	16	-	16	-
RR	0.90	0.80	0.90	0.80	0.73	1.20
Q_R (kW)	991.75	1,367.19	337.56	1,361.19	-	1,520.84
Q_C (kW)	1,514.91	991.75	1,514.91	-	1,330.35	-
$Q_{exch.}$ (kW)	-		991.75		1,159.73	
T_D (ºC)	59.79	155.28	59.79	155.28	75.79	155.23
T_B (ºC)	70.55	222.84	70.55	222.84	70.80	222.81
Capital Cost (1,000 USD/year)	346.264		334.860		319.760	
Capital Cost Reduction	-		3.29%		7.65%	
Energy Cost (1,000 USD/year)	332.940		262.520		266.930	
Energy Cost Reduction	-		21.15%		19.83%	
TAC (1,000 USD/year)	679.200		597.380		586.680	
TAC Reduction	-		12.05%		13.62%	

This paper is the second part of an study talking about the separation of a mixture of 3,000 kg/h composed by 85.8 %wt methylal, 13.9%wt MeOH and 0.3%wt water using extractive distillation (Q. Wang et al., 2012). In this part, the feed is considered the same, and also the product purities, which are 99.9%wt methylal and methylal impurities under 0.2 %wt in the MeOH product stream. The operating pressure of the LPC is set atmospheric pressure and the pressure of the HPC is chosen as 11.85 atm (1,200 kPa) after notice that it gives the best results regarding the TAC.

Before starting with the HIPSD, with some fixed values, the feasibility of the heat integration is checked by calculating the temperatures and heat duty of the condensers and reboilers with some initial values for the different variables of the system. The PSD is not optimised.

The first step done is find the minimum tray numbers and reflux ratios assuming the distillate of the second column must be at azeotropic composition of its pressure. This flow rate is determined by simple material balance. The heuristic that set the optimum reflux ratio at 1,2 times the minimum reflux ratio is assumed to determine the minimum stages number. The bottom flow rate is manipulated to reach the product purity in each column. To achieve the full HIPSD, the reflux ratio of the LPC is adjusted to make the LPC reboiler and HPC condenser heat duties equal. The feeding locations of both columns and the reflux ratio of the HPC are set to minimise the HPC reboiler heat duty. These three variables are changed one by one in an iterative sequence until obtaining the optimum values on the basis of minimising the HPC reboiler heat duty.

Then the process is repeated changing the number of trays and the HPC pressure and following the same procedure in order to find the minimum TAC. The capital costs include vessels, internals, reboilers and condensers, and operating costs considers the utilities costs and the power of all pumps.

The best results are obtained in Table 6. In this paper, only the full HIPSD results are shown, but the TAC for the process without heat integration is given (795.1x10^3 USD/year). Neither the capital nor the energy costs are given.

Table 6 Results Yu et al. (2012)

	Full HIPSD	
	LPC	HPC
N_T	16	28
N_F	5	10
N_{FD}	12	-
RR	0.83	1.34
Q_R (kW)	-	904.20
Q_C (kW)	314.64	-
$Q_{exch.}$ (kW)	605.40	
T_D (ºC)	314.64	399.73
T_B (ºC)	340.63	409.77
TAC (1,000 USD/year)	554.160	
TAC Reduction	30.30%	

Paper 6: Thermodynamic efficiency enhancement of pressure-swing distillation process via heat integration and heat pump technology (Li et al., 2019)

The HIPSD process to separate acetonitrile and ethanol is studied in this paper. The flowrate of feed stream is 100 kmol/h, and the mixture contains 70 %mol of acetonitrile (which is the bottom product of the HPC) and 30 %mol of ethanol (obtained by the bottom of the LPC). In this process, due to the composition of the feed mixture, the first column is the HPC and the second the LPC, operating at 1 atm. The product purities are fixed at 99.9 %mol in both columns.

The bottom purities are achieved by adjusting the bottom flowrate of both columns. Then an iterative sequence is developed in order to find the values that minimises the TAC, changing variables one by one, starting with the feed stages (first LPC, the recirculated feed, and then the HPC), the reflux ratio of the LPC and HPC and the trays number of the LPC and HPC, and HPC pressure. The best results obtained are for the HPC operation pressure at 7 atm, hence, the heat integration is performed at this pressure.

For partial HIPSD, the heat duty removed from the HPC condenser is given to the LPC reboiler, but in this case, the condenser heat duty in less than the reboiler heat duty, therefore, instead of needing an auxiliary reboiler, an auxiliary condenser is required.

This paper does not design a full HIPSD. The results available are presented in Table 7. The capital costs include the equipment cost of column vessels plates, and heat exchangers. The energy costs are considered the utilities and electrical costs. the TAC is calculated with a PP of 3 years.

Table 7 Results Li et al. (2019)

	PSD		Partial HIPSD	
	LPC	HPC	LPC	HPC
N_T	29	36	29	36
N_F	12	26	12	26
N_{FD}	-	18	-	18
RR	2.03	1.52	2.03	1.52
Q_R (kW)	630.60	1,745.70	-	1,745.70
Q_C (kW)	787.80	1,255.10	787.80	624.50
$Q_{exch.}$ (kW)	-		630.60	
T_D (ºC)	73.00	137.30	73.00	137.30
T_B (ºC)	82.80	159.60	82.80	159.60
Capital Cost (1,000 USD/year)	467.170		443.038	
Capital Cost Reduction	-		5.17%	
Energy Cost (1,000 USD/year)	975.429		727.818	
Energy Cost Reduction	-		25.38%	
TAC (1,000 USD/year)	1,442.599		1,170.856	
TAC Reduction	-		18.84%	

3. OBJECTIVES

The main objectives of this project are to study and optimize the separation of an azeotropic mixture composed by methanol (MeOH) and methyl acetate (MetAc) through pressure swing distillation (PSD) and heat integrated pressure swing distillation (HIPSD) and evaluate the energy savings and economic data using Aspen Plus Software and the complement Aspen Energy Analyzer. This complement has not been used in the department before.

In Figure 11 the process studied is schematically represented. The first column (LPC) is fed with a mixture of 50 %mol of MetAc and 50 %mol of MeOH and it operates at atmospheric pressure. Purified MeOH is obtained by the bottom of this column, and the distillate, a mixture on its azeotropic composition at 1 atm, is fed to the HPC. In this column, MetAc is obtained by the bottom and the distillate mixture at the corresponding azeotropic composition, is recirculated into the LPC.
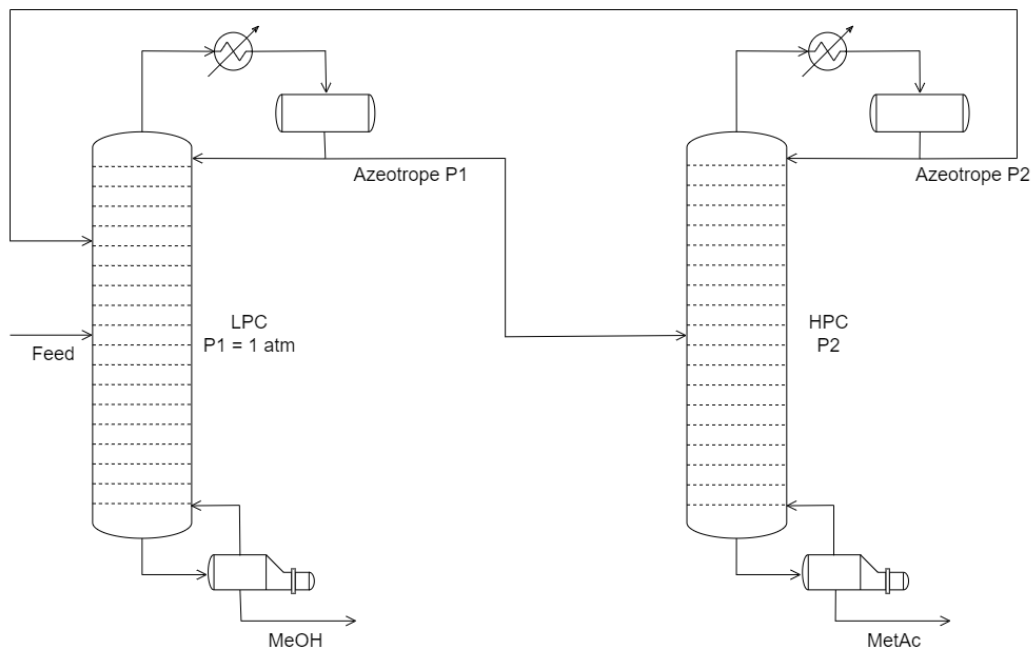

Figure 11 Schematical PSD Process Proposed

4. METHODOLOGY

Before starting with the simulations, some bibliographic research has been done. After that, the PSD process is designed and simulated using Aspen Plus V12.1. Then, for the partial HIPSD, the Temperature-Interval method is developed in the basis of the PSD simulation. Aspen Energy Analyzer is also used to calculate potential energy savings and find a solution to meet the utilities target. Also, the full HIPSD is simulated, and energy analysed in order to study the energy and economic potential saves. In both cases, the condenser-reboiler heat integration is used.

4.1. Aspen Plus Simulations

For the simulation, the UNIQ-RK method is used, as it has been seen that there is experimental data for the studied mixture, and Redlich-Kwong because of working at high pressures. The columns used are RadFrac with Equilibrium calculation type due to it is based on the liquid-vapor equilibrium stage. The condenser used is total and the reboiler type is set as kettle. The selected convergence is Strongly Non-Ideal Liquid because of the presence of azeotropic mixtures in the process. The columns are fed using above-stage convention, and the first and last stages of each column are considered the condenser and reboiler respectively. In order to optimize the columns, the Sensitivity Analysis Tool of Aspen Plus is used to study the influence of varying the number of stages and feed stages and to find the ones that make the reflux ratios achieve their optimal value.

Regarding the utilities in the simulation, low, medium, and high-pressure steam (LPS, MPS and HPS) and cooling water (CW) are introduced, and in Table 8 the utilities prices are summarised.

