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# Synthesis and Optimization of Sustainable Processes Based on Liquid-Liquid Extraction to Purify Methyl Ethyl Ketone

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ABSTRACT

Methyl-Ethyl Ketone (MEK) is a promising bulk chemical and can be produced in a biochemical route from biomass. Within this route, two azeotropes are formed because of the intermolecular interactions; thus, the purification of that mixture is difficult. In this study, a work of synthesis, design, and multi-objective optimization was carried out to generate sustainable alternatives to purify MEK, starting from a promising alternative previously reported. Those alternatives are hybrid processes that combine the advantages of using a liquid-liquid extraction column for handling the azeotropes aforementioned. All alternatives were modeled in Aspen Plus and were optimized using a hybrid stochastic optimization algorithm. As a result, interesting trends among objectives and design variables were found. Additionally, the thermally coupled alternative was shown as a promissory alternative with savings of 11%, 12% for the economic and environmental impact. Also, it showed improvements in controllability and no real penalty regarding safety issues in comparison with a case base.

## 1. Introduction

Improvements in the chemical industry in the use of renewable technology and the effective use of resources are required to reduce energy consumption, waste production, environmental impact, and costs. Process improvements are generally accomplished through an evolutionary approach, where expert expertise in process engineering and the knowledge gained from process understanding are applied. However, there are drawbacks in this method, as the search space employed is small in size in the test and error, experimental methods, to modern, creative, and more sustainable process designs.

Process synthesis should strive to find the best way to process raw materials from a variety of alternatives into particular (desired) products subject to predefined performance criteria. For this purpose, process synthesis includes the study of the problem to be resolved and the generation, evaluation, and screening of process alternatives to determine the best possible process options. Process synthesis typically takes place through three types of methods: (1) rules-based heuristic methods described from process insights and expertise; (2) programming methods based on mathematical methods where network superstructure optimization determines the best flowsheet alternative. (3) Hybrid approaches, which use the know-how, rules, and programming of systems [1]. This means that the models are used for good physical insight which helps to reduce the scope of searching for alternatives, to reduce the synthesis issue. The intensification of processes (PI) is characterized as the improvement of a process to improve the output of limiting phenomena at different scales [2].

This change could be accomplished in four fields – process structure, energy, synergy, and time – according to Van Gerven and Stankiewicz [3]. An example of PI at the process/plant level are the hybrid schemes involving external integration of at least one operation [1]. Several methods [4] have been reported for the design of complex hybrid-intensified operations within a single process. In the case of hybrid approaches, Lutze et al. [2]. suggested a framework to systematically intensify the process. Additional hybrid systems were built to intensify the specific sections of a process, such as at the molecular and phenomena [5,6]. As process intensification aims at improving process performance, synthesis and process intensification should also lead to better and more sustainable process degradation.

Additionally, to process synthesis, green technologies, are among the most effective strategies to try to apply the concepts of sustainability, circular economy, and bioeconomy in the fight to decrease greenhouse gas emissions and global warming while meeting humanity's energy requirements [7]. According to several review papers [7–9], there are

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**Table 1**
Representative mixture coming from 2,3-BD dehydration process.

| Feed Characterization | |
|---|---|
| Water/IBA/2,3-BD/MEK (%wt) | 0.18/0.07/0.1/0.65 |
| Flowrate (kg h-1) | 11,764.7 (vapor fraction zero) |
| Temperature (K) | 298 |

several characteristics that a sustainable process must have. These authors highlight the importance of economic feasibility; however, the simultaneous importance of the environmental aspect is described. On the other hand, to guarantee stable and safe processes with minimum waste generation, the importance of designing controllable and safe processes is highlighted. The sustainability of intensified processes is assessed most of the time by prioritizing economic issues and only taking an environmental aspect into account [10–12]. In this sense, there is no complete picture of the role played by other important indicators, such as process controllability, inherent security, and its connection, for example. Another important aspect that contributes to the sustainable design of processes is the raw material used in different processes. Biomass is called to be the most sustainable way to generate products that can eventually replace the production of bioproducts based on non-renewable materials and the environmental consequences they cause [13].

While there is currently relatively robust research on the production of some bio-compounds, for example, ethanol and butanol, there is still a huge variety of compounds that have the potential to substitute their counterpart from a non-renewable feedstock [14].

Among the industrial products that have recently had a relevant boom in various applications and that can be obtained from a biomass route is Methyl ethyl ketone (MEK). This chemical component is used as a solvent for various coating systems, for example, vinyl, adhesives, nitrocellulose, acrylic coatings, and many more uses [15].

Currently, MEK production is achieved through the hydration of butylene, secondary butyl alcohol (SBA) production, and SBA dehydration. Commercial-scale petroleum cracking produces butylene. SBA can be produced by hydrating 1-butene and 2-butene using acid catalysis. The hydration process takes place at about 250 Celsius and involves a 75 percent $H_2SO_4$ solution; specifically, the 1-butene/2-butene is reacted in a reactor and then transferred to a distillation column, which separates the unreactants from the 2-butanol. Dehydration of the generated SBA results in the development of MEK [16]. With this in mind, the entire process may be pointed out as a major cause of environmental issues for the direct connection with the petroleum industry. So, the production of MEK from a renewable resource may be considered a relief for such problems. Nevertheless, MEK bio-based production is not yet well based. Several works have proposed biotechnological conversion starting from pure sugar as raw material [17]. MEK might be produced by direct fermentation of sugar, however, its production is quite weak with yields of approximately 0.004 $g_{MEK}/g_{glucose}$. A quite promising alternative to produce MEK is utilizing 2,3- Butanediol (2, 3-BD) as intermediate. The interesting situation of this route is a relatively high yield on the production of 2,3- BD via fermentation, which yields have reached values near to the theoretical limit of 0.5 $g_{2,3\text{-}BD}/g_{glucose}$. Further, the direct dehydration of 2, 3- BD is performed with yields superior to 95% [18]. Notwithstanding the relatively high yields for 2, 3-BD fermentation and further dehydration, the downstream processes have been explored by only a few papers [19,20]. The mixture coming from the dehydration process of 2,3-BD is depicted in Table 1, note, in this case, a further separation process is necessary to obtain high purity MEK.

In that sense, it would be worthwhile to question whether MEK production should be generated in a sustainable process environment. One starting point is the demand for this compound. The MEK market is estimated to increase to USD 3.26 billion and its production to 1.754 million tons by 2020 [21]. Note in Fig. 1 the global growth of this compound, as well as the geographic distribution of its production [22].

Based on these ideas, and in particular, for the case of MEK purification, obtained via biomass, Sánchez-Ramírez et al. [18] have proposed an intensified process that combines the advantages of using a liquid-liquid extraction column with distillation for handling the

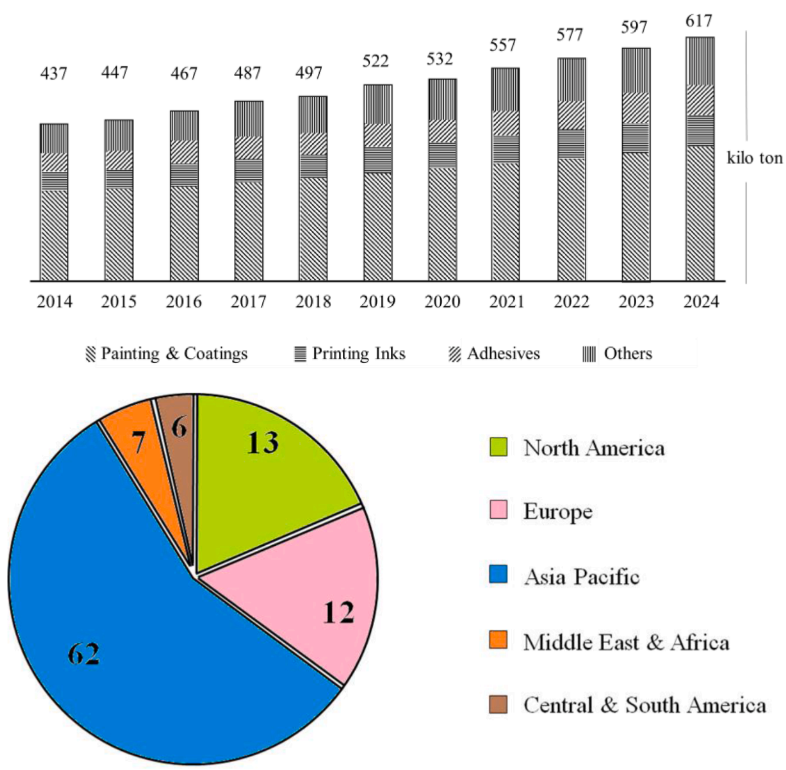


**Fig. 1.** Global market of MEK through years in kilotons and its demand by geographic region.

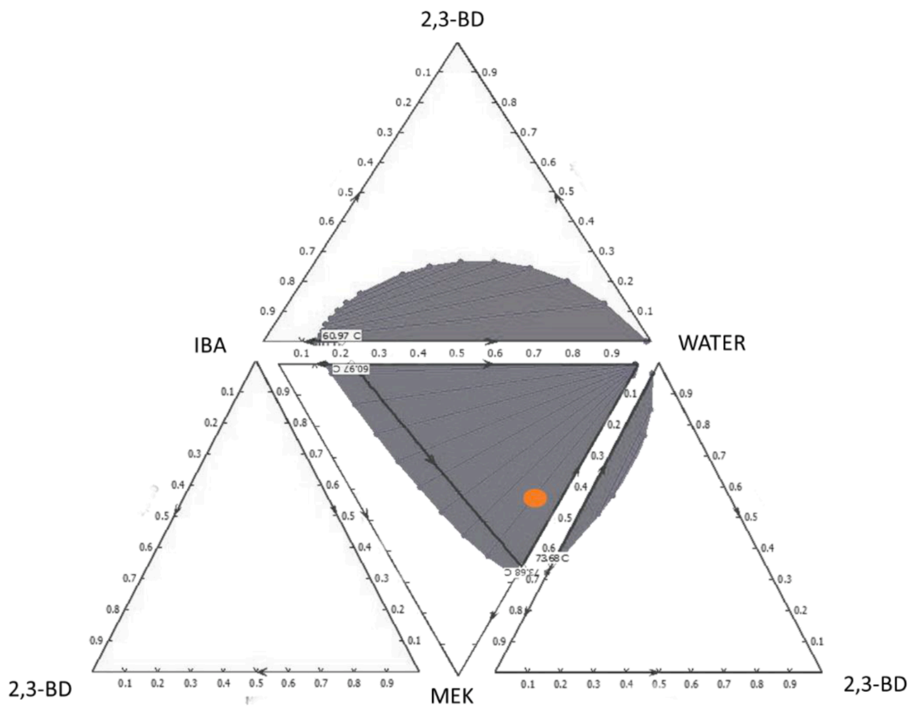


**Fig. 2.** Quaternary diagram for 2,3-BD, IBA, Water, and MEK and their heterogeneos azeotropes (mole basis) in the feed mixture.

azeotropes present in the mixture water, isobutyraldehyde, 2, 3-Butanediol, and Methyl ethyl ketone. Hybrid processes, according to Gorak et al. [23]., are the external combination of two separate unit operations for the same separation task, allowing each unit operation to be included in the operating window where it outperforms all others. Furthermore, occurring synergies enable another unit operation based on a different separation concept to cross the thermodynamic boundaries of a single unit operation. In the reference case approached in this proposal, the combination of liquid-liquid extraction and distillation columns generates a hybrid process. Some other authors also consider that the combination of distillation columns with liquid-liquid extraction columns forms a hybrid process. For example, Kraemer et al. [24] claims that a hybrid process distillation-LLX is a good alternative to separate a broth coming form ABE fermentation. To purify such a mixture, Errico et al. [25,26] outline the benefits of hybrid processes. Likewise, this type of hybrid process has been used for other types of blends. [27–31]. This kind of combination have proven their efficacy in reducing global energy consumption regarding downstream processes [25,29]. The main reason for reducing energy requirements lies on the fact that a liquid-liquid extraction (LLX) column helps in breaking the intermolecular interactions among components, consequently, the energy requirement is reduced. On the other hand, Stankiewicz and Moulinjn [32] presented a compressive review and classification of intensified process, positioning the hybrid processes as intensified processes. Subsequently, Stankiewicz et al. [33] define an intensified process as hybrid separations, where two or more separation techniques are combined with each other to deliver better separation efficiency or energy savings. Additionally, hybrid processes have shown capabilities of improvement in many performance indexes [18]. Hybrid processes are a clear example of intensified processes and therefore a way to generate sustainable processes in accordance with the circular economy and bioeconomy policies. The proposal shows huge energy savings which are consequently observed in performance parameters as total annual cost, environmental impact, dynamic behavior, and inherent safety compared to separation systems based exclusively on distillation columns. This work presents for the first time the synthesis, design, and optimization of three new highly intensified designs based on liquid-liquid extraction and compared with the design proposed by Sánchez-Ramírez et al. [18].

The objective functions used in the optimization problem are total annual cost, environmental impact, inherent safety, and dynamic behavior. All those targets were taken into account to know how to process synthesis affects the sustainability of new processes.