Table 8 Utilities Price Aspen Plus

Utility	Price (USD/kJ)
CW	2.12×10^{-7}
LPS	1.90×10^{-6}
MPS	2.20×10^{-6}
HPS	2.50×10^{-6}

To calculate total annual cost (TAC), Equation 2 is used. Capital cost includes the equipment and installed cost of the equipment and piping, and energy cost includes the utilities costs. The payback period (PP) in this project is considered 5 years.

$$TAC\ [USD/year] = \frac{Capital\ Cost\ [USD]}{PP\ [years]} + Energy\ Cost[USD/year]$$

4.2. Energy Analyzer

This project is the first in the department using Energy Analyzer, hence, in this section, an explanation about its use is presented. There are two ways to start a project in Energy Analyzer: introducing process streams directly in Energy Analyzer (Rao, 2014) and extracting process data from an existing HYSYS or Aspen file. In this work the second method is explained below.

To export data from a process simulated in Aspen, the file must be in backup file format (extension .bkp), and the simulation must be in steady state, with neither errors nor warnings. Also, economic analysis should have been performed. Once the Aspen file is suitable to be analysed, the Energy Analyzer button must be activated as Figure 12 shows.

Figure 12 Energy Analyzer Button

Once it is activated, the Energy Analyzer calculates the potential energy savings of the process. In the Energy Analyzer tab (Figure 13), the actual and target values of total, heating and cooling utilities are shown, as well as the carbon emission (yellow frame), and the economic data can be seen by selecting the cost basis instead of flow basis (green frame). Any of these data can be exported to an excel file by clicking "See report" (blue frame). By clicking "Find Design Changes" (purple frame) in Figure 13, Energy Analyzer explores different design changes to reach the utilities target
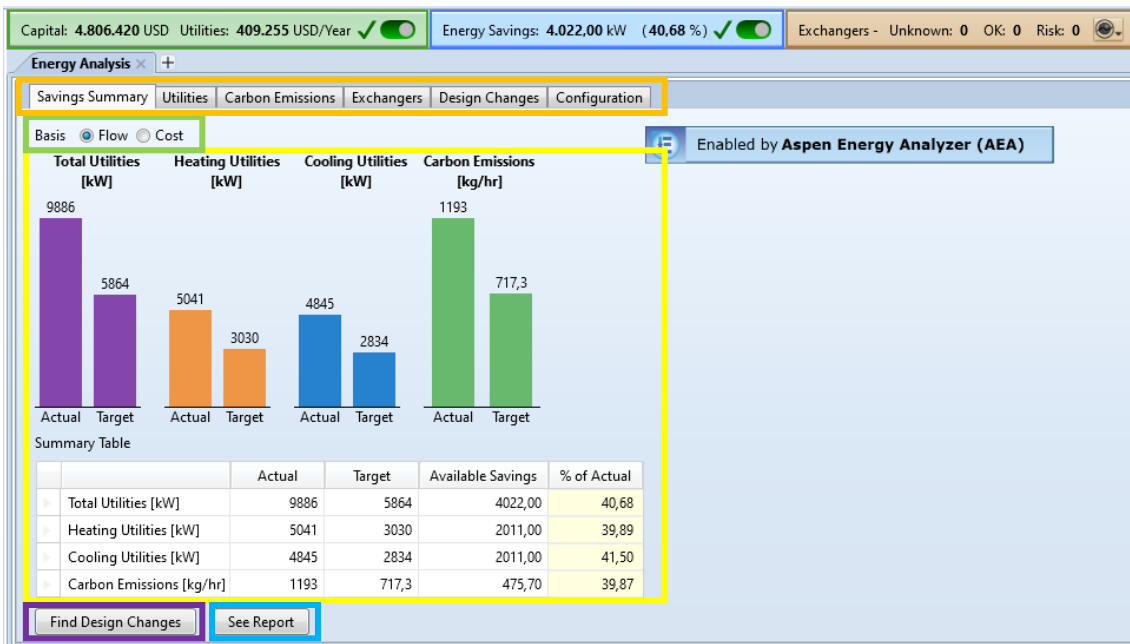
Figure 13 Energy Savings Screen

In the different tabs from the top (orange frame in Figure 13), the data obtained in the summary screen is detailed. For example, Figure 14 is displayed when "utilities" tab is opened.
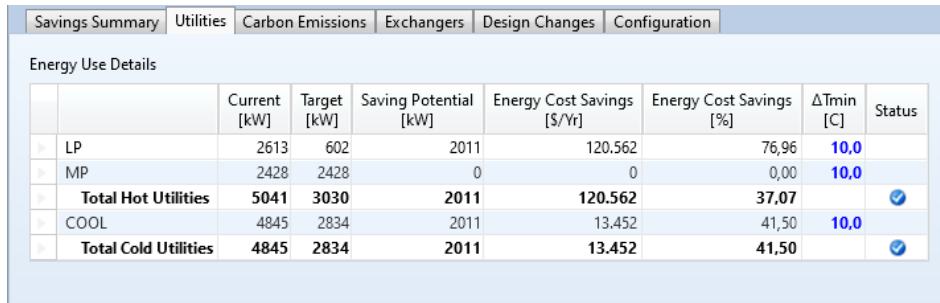

Figure 14 Utilities Tab

Also, the information about each heat exchanger is given in "Exchangers" tab (Figure 15). Finally, in the "Configuration" tab, the ΔT_{min} can be chosen, and the inlet and outlet temperatures of the utilities can be modified.
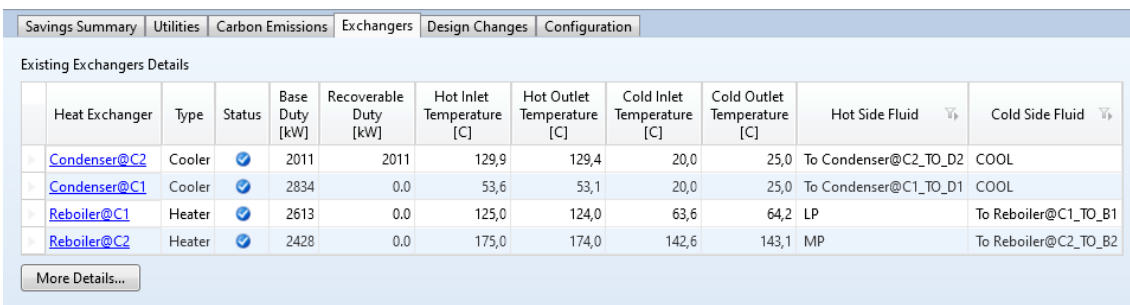

Figure 15 Heat Exchangers Information

When "Find Designs Changes" is clicked, it analyses three possibilities: modify existing heat exchangers, add new heat exchangers, and relocate existing heat exchangers. Figure 16 shows the screen with the solution found (yellow frame). Each solution generates a new scenario in Energy Analyzer.
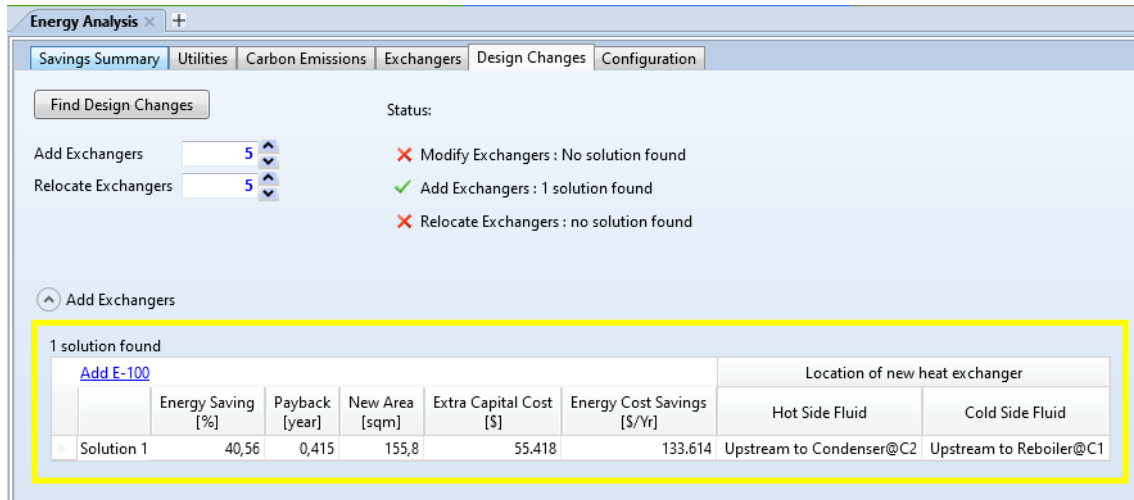

Figure 16 Found Design Changes

Then, in the Energy Analyzer environment, information about the base process and about each scenario is presented (Figure 17). In Figure 17 the energy costs and consumption for base case, solution proposed, as well as the target values are shown (yellow frame). Also, information about the potential changes in the design (green frame) and details about the heat exchangers of the scenario (blue frame) are presented. It is also possible to explore the different scenarios in the left menu (orange frame).
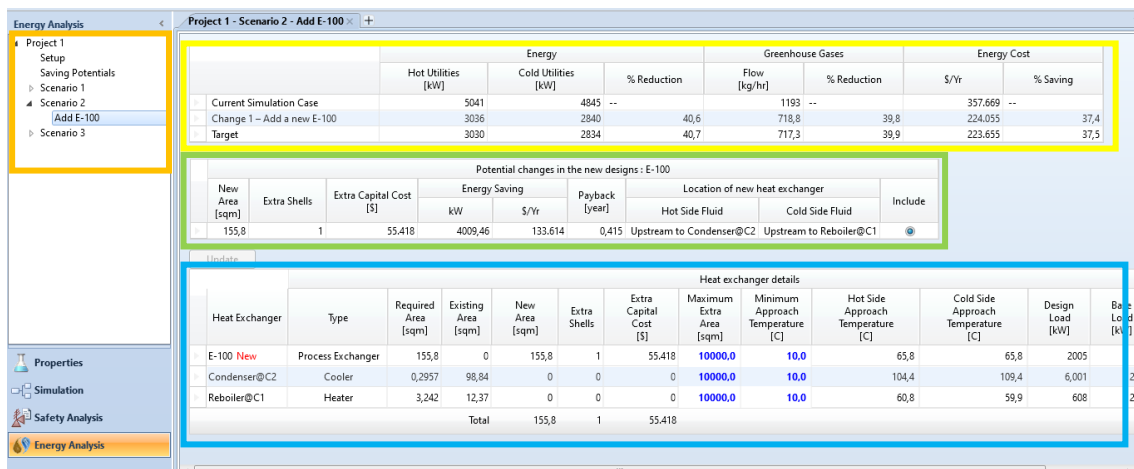