## 2. Case study and synthesis of intensified configurations

Considering the mixture presented in Table 1, because of the intermolecular interactions (See the orange point in Fig. 2), the MEK purification is challenging since two azeotropes are present in the mixture MEK/IBA/2,3-BD/Water. Fig. 2 shows the various molecular interactions in the study mixture. The gray region shows the presence of different phases. The equilibrium between the fractions of these phases is shown by the straight lines (tie lines). On the other hand, the dark gray line, as well as the outline of the triangles, represent the distillation boundaries. The orange dot represents the composition of the mixture to be separated in this case study. At atmospheric pressure, the quaternary diagram of MEK/water/IBA/2,3-BD shows two temperature-minimum azeotropes. Separating pure MEK from a dilute solution is complicated by the distillation boundary. When a solvent is added to the mixture, the liquid-liquid equilibrium will cross the distillation boundary. As a result, the organic products' miscibility difference with water may be used to isolate them in a subsequent series of distillation columns. While there are some approaches to MEK purification, the purification process does not address the mixture being purified in this work. Furthermore, they are mixtures that do not present a thermodynamic complexity of the quaternary mixture of this work. For example, Smetana et al. [34] approached the purification of the MEK-water mixture based on a membrane process. Penner et al. [35] presented the conceptual design of 4 alternatives for the purification of the MEK/IBA/2,3-BD/Water mixture, however, their proposal is entirely based on distillation columns and decanters. As reported by Marquard et al. [36], there are several technologies capable of separating this type of complex mixtures, pressure swing process, schemes assisted by entrainers, heterogeneous distillation, etc. Considering the use of the short method proposed by Marquead et al. [36] which considers the energy demand for discerning between the different possibilities, it was concluded that the use of an extended mass agent was the best option.