Figure 17 Energy Analyzer Environment

In the top section (Figure 18), there are some options to modify the scenario: add a new one or compare all the scenarios in economic and energy terms.
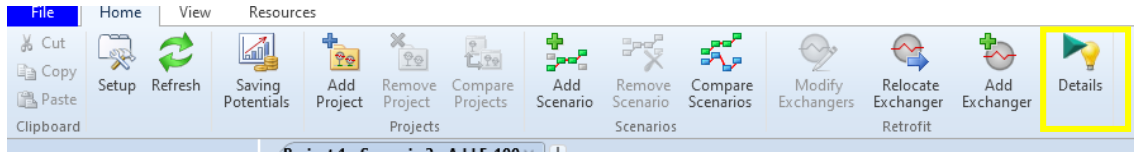

Figure 18 Top Section

By clicking in "Details" (yellow frame in Figure 18) the Energy Analyzer software opens a new window as the one presented in Figure 19. In the left side a folder menu can be seen (yellow frame), in which the different scenarios generated, including the base simulation case (SimulationBaseCase) and the solutions proposed can be explored. To see more details, it is possible to open them by double click.
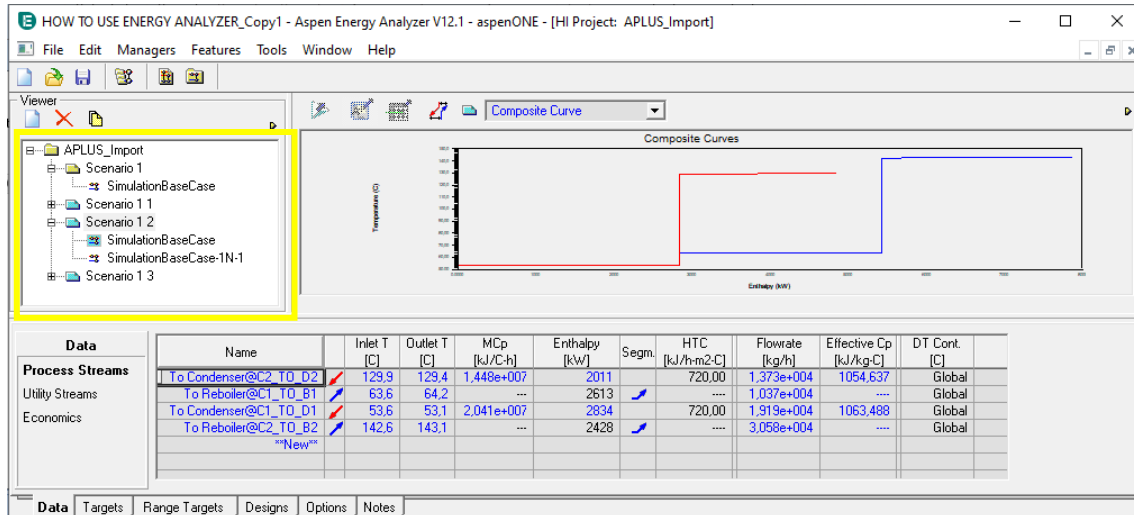

Figure 19 Energy Analyzer Window

In this case, to explain about what information can be found, the solution proposed in scenario 2 (SimulationBaseCase-1N-1) is opened (Figure 20). The graphic displayed (yellow frame) represents the process and utilities streams along with the heat exchangers. When right-clicking it, several options are displayed, including show/hide the utilities, show/hide the Pinch Lines, reorder the streams, or print the graphic. The solution can also be adjusted, adding, removing, or modifying heat exchangers. In the grey bottom part of the screen there are some tabs (blue frame) with information about economics and energy, for the base case, the target, and the solution. Also, some graphics of interest, as the grand composite curve can be obtained. If right-

clicking in the grey part (orange frame), it is possible to print the datasheet with the main information, that can be chosen by the user.

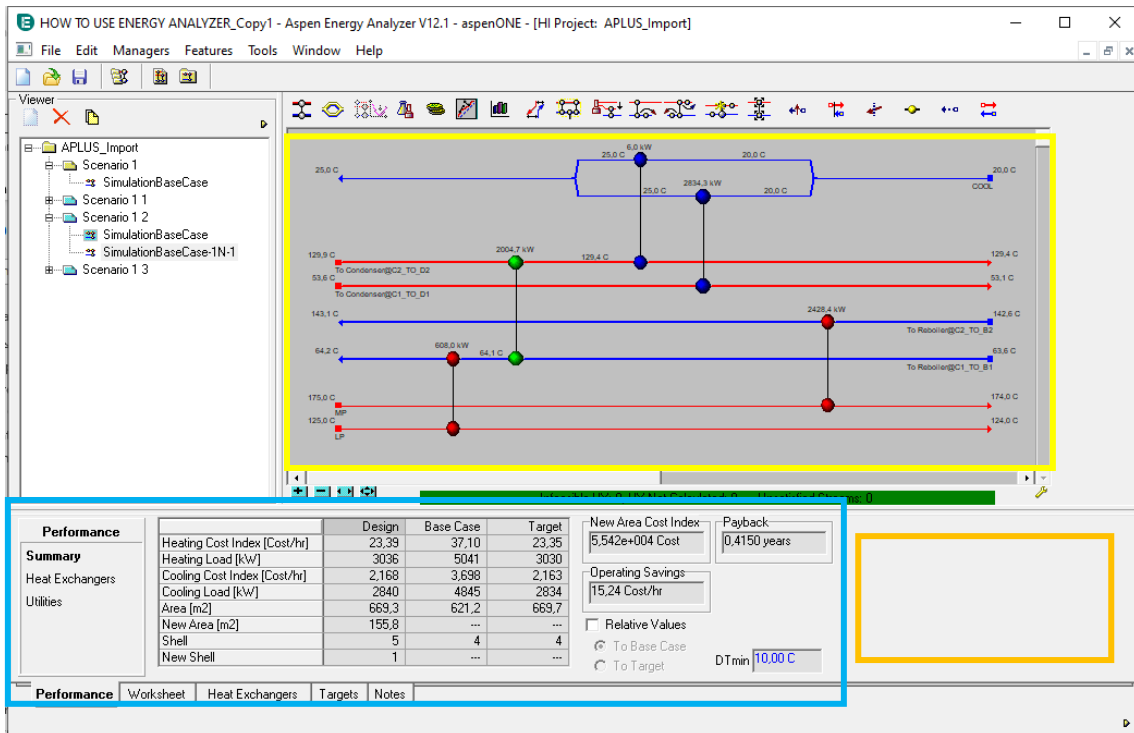*Figure 20 Solution Window*

The file can be saved and opened later by clicking the file using Windows explorer. Clicking in "Manager", the tab shown in Figure 21 allows to open the file, named "APLUS_Import" and review or edit it.
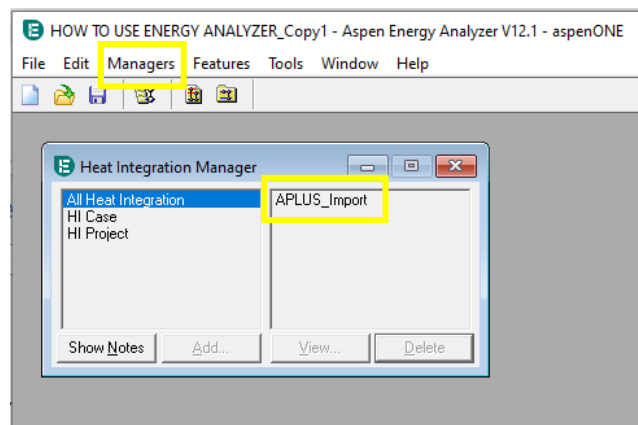

Figure 21 Open a File

Once the methodology and the tools used are described, the simulations performed and the results obtained are explained in the next chapters.

5. PRESSURE SWING DISTILLATION DESIGN

As said before, to design a PSD process, is important to know the equilibrium and azeotropic data of the feed mixture. In this work, the information of the feed mixture is shown in Table 9.

Table 9 Feed Mixture Conditions

Pressure (atm)		1
Vapor Fraction		0
Flow Rate (kmol/h)		100
Molar	MeOH	0.5
Fraction	MetAC	0.5

Once the feed mixture is fixed, the equilibrium and azeotropic data for 1 atm is obtained using Aspen Plus (UNIQUAC-RK model) and can be seen in Figure 22. As it can be seen from this graphic, the azeotropic composition for the mixture at atmospheric pressure is 33.5 %mol MeOH and 66.5 %mol MetAc.
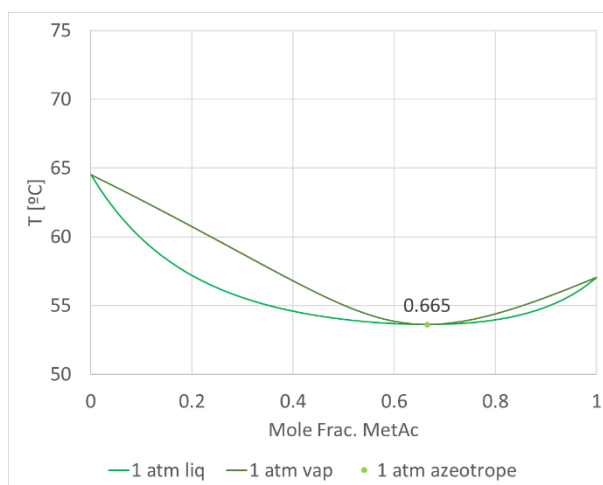
Figure 22 Txy Phase Diagram of the Mixture MeOH – MetAc for 1 atm

For the HPC, the pressure is fixed at 10 atm, as most of the consulted literature choose similar values, and after checking that the azeotropic composition variation is wide enough. In Figure 23 the Txy phase diagram for the mixture at 10 atm can be seen, and from these data, the azeotropic composition for this pressure is 55 %mol MeOH and 45%mol MetAc, which means a variation of around 33 % taking MetAc as base.
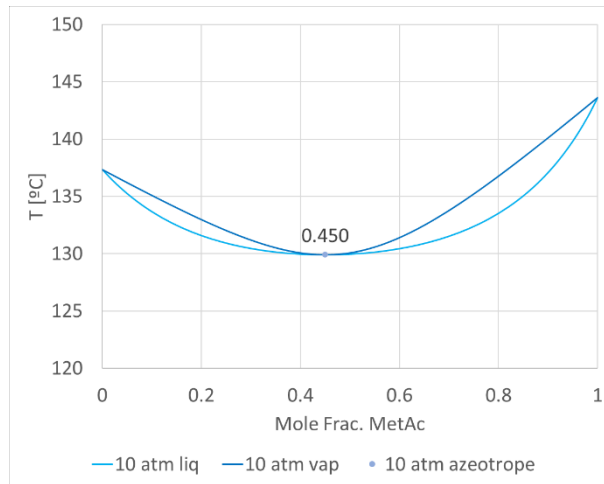
Figure 23 Txy Phase Diagram of the Mixture MeOH – MetAc for 10 atm

As seen in the literature, for this mixture the first column should operate at low pressure and the second at high pressure in order to use only two columns instead of three, thus this is the order selected in this work. According to this column sequence and considering that the mixture is a minimum boiling point azeotropic mixture, in the LPC MeOH is obtained in bottoms, and MetAc is obtained in bottoms of the HPC.
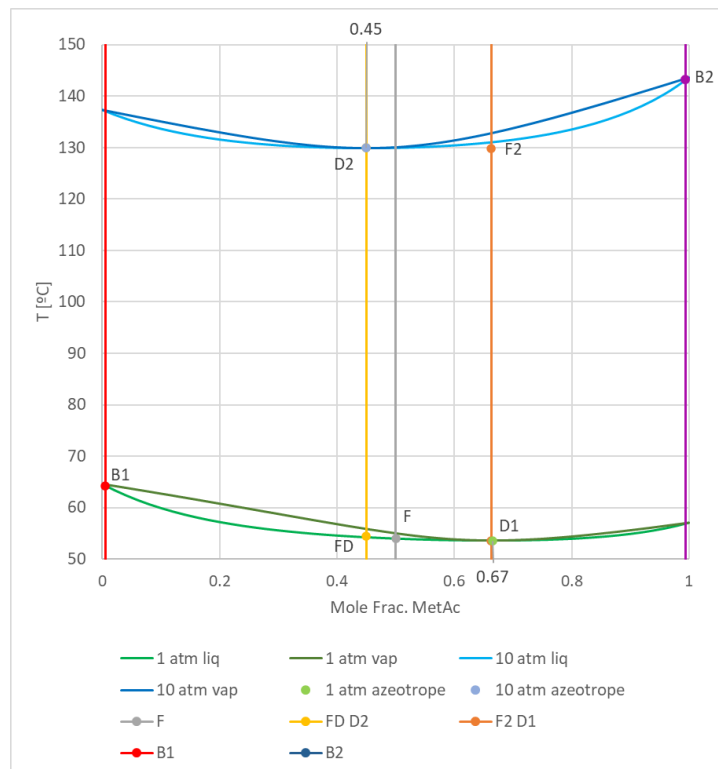

Figure 24 Txy Phase Diagram of the Mixture MeOH – MetAc for 1 and 10 atm

In Figure 24, the equilibrium data for both 1 and 10 atm are displayed. Over the graphic, it is represented the PSD process proposed. As explained before, by changing

the pressure, the azeotropic composition can be overpassed and both components can be obtained separately (B_1 and B_2).

To start with the simulation in Aspen Plus, the first step preformed is to calculate the bottom and distillate rates by global balances. For this step, separator equipment (column type) is used. This simulation solves mass balances, and its flowsheet can be seen in Figure 25.
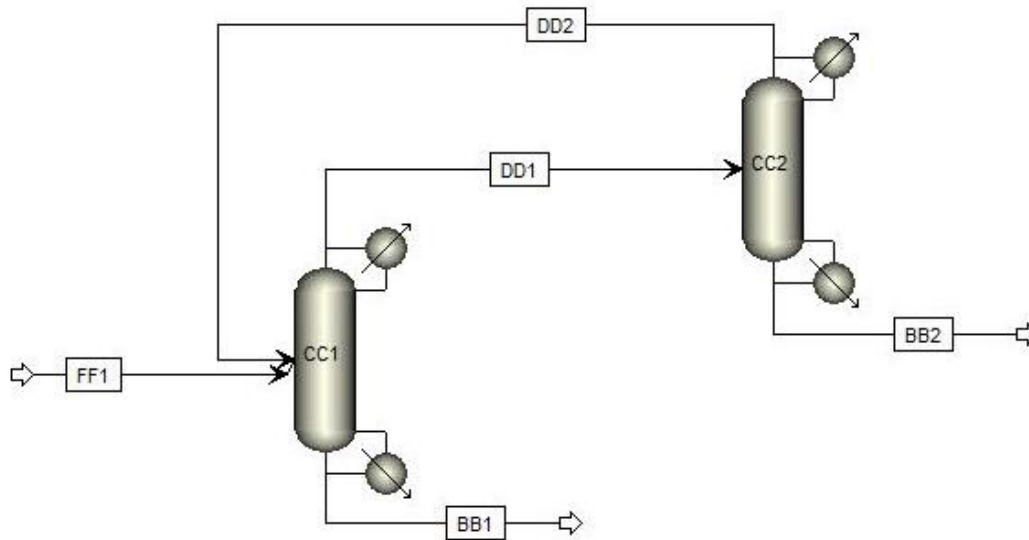
Figure 25 Global Molar Balance Flowsheet

The feed (FF1) information is specified in Table 9. The specification for the first and second separator (CC1 and CC2) are shown in Table 10. These specifications have been set in order to obtain pure MetAc, and the azeotropic composition at 1 atm in the distillate of the first column (DD1) and all the MeOH and the azeotropic composition for 10 atm in the distillate of the second column (DD2).

Table 10 Separators Specifications for Global Balance

		CC2	CC2
Outlet stream		DD1	DD2
Stream specification		Split fraction	Split fraction
Split fraction	Component	MetAc	MeOH
	Value	1	1
Mole fraction	Component	MeOH	MetAc
	Value	0.335	0.450

The purpose of this mass balance simulation is to obtain a close approximation of every stream flow of the process, as they are used as initialization data for the rigorous simulation. These values are summarised in Table 11.

Table 11 Global Molar Balance Stream Results

Streams	Mole Flow (kmol/h)	Mole Fraction	
		MetAc	MeOH
FF1	100.000	0.500	0.500
DD1	127.907	0.665	0.335
BB1	50.000	0.000	1.000
DD2	77.907	0.450	0.550
BB2	50.000	1.000	0.000

Once the global balances are solved, the rigorous simulations are carried out using the RadFrac block as column model.

In order to ensure a system convergence, the simulation has been done step by step, starting solely with the LPC, then adding the HPC and finally closing the recirculation stream. For the first step, both feed streams are introduced to the LPC: the feed mixture (F1) and the recirculated distillate from the second column (FD). Both are introduced at 1 atm and with a vapor fraction = 0. For F1, the mole flow rate and mole fraction are determined by Table 9, FD flow and composition is determined from Table 11 (DD2). Regarding the column, firstly the number of stages is set to 100 (a big number to ensure convergence), and the feed stages were selected at 50 (F1) and 55 (FD). The bottom rate is 50 kmol/h as calculated in the global balance, and the reflux ratio is 50 as initial value. Using the Design Specification tool from Aspen Plus, the bottom purity of MeOH is fixed at 0.9945 varying the reflux ratio to obtain the minimum reflux ratio. As the optimal reflux ratio is known as 1.3 the minimum reflux ratio (D. Seider et al., 2016), the number of stages and feed stages are varied to reach the minimum reflux ratio using the Sensitivity Analysis Tool.

For the second column, the distillate of the LPC (D1) is introduced as a feed (F2) passing through a pump in order to increase the pressure from 1 atm to 10 atm. In this column, the distillate rate is fixed at 77.91 kmol/h (DD2 obtained in the mass balance) and the same procedure is performed to obtain the number of stages and feed stage that accomplish the optimal reflux ratio fixing the MetAc purity of the bottom also at 0.9945. When both columns are optimised, the distillate of the HPC is recirculated to the LPC. The data for both columns can be seen in Table 12.

Table 12 Columns Results

Variables	LPC (C1)	HPC (C2)
P (atm)	1	10
N_T	29	44
N_F / N_{FD}	22 / 23	36
RR	1.50	2.46
Q_{COND} (kW)	2,834.33	2,010.73
Q_{REB} (kW)	2,612.75	2,428.39

The flowsheet of the process is represented in Figure 26.
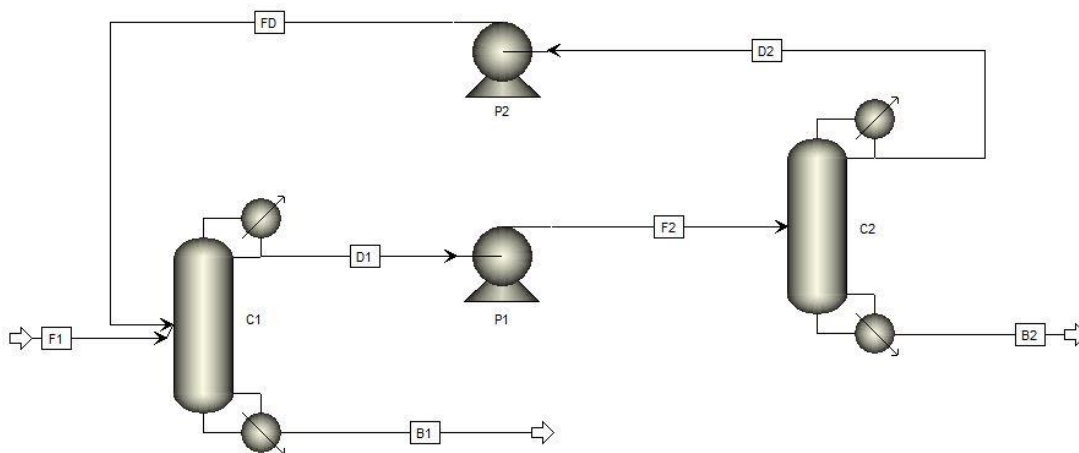
Figure 26 PSD Flowsheet

And in Table 13 the stream results are summarised.