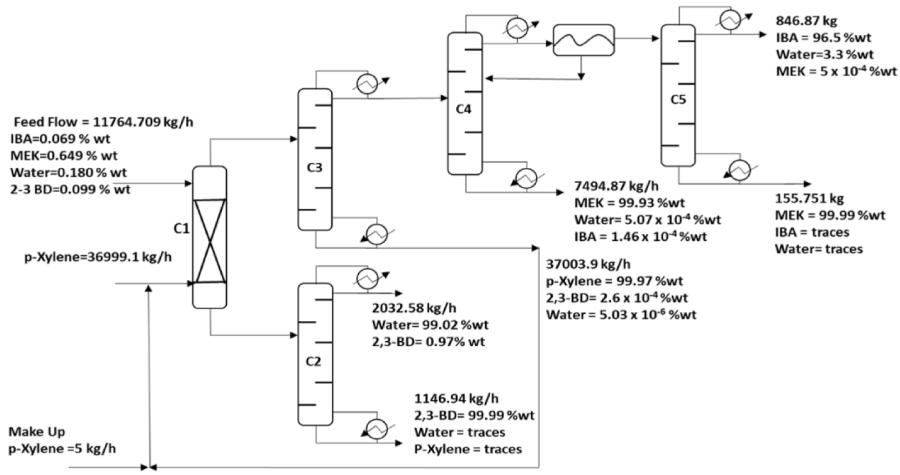


**Fig. 3.** Reference case from [18] for the synthesis, design and optimization work developed in this proposal.

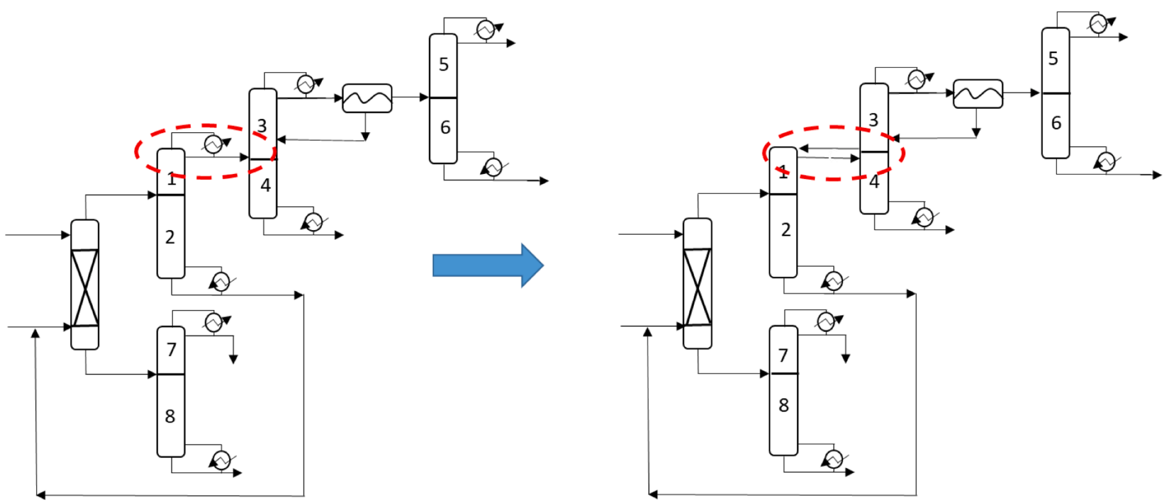


**Fig. 4.** substitution of the column condenser by a thermal coupling to obtain a thermally coupled scheme.

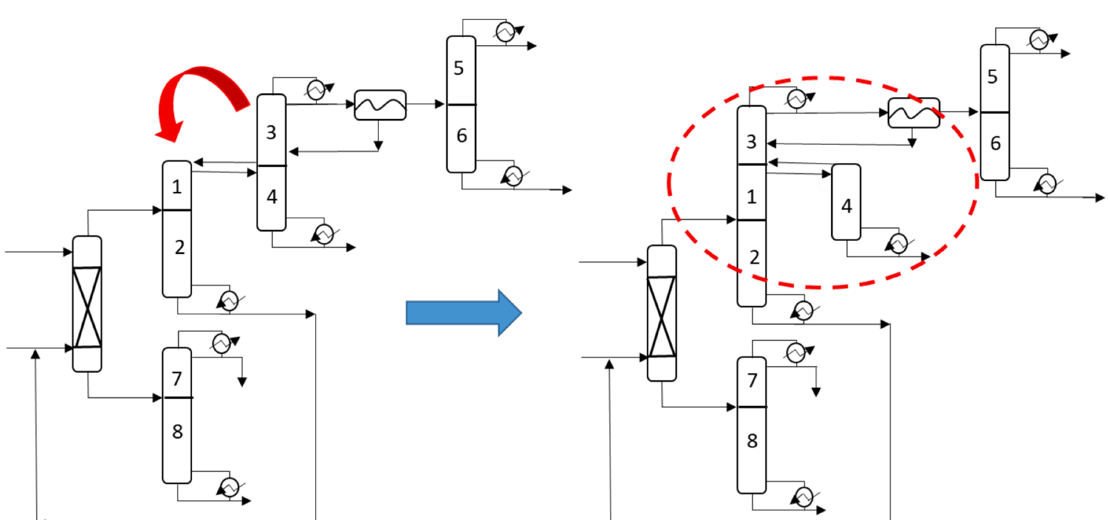


**Fig. 5.** Movement of column section #3 to generate a thermodynamically equivalent scheme.

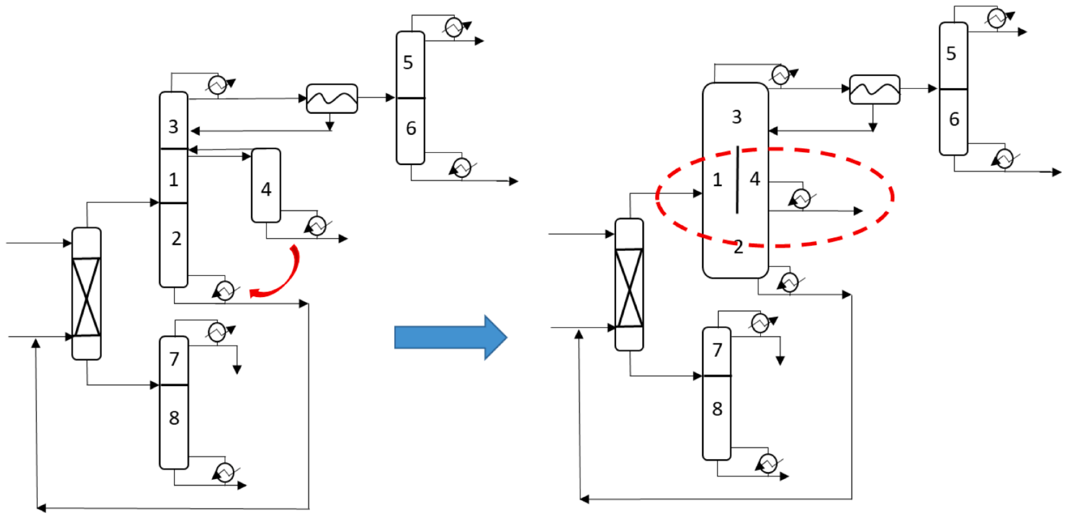


**Fig. 6.** Adding column Section 4 to generate a DWC scheme.

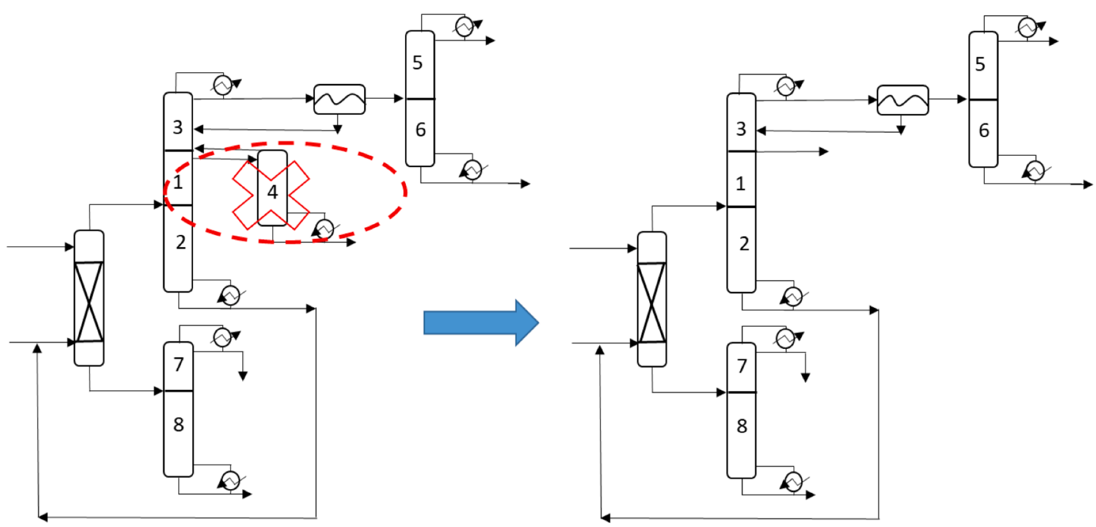


**Fig. 7.** Elimination of column section #4 to generate a intensified scheme.

The choice of the external mass agent is an important aspect, and must take into account the nature of the mixture to be separated and the molecular mechanisms of the mixture [37,38]. In particular, ketone groups generate molecular interactions that hinder the separation and purification of these compounds [39–42].

In this proposal, is taken as a starting point the scheme presented in Fig. 3 [18]. The base case consists of a liquid-liquid extraction column (C1), followed by some conventional distillation columns (C2, C3, and C5) and an azeotropic distillation column (C4). This proposal notably improved the performance (cost, energy requirements, etc.) of a set of four separation scheme based on distillation columns and azeotropic columns. The solvent used is p-xylene. From such scheme, a synthesis work will be applied in order to promote better sustainable indexes. The synthesis work consists of, starting from the base case, applying thermal couplings, movement/elimination/integration of column sections.

## 2.1. *Synthesis of intensified configurations*

The methodology to generate new alternatives is based on the introduction of thermal couplings, transposition/movement of section (understanding a column section as a portion of any conventional column not truncated by mass or heat streams [43,44]), and process intensification. Although this methodology is not complicated, its orderly and logically structured procedure has made it possible to obtain very good results in terms of energy, economic and environmental savings [25,26]. Briefly, the methodology is described in four steps applied to the conventional columns:

i) Application of thermal couplings

Starting from the topology presented in Fig. 3, it is possible to generate a modified thermally coupling scheme if a heat exchanger (reboiler or condenser) is directly connected to a non-product stream is replaced with a liquid/vapor stream. The right scheme of Fig. 4 were obtained by substituting the condenser and replaced by a vapor/liquid stream coming from the next column, feed it at the top of the second column.

i) Transposition of column section to generate a dividing wall column

Once the thermal couplings are already introduced, note that there are some column sections where either a condenser or reboiler provides a common reflux ratio/vapor boil-up between adjacent columns. With such consideration, it is possible to transpose column sections to