Table 13 PSD Stream Results

	F1	FD	B1	D1	F2	B2	D2
From	-	P2	C1	C1	P1	C2	C2
To	C1	C1	-	P1	C2	-	P2
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature (ºC)	53.99	129.82	64.20	53.62	54.53	143.14	129.91
Pressure (atm)	1	1	1	1	10	10	10
Molar Vapor Fraction	0	0	0	0	0	0	0
Molar Liquid Fraction	1	1	1	1	1	1	1
Mole Flow (kmol/h)	100.00	77.91	50.00	127.91	127.91	50.00	77.91
MeOH Mole Fraction	0.5000	0.5496	0.9945	0.3369	0.3369	0.0055	0.5496
MetAc Mole Fraction	0.5000	0.4504	0.0055	0.6631	0.6631	0.9945	0.4504
Mass Flow (kg/h)	5,306.08	3,971.40	1,613.67	7,663.81	7,663.81	3,692.41	3,971.40

In order to obtain economic results of operating costs, utilities are introduced into Aspen Plus to use them in the reboilers and condensers. The utilities available are CW, LPS, MPS and HPS, and their temperatures are in Table 14.

Table 14 Utilities Temperatures

Name	Type		Temperature (ºC)	
			Inlet	Outlet
CW	WATER	Cooling Utility	20	25
HPS	STEAM	Heating Utility	250	249
MPS	STEAM	Heating Utility	175	174
LPS	STEAM	Heating Utility	125	124

Taking into account the temperatures of the streams cooled and heated in the condensers and reboilers where the utilities are used, CW is used to condensate the distillates of both columns (2,834.33 kW and 2,010.73 kW), LPS is used to provide heat to the LPC reboiler (2,612.75 kW) and MPS is used in the HPC reboiler (2,428.39 kW). The capital cost (including the equipment and installed cost of the columns with condensers and reboilers) calculated for this process is 2,673,500 USD and the energy cost (including only the utilities) 357,669 USD/year. The Total Annual Cost (TAC) obtained, considering a Payback Period (PP) of 5 years is 892,369 USD/year.

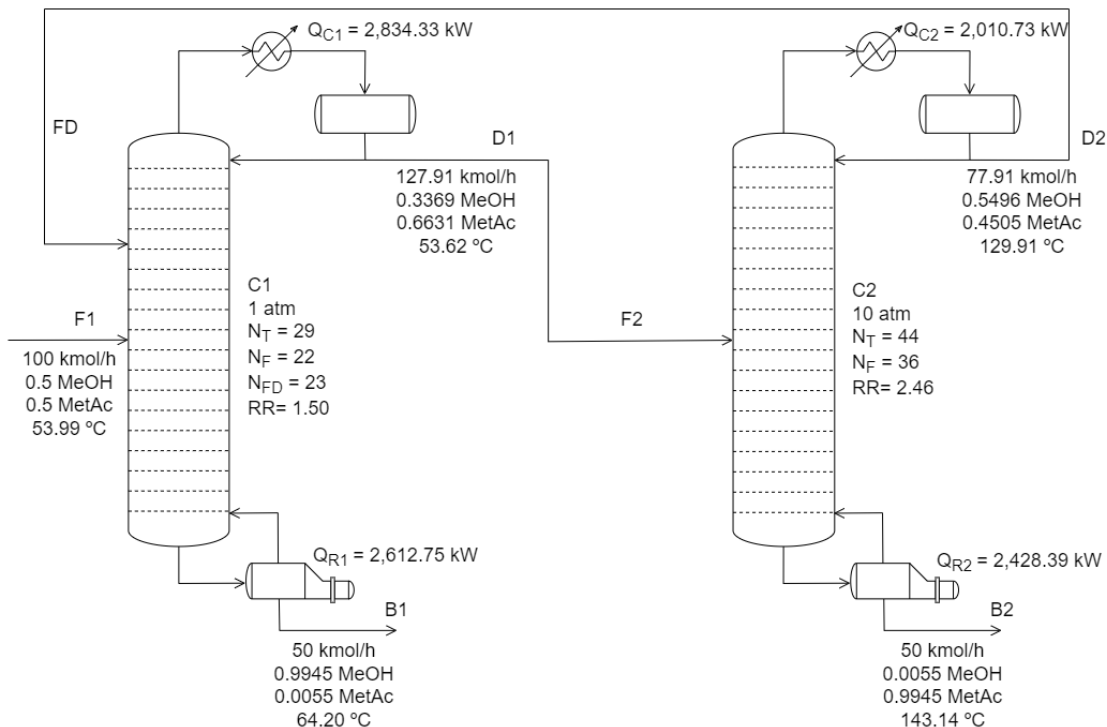In Figure 27, a schematic flowsheet is represented with some of the main data.

Figure 27 PSD Process Results Flow Diagram

6. HEAT INTEGRATED PRESSURE SWING DISTILLATION DESIGN

Once the PSD process for the feed mixture selected is done, heat integration is designed with the purpose of reducing energy requirements and reducing operating costs. Both types, partial and full heat integration are designed and simulated in this project.

6.1. Partial Heat Integration

As explained before, partial heat integration consists of reducing the energy requirements without modifying anything from the original PSD process. This method is performed by the Temperature-Interval method and using Aspen Energy Analyzer.

6.1.1. Temperature-Interval Method

The first step to design heat exchanger network (HEN) is determine the minimum energy requirements (MER) target, by the Temperature-Interval method, with a ΔT_{min} of 15 ºC as it is generally used in processes with this range of temperatures. In Table 15 the streams involved in the HEN with the necessary data obtained from Aspen are displayed.

Table 15 Stream Data for Partial Heat Integration

			Adjusted Tempertaures				
STREAM	T_i (ºC)	T_f (ºC)	T_i (ºC)	T_f (ºC)	ΔT (ºC)	ΔH (kW)	C (kW/ºC)
H_1	54.62	53.62	54.62	53.62	1	2,834.33	2,834.33
H_2	130.91	129.91	130.91	129.91	1	2,010.73	2,010.73
C_1	63.20	64.20	78.20	79.20	1	2,612.75	2,612.75
C_2	142.14	143.14	157.14	158.14	1	2,428.39	2,428.39

H_1 corresponds to the stream cooled in the LPC condenser, H_2 to the stream cooled in the HPC condenser, and C_1 and C_2 are the streams heated in the LPC and HPC reboilers respectively. In Figure 27, which represents the PSD process, H_1 is the stream condensed in Q_{C1}, H_2 the one condensed in Q_{C2}, and C_1 and C_2 the streams vaporised in Q_{R1} and Q_{R2}.

In Table 16, the interval method is developed for the streams mentioned above. As it can be seen, there are two pinch temperatures, $T_{pinch\ 1} = 78.20$ ºC and

$T_{pinch\ 2}$ = 54.62 ºC. From this table, it is also possible to know the minimum usage of heating, which is 3,030.42 kW and the minimum usage of cooling, which is 2,834.33 kW.

Table 16 Temperature-Interval Method for Partial Heat Integration

Interval	T_i (ºC)	T_f (ºC)	H_1	H_2	C_1	C_2	Interval C	ΔH (kW)	Q_{Hmin} = 0	Q_{Hmin} = 3,030.42	
1	158.14	157.14				X	-2,428.39	-2,428.39	-2,428.39	602.03	
2	157.14	130.91					0.00	0.00	-2,428.39	602.03	
3	130.91	129.91		X			2,010.73	2,010.73	-417.66	2,612.75	
4	129.91	79.20					0.00	0.00	-417.66	2,612.75	
5	79.20	78.20			X		-2,612.75	-2,612.75	-3,030.42	0.00	Pinch 1
6	78.20	54.62					0.00	0.00	-3,030.42	0.00	Pinch 2
7	54.62	53.62	X				2,834.33	2,834.33	-196.09	2,834.33	= Q_{Cmin}
	53.62										

Once the MER targeting is done, the streams are represented in Figure 28. As it can be seen H_1 cannot exchange heat with any other stream.

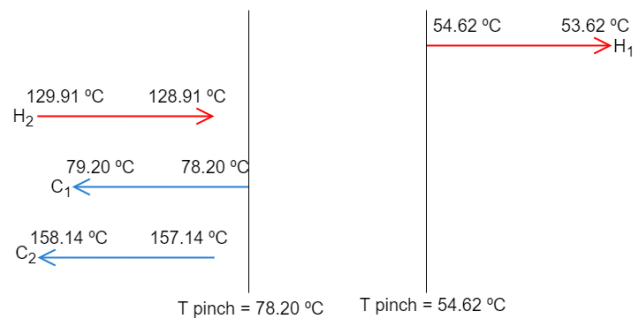*Figure 28 Pinch Analysis*

On the heating services area there are three streams (H_2, C_1 and C_2), and there is only one possible heat exchange, which is between H_2 and C_1 owing to considering the temperatures of the streams, the exchange between H_2 and C_2 is not possible (the final temperature of the hot stream is lower than the initial temperature of the cold stream). All the heat removed from H_2 (2,010.73 kW) is given to C_1, and the residual heat required (602.03 kW) to heat C_1 from 78.97 ºC to 79.20 ºC, is given by utilities. In Figure 29 the HEN proposed is shown. With this HEN, the MER target is reached, getting a reduction of 39.89 % for heating services and 41.50 % for cooling services.
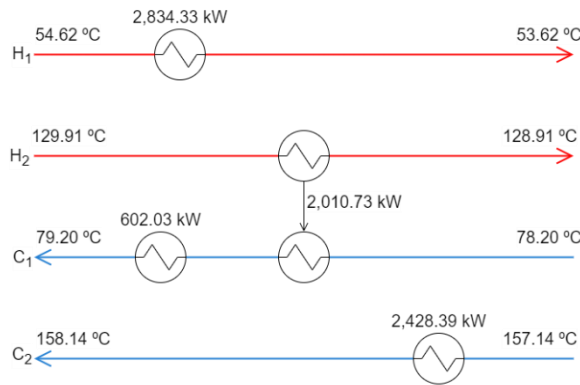
Figure 29 Partial HIPSD HEN

6.1.2. Aspen Energy Analyzer

Regarding the simulation, from the PSD process represented in Figure 26, using the Energy Analyzer environment and introducing the $\Delta T_{min} = 15$ ºC, the saving energy results are obtained. Energy Analyzer estimates that 40.68 % of the utilities (39.89 % of heating utilities and 41.50 % of cooling utilities) can be saved. In Figure 30, the actual and target values of utilities for this process are represented.
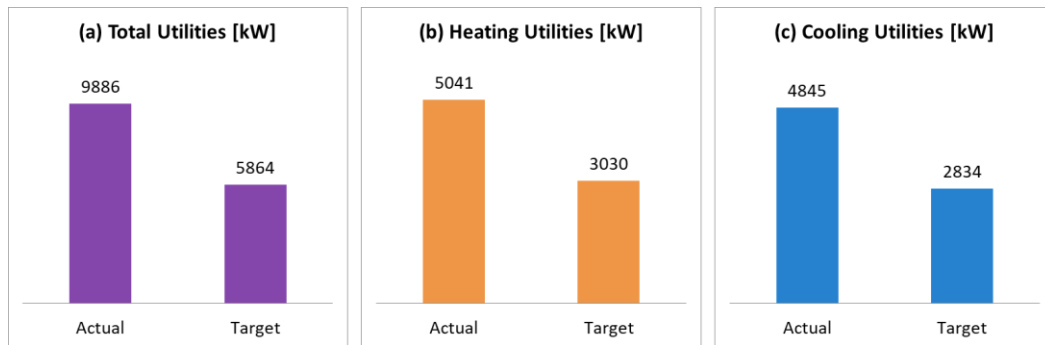
Figure 30 Energy Savings (a) Total Utilities (b) Heating Utilities (c) Cooling Utilities

After checking the option of changing heat exchangers areas, adding a heat exchanger and change the position of some heat exchanger, Energy Analyzer proposes a design change to reach the target values of utilities. This solution involves adding a heat exchanger between the condenser of the HPC and the reboiler of the LPC.

From Aspen Energy Analyzer, also the following graphics are obtained. In Figure 31 the process streams are represented with Pinch temperatures. On each stream the heat exchanged using utilities are represented by a red or blue point, depending on if it is a heating or cooling utility respectively. In Figure 32, the HEN for the solution proposed by Aspen Energy Analyzer is represented. The streams represented from top

to bottom are CW, H_1, H_2, C_1, C_2, LP and MP. As it can be seen, the utilities target is achieved, and all the heat removed from the HPC condenser is given to the LPC reboiler (2,010.7 kW) (white point) and the remaining heat required by this reboiler (602.2 kW) is provided by LPS.
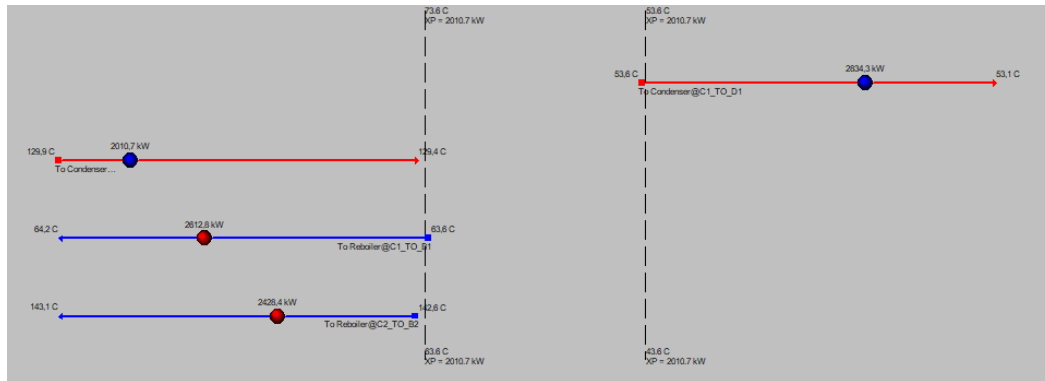
Figure 31 Process Streams - Aspen Energy Analyzer
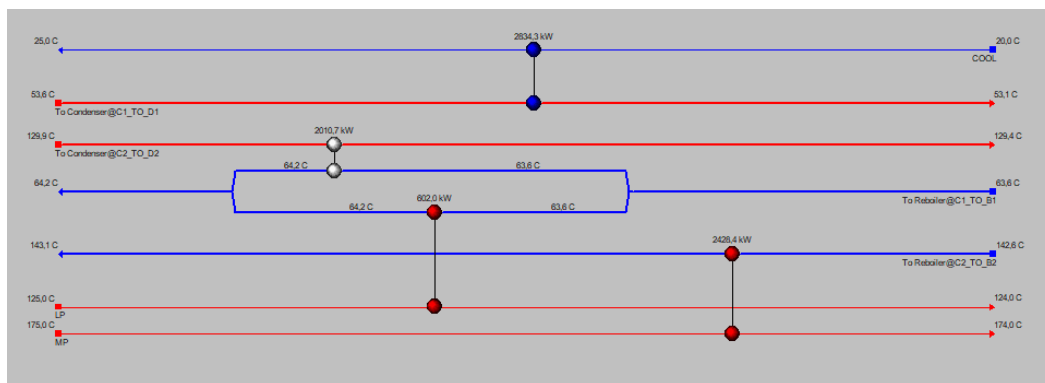
Figure 32 HEN - Aspen Energy Analyzer

The extra capital costs due to the new exchanger is 55,528 USD with a PP of about a year and a half so the resulting capital cost is 2,729,028 USD for partial HIPSD, the energy costs are reduced up to 223,655 USD/year. The TAC obtained for this process is 769,461 USD/year (with a PP of 5 years).

6.2. Full Heat Integration

To develop the full HIPSD, the main requirement is that the reboiler heat duty of the LPC and the condenser heat duty of the HPC are equal to allow to exchange all the heat among them. To achieve this requisite, the PSD process developed above (5.PRESSURE SWING DISTILLATION DESIGN) is modified. In the original PSD process, the bottom purities of both columns are obtained by varying the reflux ratios. In this case, the LPC reflux ratio is adjusted to equalise the heat duties of the LPC reboiler and

HPC condenser, and the bottom purity of the LPC is achieved by varying the bottom rate and in the HPC by changing the distillate rate. These manipulations are automatised by designs specifications. Also, the influence of the reflux ratio of the LPC on the reboiler heat duty of the HPC is analysed using the Sensitivity Analysis Tool, in order to fix this reflux ratio at the value that minimises the HPC reboiler heat duty, as seen in the literature. In Figure 33, a representation of the PSD process with the results for the columns is shown.
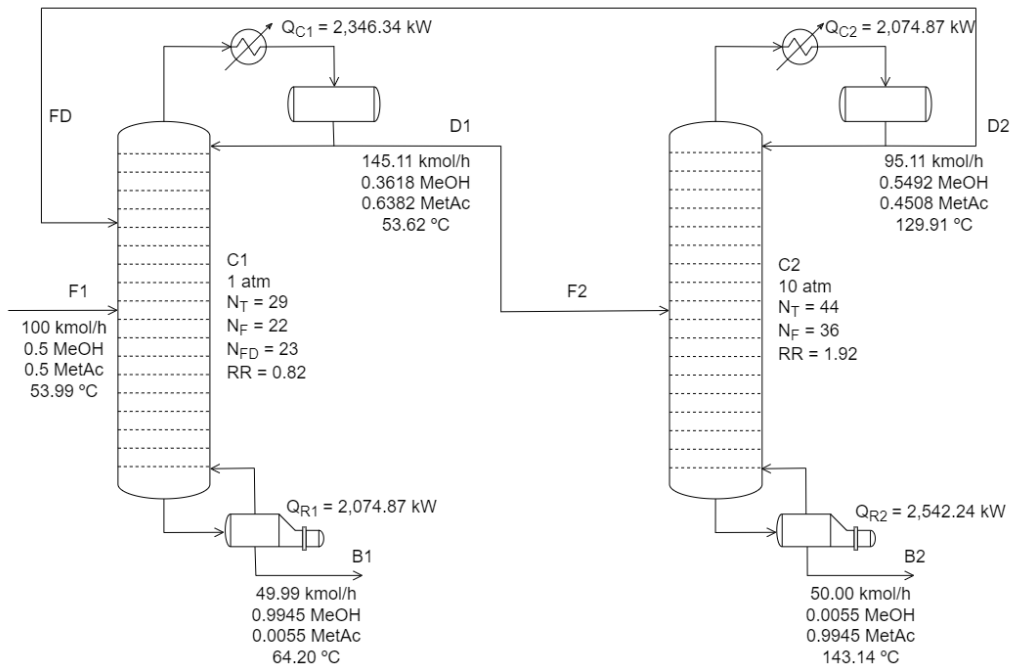
Figure 33 Modified PSD for Full HIPSD Process Flow Diagram

And in Table 17, the new stream results are summarised.

Table 17 Modified PSD Stream Results

	F1	FD	B1	D1	F2	B2	D2
From	-	P2	C1	C1	P1	C2	C2
To	C1	C1	-	P1	C2	-	P2
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Temperature (ºC)	53.99	129.82	64.20	53.62	54.53	143.14	129.91
Pressure (atm)	1	1	1	1	10	10	10
Molar Vapor Fraction	0	0	0	0	0	0	0
Molar Liquid Fraction	1	1	1	1	1	1	1
Mole Flow (kmol/h)	100.00	95.11	49.99	145.11	145.11	50.00	95.11
MeOH Mole Fraction	0.5000	0.5492	0.9945	0.3618	0.3618	0.0055	0.5492
MetAc Mole Fraction	0.5000	0.4508	0.0055	0.6382	0.6382	0.9945	0.4508
Mass Flow (kg/h)	5,306.08	4,849.97	1,613.51	8,542.50	8,542.50	3,692.53	4,849.97

In Table 18, the main energy and economic data obtained for this process is shown.

Table 18 Economic Data for Modified PSD

Equipment Cost (USD)	768,400.00
Total Installed Cost (USD)	1,835,300.00
Capital Cost (USD)	2,603,700.00
Heating Utilities (USD/year)	300,897.86
Cooling Utilities (USD/year)	29,578.24
Total Utilities Cost (USD/Year)	330,476.10
PP (years)	5
TAC (USD/years)	851,216.10

6.2.1. Temperature-Interval Method

The same procedure followed in section 6.1.1, Temperature-Interval Method is developed for the modified PSD, also with an ΔT_{min} of 15 ºC. In Table 19 the streams involved in the heat exchange process are summarised and in Table 20, the Temperature-Interval method is developed.

Table 19 Stream Data for Full Heat Integration

			Adjusted Tempertaures				
STREAM	Ti (ºC)	Tf (ºC)	Ti (ºC)	Tf (ºC)	ΔT (ºC)	ΔH (kW)	Fcp (kW/ºC)
H_1	54.62	53.62	54.62	53.62	1	2,346.33	2,346.33
H_2	130.91	129.91	130.91	129.91	1	2,074.80	2,074.80
C_1	63.20	64.20	78.20	79.20	1	2,074.80	2,074.80
C_2	142.14	143.14	157.14	158.14	1	2,542.16	2,542.16

The heating utilities target in this case is 2,542.16 kW and for the cooling utilities is 2,346.33 kW.