**Table 2**
Unit eco-indicator used to measure eco-indicator 99 in both case studies [24].

| Impact category | Steel (points/kg) | Steam (points/kg) | Electricity (points/kWh) |
|---|---|---|---|
| Carcinogenic | $6.320\times10^{-3}$ | $1.180\times10^{-4}$ | $4.360\times10^{-4}$ |
| Climate change | $1.310\times10^{-2}$ | $1.600\times10^{-3}$ | $3.610\times10^{-6}$ |
| Ionizing radiation | $4.510\times10^{-4}$ | $1.130\times10^{-3}$ | $8.240\times10^{-4}$ |
| Ozone depletion | $4.550\times10^{-6}$ | $2.100\times10^{-6}$ | $1.210\times10^{-4}$ |
| Respiratory effects | $8.010\times10^{-2}$ | $7.870\times10^{-7}$ | $1.350\times10^{-6}$ |
| Acidification | $2.710\times10^{-3}$ | $1.210\times10^{-2}$ | $2.810\times10^{-4}$ |
| Ecotoxicity | $7.450\times10^{-2}$ | $2.800\times10^{-3}$ | $1.670\times10^{-4}$ |
| Land Occupation | $3.730\times10^{-3}$ | $8.580\times10^{-5}$ | $4.680\times10^{-4}$ |
| Fossil fuels | $5.930\times10^{-2}$ | $1.250\times10^{-2}$ | $1.200\times10^{-3}$ |
| Mineral extraction | $7.420\times10^{-2}$ | $8.820\times10^{-6}$ | $5.700\times10^{-6}$ |

generate thermally coupled sequences. Note the right scheme of Fig. 5 was obtained from the corresponding thermally coupled sequence moving Section 3 above Section 1. This schemes is a Thermodynamic equivalent scheme of the thermally coupled sequences in Fig. 4.

So far, we have thermodynamic schemes with either a side stripper/rectifier. We can follow two different paths to intensify the process.

i) DWC synthesis: To obtain a dividing wall column is only necessary to incorporate the single side section into the first column, see in the right scheme of Fig. 6 that a stripping section (column Section 4) is collocated inside the column, as result, a DWC with two reboilers is obtained.
ii) Elimination of column Section: Again, starting from the thermodynamic equivalent schemes, the methodology is quite simple; only it is necessary to eliminate the column Section 4 and adding instead a side stream. As result, the righ scheme in Fig. 7 show the intensified scheme.

## 3. Sustainable indexes

In order to evaluate all alternatives developed in a framework of sustainable process, it is necessary to define some metrics. Sustainable development is defined as 'development that meets the needs of the present without compromising the ability of future generations to meet their own needs'. Sustainable development lies at the overlap of social, environmental, and economic development [45]. Green chemistry can be seen as a tool by which sustainable development can be achieved. The application of green chemistry is relevant to social, environmental, and economic concerns. According to concepts reported by Jiménez-Gonzalez et al. [7] should consider incorporating "green metrics" when designing a process towards the broader goal of environmental sustainability. Among those green metrics should be highlighted the aspects of environmental, economics, safety, and process control. In the same sense, modification in the topology of intensified configurations for the same downstream process can also modify sustainable indexes [46].

### 3.1. Economical index

As has been described, for economic purposes, all designs were compared employing the total annual cost (TAC) and the selling price. To calculate the total annual cost (TAC), it was used the method published by Turton et al. [47]. the cost approximation is described in equation 1.

$$TAC = \frac{\sum_{i=1}^{n} C_{TM,i}}{r} + \sum_{j=1}^{n} C_{ut,j} \quad (1)$$

The economic study performed considers 10 years as the recovery period. The plant is assumed to run 8500 h/year. Besides, the following heating and cooling costs were taken into account: high-pressure (HP) steam (42 bar, 254 °C, \$9.88 GJ$^{-1}$), medium-pressure (MP) steam (11 bar, 184 °C, \$8.22 GJ$^{-1}$), low-pressure (LP) steam (6 bar, 160 °C, \$7.78 GJ$^{-1}$), and cooling water (\$0.72 GJ−1) [48].

### 3.2. Environmental index

The Eco-Indicator 99 (EI99) was used to evaluate the sustainability of the processes and to quantify the environmental impact due to the multiple activities performed in the process. This methodology is based on the life cycle assessment. The approach was proposed by Goedkoop and Spriensma [49]. The EI99 has proven to be an important method to evaluate the overall environmental impact related to chemical processes. Some authors – such as Quiroz-Ramirez et al. [50], Contreras-Vargas et al. [51], among others – have demonstrated that applying the EI99 during the design and synthesis phases can lead to important improvements and reductions of wastes, and the index was applied successfully in screening different alternatives giving as results the optimal configuration with the lowest environmental impact and cost. The eco-indicator 99 is calculated as follow:

$$EI99 = \sum_{b}\sum_{d}\sum_{k\in K}\delta_d\omega_d\beta_b\alpha_{b,k} \quad (2)$$

Where $\beta_b$ represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical b released to the environment, $\omega_d$ is a weighting factor for damage in category d, and $\delta_d$ is the normalization factor for damage of category d. The EI99 methodology considers 11 impact categories aggregated into three major damages categories: human health, ecosystem quality, and resource depletion. The scale is chosen in such a way that the value of 1 Pt (point) is representative of one-thousandth of the yearly environmental load of one average European inhabitant. To analyze the schemes considered as cases of study, the impact calculation of three factors was considered as the most important: steam (used in column reboiler), electricity (used for pumping), and steel (to build a reactor, distillation column, and accessories). Furthermore, in the presented approach the hierarchical perspective was considered to balance the short- and long-term effects. The normalization set is based on a damage calculation for all relevant emissions, extractions, and land-uses. The values for those three factors are summarized in Table 2.

### 3.3. Inherent safety index

Process safety quantified by the individual risk (IR) index. The IR can be defined as the risk of injury or decease to a person in the vicinity of a hazard [52]. The main objective of this index is the estimation of likelihood affectation caused by the specific incident that occurs with a certain frequency. The IR does not depend on the number of people exposed. The mathematical expression for calculating individual risk is the following:

$$IR = \sum f_i P_{x,y} \quad (3)$$

Where $f_i$ is the occurrence frequency of incident $i$, whereas $P_{x,y}$ is the probability of injury or decease caused by the incident $i$. In this work, an irreversible injury (decease) is used, for which more data are recorded. The calculation of IR can be carried out through quantitative risk analysis (QRA), which is a methodology used to identify incidents and accidents and their consequences. The QRA starts with the identification of possible incidents, for distillation columns are identified continuous and instantaneous releases. A continuous release is produced mainly by a rupture in a pipeline or partial rupture on a process vessel causing a leak. The instantaneous release consists of the total loss of matter from the process equipment originated by a catastrophic rupture of the vessel.

**Table 3**
Range and type of variables used in the calculation of objective functions.

| Type of Variable | | Search Range |
|---|---|---|
| Number of Stages | Discrete | 5–100 |
| Feed Stages | Discrete | 4–99 |
| Side Stream Stage | Discrete | 4–99 |
| Reflux Ratio | Continuous | 0.1–75 |
| Distillate Rate | Continuous | 10–248 (kmol $h^{-1}$) |
| Diameter | Continuous | 0.9–5 (meters) |
| Solvent | Continuous | 124–496 (kmol $h^{-1}$) |

These incidents were determined through hazard and operability study (HAZOP). The frequencies for each incident ($f_i$) were taken according to the previously reported values by the American Institute of Chemical Engineers [52] and using the event tree diagrams obtained with all probabilities of instantaneous and continuous incidents, along with their respective frequencies. Accordingly, instantaneous incidents are: boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), flash fire, and toxic release, whereas the continuous release incidents are: jet fire, flash fire, and toxic release.