Table 20 Temperature-Interval Method for Full Heat Integration

Interval	T_i (ºC)	T_f (ºC)	H_1	H_2	C_1	C_2	Interval C	ΔH (kW)	Q_{Hmin} = 0	Q_{Hmin} = 2,542.16	
1	158.14	157.14				X	-2,542.16	-2,542.16	-2,542.16	0.00	Pinch 1
2	157.14	130.91					0.00	0.00	-2,542.16	0.00	Pinch 2
3	130.91	129.91		X			2,074.80	2,074.80	-467.37	2,074.80	
4	129.91	79.20					0.00	0.00	-467.37	2,074.80	
5	79.20	78.20			X		-2,074.80	-2,074.80	-2,542.16	0.00	Pinch 3
6	78.20	54.62					0.00	0.00	-2,542.16	0.00	Pinch 4
7	54.62	53.62	X				2,346.33	2,346.33	-195.84	2,346.33	= Q_{Cmin}
	53.62										

As seen in Figure 34, the only heat exchange feasible, taking into account temperatures and at which side of the pinch the streams are, is between C_1 and H_2. In this case, as the heat duty of both streams are the same (2,074.80 kW), there is no

need of utilities for none of them. With this heat exchange, the utilities target is achieved.
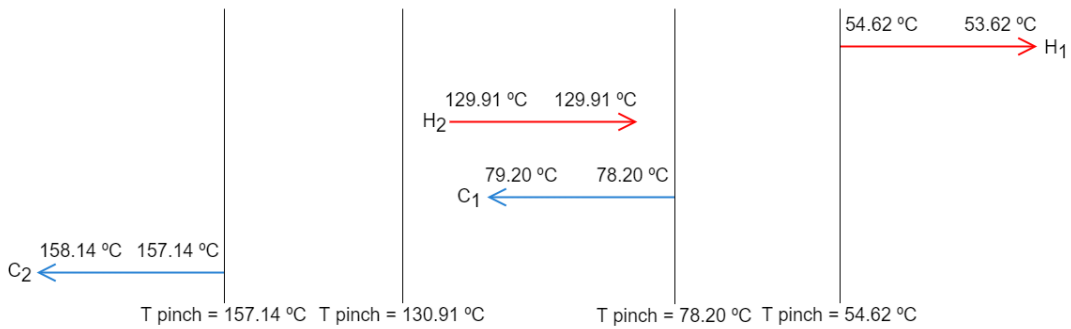
Figure 34 Pinch Analysis

In Figure 35 the HEN proposed is represented.
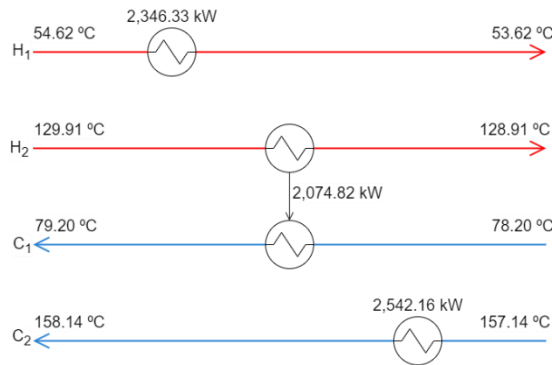
Figure 35 Full HIPSD HEN

6.2.2. Aspen Energy Analyzer

Aspen Energy Analyzer is used as well in this part of the project on the basis of the modified PSD process. As seen in Figure 36, the utilities requirements of the modified PSD can be reduced about a 46 %.
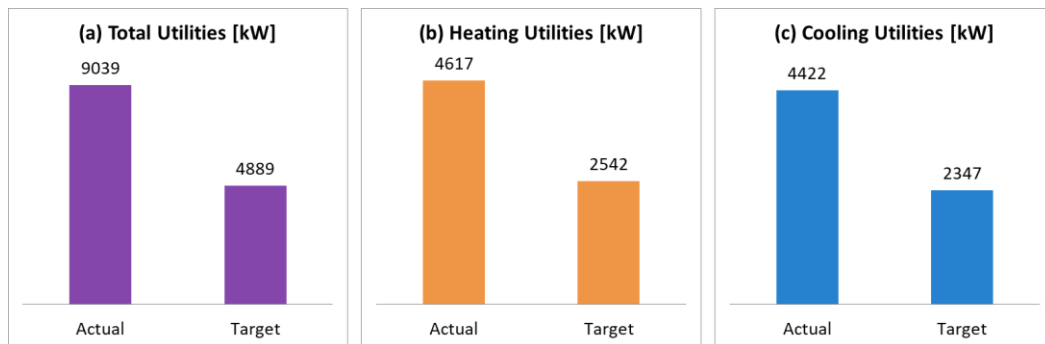
Figure 36 Energy Savings (a) Total Utilities (b) Heating Utilities (c) Cooling Utilities

Also in this process, the solution proposed by Aspen Energy Analyzer involves adding a heat exchanger between the HPC condenser and LPC reboiler.

The following graphics are obtained from Aspen Energy Analyzer. In Figure 37 the process streams are represented with the pinch temperatures as well. The red and blue points represent the heat exchanges with heating and cooling utilities respectively.
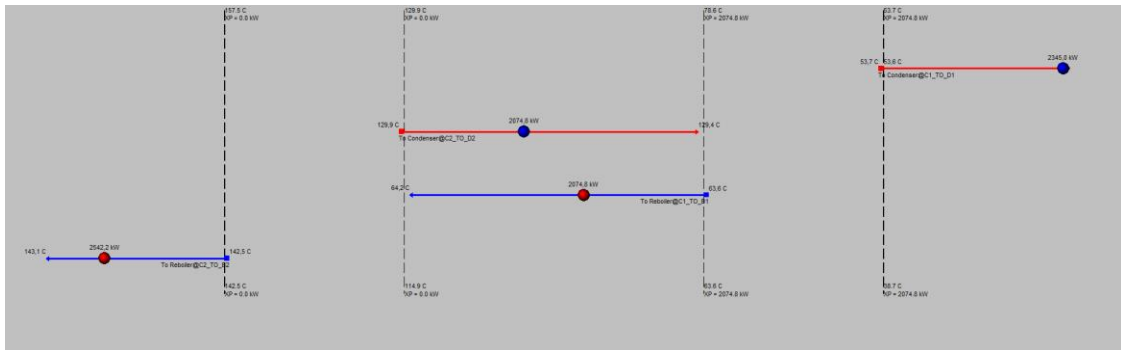
Figure 37 Process Streams - Aspen Energy Analyzer

After adding the exchanger proposed by Aspen Energy Analyzer (green points), the HEN obtained is represented in Figure 38. The streams represented from top to down are CW, H_1, H_2, C_1, C_2, LP and MP.
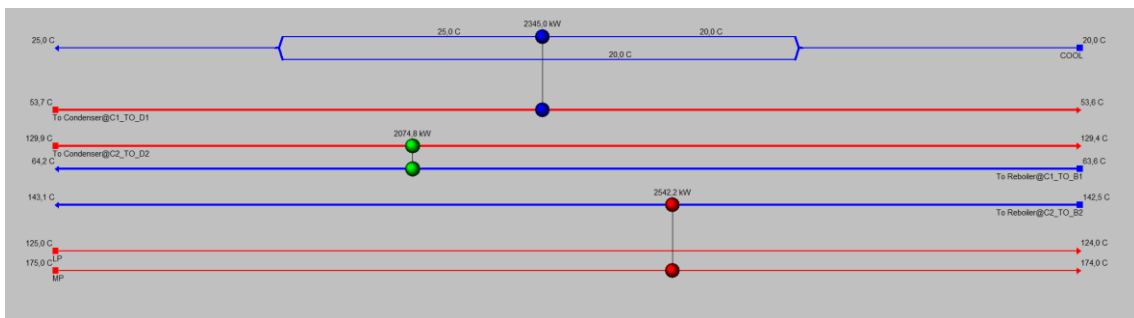
Figure 38 HEN - Aspen Energy Analyzer

The addition of this exchange represents an extra capital cost of 56,763 USD which means a total capital of 2,660,463 USD, and the energy cost of his process is 192,182 USD/year. This results in a TAC of 724,275 USD/year (with a PP of 5 years).

7. RESULTS DISCUSSION AND COMPARISON

From the literature research, it has been found that in all the PSD processes studied, the partial and full HIPSD are feasible, due to in all the cases, the temperatures differences and heat duties are suitable. In Table 21, the different savings obtained in each paper described in section 2.6 (Related Literature) are summarised. From this data, it can be seen that the two papers found about the studied mixture (Zhang et al., (2016) and K. Wang et al., (2019)) achieve similar saving for both HIPSD, and in both cases, the optimum results are obtained for the full HIPS. If taking into account all the results, including other mixtures besides the studied mixture, it can be seen that in all the cases the best results for capital costs and TAC are obtained with the full heat integration. Also, the energy costs are more reduced with the full HIPSD in all the papers except in paper 4 (Zhu et al., 2015), in which the partial HIPSD involves more energy costs savings than the full HIPSD. It is possible since in this paper, the full HIPSD is designed to minimise the TAC and not the energy costs.

Table 21 Literature Savings Results

	Paper	HIPSD	Capital Costs Reduction	Energy Costs Reduction	TAC Reduction
Studied Mixture	Paper 1 (Zhang et al., 2016)	Partial	13.87%	33.50%	25.40%
		Full	17.45%	35.06%	27.68%
	Paper 2 (K. Wang et al., 2019)	Partial	13.56%	35.31%	27.02%
		Full	15.63%	39.17%	30.20%
	Paper 3 (Chen et al., 2018)	Partial	-	-	-
		Full	-	-	-
Other Mixtures	Paper 4 (Zhu et al., 2015)	Partial	3.29%	21.15%	12.05%
		Full	7.65%	19.83%	13.62%
	Paper 5 (Yu et al., 2012)	Partial	-	-	-
		Full	-	-	30.30%
	Paper 6 (Li et al., 2019)	Partial	5.17%	25.38%	18.84%
		Full	-	-	-

Regarding the simulation, for the feed mixture (Table 9), the product and distillates stream results obtained in each process simulated are shown in Table 22. The modifications done to the PSD process to design the full HIPSD involve the modification of the LPC bottom flow rate and the HPC distillate flow rate. In the case of the bottoms flow rates, the values obtained in the full HIPSD do not differ a lot form

the values obtained in the PSD process as the bottom purities are fixed. However, in the case of the distillate flow rates, the values are considerably different and this variation involves a variation on the distillate compositions. These compositions are more different from the azeotropic point, but since the distillates are not product (the distillate of the LPC is the fed of the HPC, and the HPC distillate is recirculated into the LPC), the compositions do no need to be fixed values.

Table 22 Bottom and Distillate Streams

	PSD		Partial HIPSD		Full HIPSD	
	LPC	HPC	LPC	HPC	LPC	HPC
Bottom rate (kmol/h)	50.000	50.000	50.000	50.000	49.995	50.002
MeOH mole frac	0.9945	0.0055	0.9945	0.0055	0.9945	0.0055
MetAc mole frac	0.0055	0.9945	0.0055	0.9945	0.0055	0.9945
Distillate rate (kmol/h)	127.910	77.910	127.910	77.910	145.109	95.108
MeOH mole frac	0.3369	0.5496	0.3369	0.5496	0.3618	0.5492
MetAc mole frac	0.6631	0.4504	0.6631	0.4504	0.6382	0.4508

The results obtained for PSD, partial and full HIPSD are summarised in Table 23. As explained before, for the partial HIPSD any variable is manipulated from the PSD process. For the full HIPSD, the reflux ratios of both columns, the LPC bottom rate and HPC distillate rate are manipulated in order to equalise the heat duties and minimise the heating utilities needed.

One point to be commented is that the reflux ratios of both columns in full HIPSD is lower than the minimum reflux ratio found when optimising the PSD (5.PRESSURE SWING DISTILLATION DESIGN). It is possible due to in PSD the bottom flow rate of the LPC and the distillate of the HPC are fixed to reach the azeotropic composition in the distillates. In the full HIPSD, these flow rates are not fixed, but they are adjusted to reach the product purities, and the reflux ratios are manipulated to achieve the heat duty requirements to design the full heat integration (as shown in Table 22). In this case, the distillate compositions are more separated than the azeotropic composition, and as the bottom and distillate rates are not fixed, the reflux ratios needed are lower.

Table 23 Simulation Results

	PSD		Partial HIPSD		Full HIPSD	
	LPC	HPC	LPC	HPC	LPC	HPC
Pressure (atm)	1	10	1	10	1	10
N_T	29	44	29	44	29	44
N_F	22	36	22	36	22	36
N_{FD}	23	-	23	-	23	-
RR	1.50	2.46	1.50	2.46	0.82	1.92
Q_R (kW)	2,613	2,428	602	2,428	-	2,542
Q_C (kW)	2,834	2,011	2,834	-	2,346	-
$Q_{exch.}$ (kW)	-		2011		2075	
T_D (ºC)	53.62	129.91	53.62	129.91	53.63	129.91
T_B (ºC)	64.20	143.14	64.20	143.14	64.20	143.14
PP (years)	5		5		5	
Capital Cost (1,000 USD/year)	534.700		545.806		532.093	
Capital Cost Reduction	-		-2.08%		0.49%	
Energy Cost (1,000 USD/year)	357.669		223.655		192.182	
Energy Cost Reduction	-		37.47%		46.27%	
TAC (1,000 USD/year)	892.369		769.461		724.275	
TAC Reduction	-		13.77%		18.84%	

With regards to the economic results, the bests results are also obtained for the full HIPSD process, as expected taking into account the literature results (Table 21). In this case, however, the capital costs for the partial HIPSD are higher than the PSD, and for full HIPSD are lower, but the savings are much lower than the ones obtained in the literature. That could be because, in this work for heat integrated processes, the capital cost has been calculated by adding the capital cost that the new exchanger (to heat integration between both columns) implies, as this is the information that Energy Analyzer gives. For the full HIPSD, the costs have been calculated in the same way, but in this case, the capital cost is added to a modified base PSD, which has lower capital costs than original PSD, and that is why, even the capital costs have been increased, they are lower than for the original PSD process. In the literature, instead of adding the cost of the new heat exchanger, they eliminate the cost that the reboiler and / or the condenser removed represent and the capital costs is calculated as only a heat exchanger acts as the LPC reboiler and the HPC condenser at the same time.

The energy costs savings for partial HIPSD are at the same range that the ones obtained in the literature. For the full HIPSD, energy savings obtained are higher, and that could be because, generally, in the literature, the PSD process is designed taking account TAC, optimising the process to reach the minimum TAC, whereas in this project, the PSD has been designed in the basis of the heuristic of the optimum reflux ratio.

Talking about the TAC results, the percentages of savings obtained in this work are lower than the ones obtained in the literature for this mixture (18.84 % with full HIPSD in the simulations in front of 27.68 % obtained by Zhang et al., (2016)). But considering the results obtained for the capital costs savings (in the simulations performed presents a very low percentage and in the partial HIPSD even they are higher than PSD) these results for TAC reduction were expected.

In Table 24, a comparison of the economic results obtained in this project and in paper 1 (Zhang et al., 2016) is shown, since the feed mixture and conditions are the same. In this table, the points commented above can be observed, like for example, the difference in the capital costs savings and that the energy costs saving in the simulations done are a little higher than the savings found in the literature.

Table 24 Comparison Simulation - Paper 1

	Simulation			Paper 1 (Zhang et al., 2016)		
	PSD	Partial HIPSD	Full HIPSD	PSD	Partial HIPSD	Full HIPSD
Capital Cost (1,000 USD/year)	535	546	532	728	627	601
Capital Cost Reduction	-	-2.08%	0.49%	-	13.87%	17.45%
Energy Cost (1,000 USD/year)	358	224	192	1,024	681	665
Energy Cost Reduction	-	37.47%	46.27%	-	33.50%	35.06%
TAC (1,000 USD/year)	892.369	769.461	724.275	1,752	1,307	1,267
TAC Reduction	-	13.77%	18.84%	-	25.40%	27.68%

However, in this project the heat integration has been performed mainly to study the energy savings as the high energy consumption is one of the most inconvenient points of the PSD, and considering these results, it has been found that effectively, energy consumption is reduced.

8. CONCLUSIONS

From the development of this work the following conclusions can be drawn:

The fact that in the PSD process there is more than one column, and at least one of them operates at high pressure, widely increments the energy requirements. This point can be partially solved by implanting partial or full heat integration, and in general, the bests results are obtained by using full HIPSD.

For the binary azeotropic mixture studied in this work (50 %mol MeOH – 50 %mol MetAc), the PSD consists of two columns, one operating at ambient pressure (LPC), and the other working at 10 atm (HPC). The sequence of distillation is determined by the feed composition and the type of azeotrope. In this case, taking into account that the mixture presents a minimum boiling point azeotrope (represented in Figure 24), the first column should be the LPC.

Heat integration is not a simple issue to design, since depending on the streams of the process to be studied, there may be infinite possibilities when crossing them. The studied process is considered relatively simple since it presents a reduced number of streams, and as it has been seen, the majority of the papers about HIPSD processes only study the energy exchange between the LPC reboiler and the HPC condenser, considering that the reboilers represent most of the energy consumption of the process. Therefore, although the other exchanges (such as heating the feed stream to its bubble point or cooling the products for their later storage) are also feasible, they are practically negligible compared to the consumption of the reboilers, and that is why these cases are not analysed.

For HIPSD, the heat duty removed from the HPC condenser is used in the LPC reboiler. When the heat duties are not equal, an auxiliary reboiler is needed.

For the studied mixture and the simulations done in this project, the bests results are obtained for the full HIPSD, obtaining a 0.49 % reduction in capital costs, 46.27 %, in energy costs and 18.84 % in the TAC in front of a -2.08 %, 37.47 % and 13.77 % respectively for the partial HIPSD. The results obtained for the capital costs cannot be compared to the ones found in the literature owing to the way of how they have been calculated is not the same. Regarding the energy costs, the savings achieved are 37.5 %

and 46.3 % for partial and full HIPSD respectively. These results are slightly higher than the ones obtained in the literature related to this mixture (33 % and 35 % obtained by Zhang et al., (2016), whose paper is about the same feed mixture).

The procedures of heat integration have been developed by the Temperature-Interval method and using Aspen Energy Analyzer, and the same results have been obtained. Hence, Aspen Energy Analyzer can be considered a good tool to optimize processes with the aim of minimising the energy requirements, since it is a fast tool to find the minimum heating and cooling utilities requirements and explore different scenarios to find the best option to reach the energy target. Energy Analyzer also allows to explore different economic and energy results and to obtain different graphics.

Another point to consider is that when developing the full HIPSD, the reflux ratios achieve lower values than the minimums found when optimising the PSD because the distillate and bottoms flow rates are not fixed, in spite of the distillate composition of both columns are more different from the azeotropic composition. Hence, without fixing the flow rates and distillate composition, the reflux ratios can be decreased keeping the product flow rates and purities.

To sum up, the objectives of this project have been accomplished, since a PSD process has been designed to separate the MetAc – MeOH mixture successfully, and heat integration has been implemented reducing the energy costs of the process up to a 46 %. Regarding Aspen Energy Analyzer, it is a promising tool to continue being explored due to the fact that it develops techniques such Pinch analysis in a few seconds, and proposes different possible solutions, with the chance to compare them and choose the most suitable for the studied project.

9. FUTURE WORK

After developing this work, the following points are some suggestions to continue and improve it:

- A study about the influence of ΔT_{min} on the final results or other variables such as the HPC pressure.

- A deeper study about the variation of the capital costs when the heat integration is implemented.

- Continue using the complement Aspen Energy Analyzer in order to explore all the possibilities that it presents.

10. NOTATION

CW	cooling water
ESA	energy separating agents
HEN	heat exchanger network
HIPSD	heat integrated pressure swing distillation
HPC	high pressure column
HPS	high pressure steam
LPC	low pressure column
LPS	low pressure steam
MeOH	methanol
MER	minimum energy requirement
MetAc	methyl acetate
MPS	medium pressure steam
MSA	mass separating agents
N_F	feed tray
N_{FD}	recirculated feed tray
N_T	number of trays
PP	payback period
PSD	pressure swing distillation
PVA	polyvinyl alcohol
Q_C	condenser heat duty
$Q_{exch.}$	exchanged heat duty between the LPC reboiler and HPC condenser
Q_R	reboiler heat duty
RR	reflux ratio
TAC	total annual cost
T_B	bottom temperature
T_D	distillate temperature
ΔH	enthalpy difference
ΔT_{min}	minimum approach temperature

11. REFERENCES AND NOTES

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