### 3.4. Control properties index

One of the basic and most important tools of modern numerical analysis is the Singular value decomposition (SVD). There are numerous important applications of the SVD when quantitative and qualitative information is desired about linear maps. One important use of the SVD is in the study of the theoretical control properties in a chemical process. One definition of SVD is:

$$G = V\Sigma W^H \quad (4)$$

Here, $G$ is the matrix target for SVD analysis, Σ is a diagonal matrix which consists of the singular values of $G$, $V$ is a matrix which contains the left-singular vector of $G$ and $W$ is the matrix composed by the left-singular vectors of $g$ (more details about mathematic fundaments in Klema and Laub, [53].

In the case where the SVD is used for the study of the theoretical control properties, two parameters are of interest: the minimum singular value ($\sigma\cdot$) the maximum singular value ($\sigma\cdot$), and its ratio known as condition number ($\gamma$):

$$\gamma = \frac{\sigma^*}{\sigma_*} \quad (5)$$

The minimum singular value is a measure of the invertibility of the system and represents a clue of potential problems of the system under feedback control. The condition number reflects the sensitivity of the system to uncertainties in process parameters and modeling errors. These parameters provide a qualitative assessment of the theoretical control properties of the alternate designs. The systems with higher minimum singular values and lower condition numbers are expected to show the best dynamic performance under feedback control [54]. The SVD technique requires a transfer function matrix ($G$) around the optimum design of the distillation sequences and registering the dynamic responses of product composition. Cabrera-Ruiz et al. [55] have recently demonstrated the use of the condition number as an index of dynamic performance and even as an objective function in a process of simultaneous optimization design-control.

## 4. Optimization strategy and objective function

All the sustainable metrics were evaluated in the early design stage through a multi-objective optimization. The method selected for optimizing intensified process is the differential evolution with Tabu list also called DETL. The DETL is a stochastic global search technique where the search for global optimum is carried out in all the feasible regions by an iterative procedure. The method was proposed by Srinivas and Rangaiah [56], it has proven to have several advantages compared to other optimization methods. For example, the DETL has a faster convergence of global optimum vicinity, smaller computational efforts, less computational time to strongly solve nonlinear and non-convex problems. Another advantage of DETL is its ability to memorize solutions previously checked, hence avoiding the evaluation of solutions previously tested. This ability reduces the computational time required to obtain the optimal solution. The differential method with Tabu list has been applied successfully to a wide range of different problems in the chemical industry [57–59].

The DETL method consists of four basic steps based on the biological evolution theory, these steps are: i) Initialization, ii) Mutation, iii) Crossover, iv) Selection. The parameters used for DETL were taken from Rangaiah [60].

These four targets already listed will be considered in the objective function defined as follow:

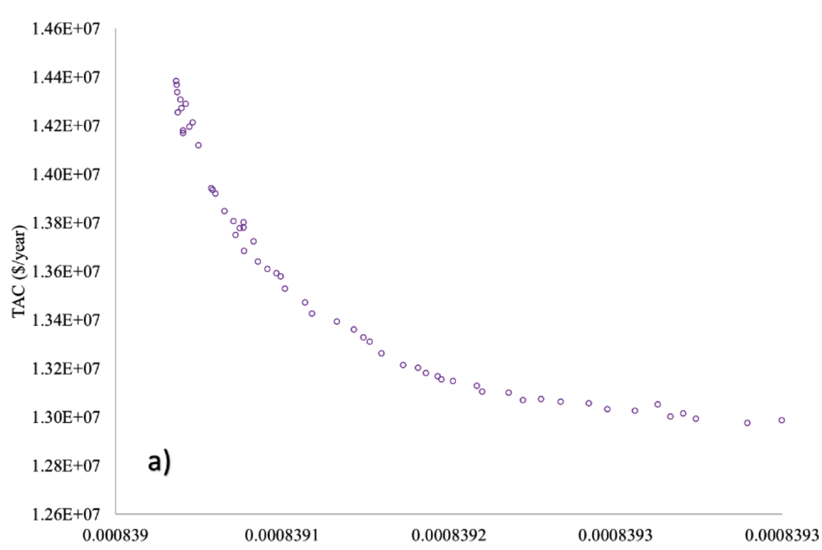


**Fig. 8.** Pareto fronts evaluating: a) TAC and IR for the intensified alternative, b) EI99 and IR for the thermally coupled scheme, c) Condition number and IR for the thermodynamic equivalent scheme, and d) TAC and EI99 for the reference case.

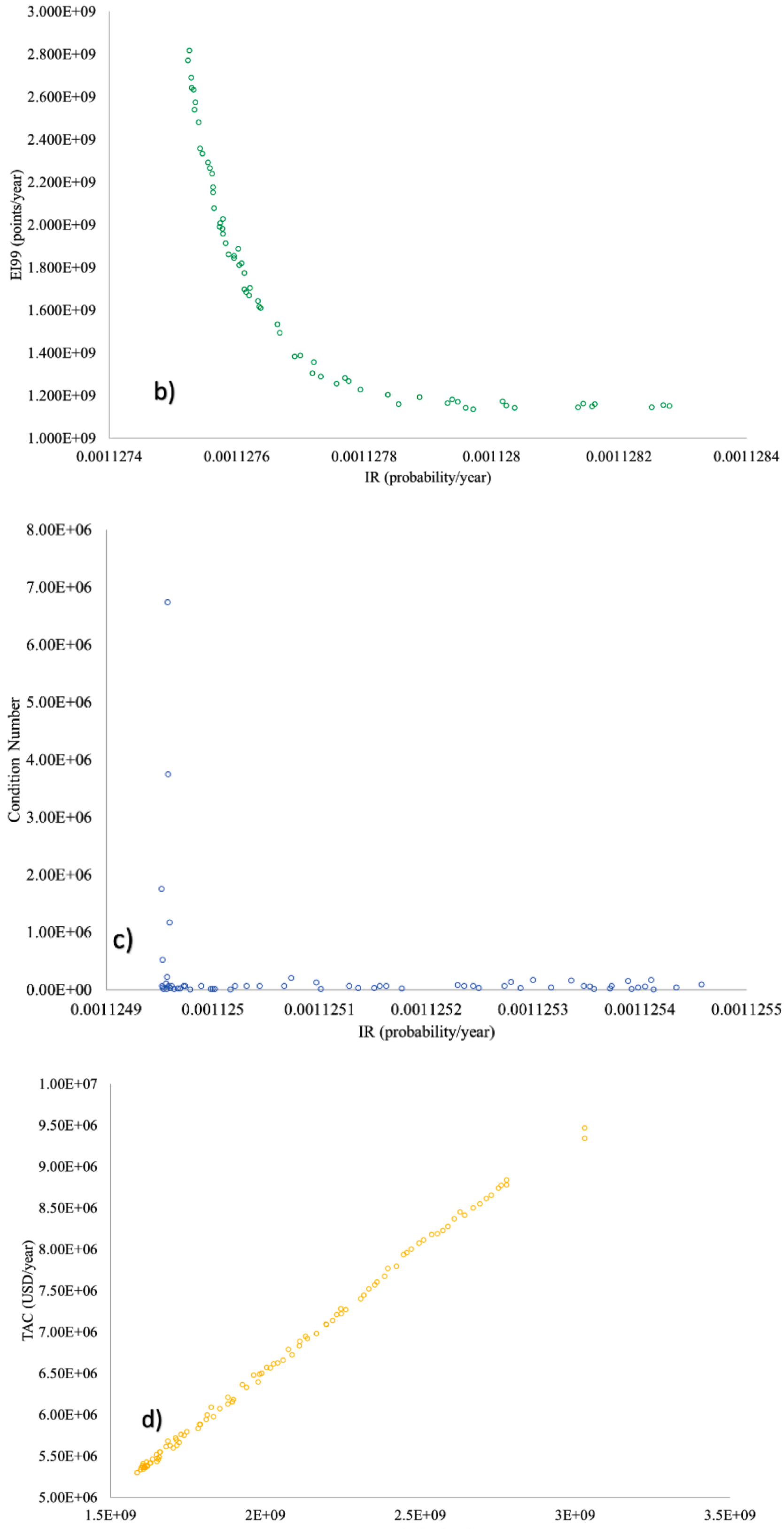


**Fig. 8.** (*continued*).

$$\min(TAC, EI99, IR, \gamma) = f\left(N_{tn}, N_{fn}, R_{rn}, F_{rn}, P_{cn}, FC_{cn}\right)$$
$$Subject to \vec{x_m} > \vec{y_m} \quad (6)$$

Where TAC is the total annual cost, EI99 is the eco-indicator 99, IR is the individual risk, γ is the condition number. $N_{tn}$ is the column stages, $N_{fn}$ is the feed stage, $R_{rn}$ is the reflux ratio, $F_{rn}$ is either distillate or bottom flux. Many physicochemical properties are considered for IR measurement, such as combustion heat of molecular weight

**Table 4**
Objective functions of all alternatives.

| | Case Base | Thermally Coupled | DWC | Intensified |
|---|---|---|---|---|
| **TAC ($ $y^{-1}$)** | $6.72\times10^{6}$ | $6.02\times10^{6}$ | $5.86\times10^{6}$ | $1.33\times10^{7}$ |
| **Eco-Ind (Points $y^{-1}$)** | $2.09\times10^{9}$ | $1.23\times10^{9}$ | $1.23\times10^{9}$ | $4.72\times10^{9}$ |
| **IR (Probability y-1)** | $1.13\times10^{-3}$ | $1.13\times10^{-3}$ | $8.45\times10^{-4}$ | $8.39\times10^{-4}$ |
| **Condition Number** | $2.01\times10^{3}$ | $1.72\times10^{2}$ | $3.94\times10^{4}$ | $8.01\times10^{5}$ |

combustion, LC50, and so on; $y_m$ and $x_m$ are the vectors of the acquired and needed purities for the components of $m_{th}$, respectively. Around 25 variables, continuous or discrete, were considered in this multi-objective optimization exercise. The flows and their respective purities of the compounds of interest were treated as constraints. In the optimization process, Table 3 shows the form of variables used and the search range.

Average limits of industrial distillation columns were considered for variables relating to the physical aspect of the distillation columns [23]. The variables to be monitored for the control analysis were the purity of 2,3-BD, IBA, MEK, and water. Besides, distillate flows and heat duties associated with the output currents of said products were taken into account as manipulable variables. In order to use MEK for industrial purposes, the purity of the commodity was at least 99.5% wt for MEK, 99.5%wt for 2, 3-BD and 95% wt for IBA in all processes [61]. P-xylene recovery is also obtained above 99.9% wt in the case of the solvent.

## 5. Results

Once the optimization process was completed for each synthetized alternative, several Pareto fronts were obtained. Remember that in the optimization process are evaluated four objective functions at the same time; in such a way that a Pareto front was obtained with those targets for each separation alternative. Despite the four objective functions were evaluated at the same time, the Pareto fronts in Fig. 8 are presented as 2D Pareto fronts for better understanding in the trends of the objective functions. After 200,000 evaluations, all Pareto Fronts were collected. There was then no noticeable change in objective functions, and it was considered that the DETL approach achieved convergence according to the evaluation criteria. The results shown here are also the best solution. In all methods, the product purities are 99.5% WT MEK, 99.5% WTP, 3% BD, and 95% IBA. In the Pareto fronts, it is easy to observe the competition that exists in the objective functions, due to the impact that the design variables have on them. Several variables can play for and against the objective functions. For example, column diameter directly affects the cost-controllability relationship. That is, the diameter should be large enough to improve controllability but not so

**Table 5**
Design parameters of the thermally coupled scheme.

| | LLX | C2 | C3 | C4 | C5 |
|---|---|---|---|---|---|
| Number of stages | 10 | 27 | 100 | 65 | 70 |
| Reflux ratio | | 1.33 | — | 22.32 | 2.67 |
| Interconnection liquid flow (kmol/h) | | — | 82.63 | — | — |
| Feed stage | 1, 10 | 4 | 27 | 12 | 56 |
| Column diameter (m) | 1.455 | 1.32 | 1.182 | 1.05 | 1.369 |
| Operative pressure (kPa) | 101.353 | 101.353 | 101.353 | 101.353 | 101.353 |
| Distillate or Bottoms (D or B) flowrate (kmol $h^{-1}$) | | 111.997 (D) | 123.297 (B) | 19.068 (D) | 2.05 (B) |
| Condenser duty (cal/s) | | 717,646 | — | 1,001,517 | 101,444 |
| Reboiler duty (cal/s) | | 855,731 | 1,029,802 | 555,011 | 109,314 |

**Table 6**
Design parameters of the DWC scheme.

| | LLX | C2 | DWC | C5 |
|---|---|---|---|---|
| Number of stages | 10 | 27 | 117 | 70 |
| Reflux ratio | | 1.33 | 22.45 | 2.67 |
| Dividing Wall | | — | 48, (17–65) | — |
| Feed stage | 1, 10 | 4 | 27 | 56 |
| Column diameter (m) | 1.455 | 1.32 | 2.148 | 1.369 |
| Operative pressure (kPa) | 101.353 | 101.353 | 101.353 | 101.353 |
| Distillate or Bottoms (D or B) flowrate (kmol $h^{-1}$) | | 111.997 (D) | 123.297 (B) | 2.05 (B) |
| Condenser duty (cal/s) | | 717,646 | 1,501,205 | 101,444 |
| Reboiler duty (cal/s) | | 855,731 | 1,584,813 | 109,314 |

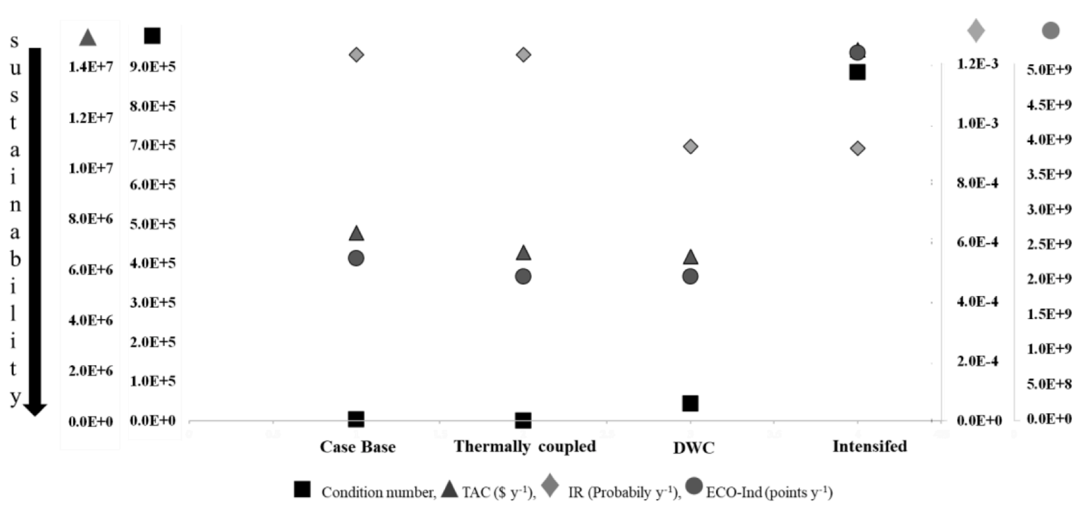


**Fig. 9.** General perspective of all objective functions for all the separation alternatives.

**Table 7**
Design parameters of the intensified scheme.

| | LLX | C2 | C3 | C5 |
|---|---|---|---|---|
| Number of stages | 10 | 27 | 104 | 65 |
| Reflux ratio | | 1.33 | 95.0318 | 2.55 |
| Feed stage | 1, 10 | 4 | 87 | 21 |
| Column diameter (m) | 1.455 | 1.32 | 1.188 | 1.34 |
| Operative pressure (kPa) | 101.35 | 101.353 | 101.353 | 101.353 |
| Distillate or Bottoms (D or B) flowrate (kmol $h^{-1}$) | | 111.997 (D) | 123.297 (B) | 2.06 (B) |
| Condenser duty (cal/s) | | 717,646 | 5,099,931 | 99,732 |
| Reboiler duty (cal/s) | | 855,731 | 5,682,588 | 109,548 |

large as to exponentially increase cost. This phenomenon is relatively similar to what happens with the reflux ratio.

The inherent safety calculation is highly influenced by the amount of matter inside the column where the calculation is made. In that sense, large distillate/bottom flows minimize the probability of an accident, but directly affect the mass balance and the recovery and purity constraints. The reflux ratio plays a similar role. For example, because there is a considerable amount of water held in the effluent, a high reflux ratio will generate dilute internal flows. This behavior will decrease the probability of a catastrophic event but will increase the reboiler duty, which will have an impact on the total annual cost and environmental impact.

Another important connection is the present one between the total annual cost and the environmental impact. According to Table 2, the calculation of the environmental impact considers the impact of construction steel, heating steam, and electricity for pumping. Therefore, to find a balance between these two objective functions, it is necessary to find a design, for example, that does not have too few balancing stages so as not to require such a high thermal load that would have a high environmental/cost impact due to the use of steam, but also does not have so many balancing stages that the environmental/cost impact caused by the steel would be considerable.

Considering all the above, the objective functions shown in Table 4 show the trends observed in the multi-objective optimization.

In this particular purification process, the immediate application of a thermal coupling involved an immediate 11% decrease in total annual cost. This decrease is mostly due to the savings generated by avoiding the re-mixing of compounds in a conventional column. Also, the savings were also due to the cost associated with the condenser in column 3. In the other objective functions, there was also a considerable improvement, for example, there was a 12% reduction in environmental impact and an improvement in controllability. However, the probability of a catastrophic event remained very similar.

Starting from the thermally coupled configuration, the thermodynamically equivalent configuration was generated. In terms of energy consumption, it has been shown on several occasions [19,25] that this type of configuration originated by a movement of sections is equivalent to the coupled schemes. However, once lateral stripping is incorporated into column 2, there should be an improvement in the total annual cost. According to Table 4, the cost improvement is approximately 4% which is immediately due to the capital cost savings. The environmental impact logically remains the same, but controllability is affected. That is, due to the topological change, controllability is diminished. Finally, due to the elimination of stripping, a counterproductive effect is generated in all indicators. Although in several studies this methodology of section elimination has proved favorable [25,46], for this particular mixture no improvement was observed. This negative effect is particularly because, once a column section was eliminated, the energy requirements of column 2 increased considerably.

Finally, analyzing the results in a sustainability framework, process synthesis plays a fundamental role. An interesting aspect is a variation in sustainability as the synthesis work progresses and as the separation process intensifies. Starting from the conventional scheme, the scheme intensifies stage by stage. By including a thermal coupling, the conventional scheme topologically acquires an advance towards intensification. Once the movement of a column section is made, and it is integrated into the form of a DWC, the scheme acquires a number of equipment for separation equal to that with the intensified scheme.

Considering only the capital cost, as the degree of intensification increases, the number of equipment is reduced and with it the cost. However, overall, the cost of services has a considerable impact on reboiler duty, especially in the intensified scheme. Energy consumption goes hand in hand with eco-indicator 99; the environmental impact is reduced with the use of less steel for equipment construction, but increases as energy requirements increase as well. In the case of inherent safety, while the number of pieces of equipment is conserved, the probability of catastrophe is conserved. On the other hand, in schemes with a smaller number of equipment, the probability of catastrophe decreases.

In the particular case of this mixture, the addition of a thermal

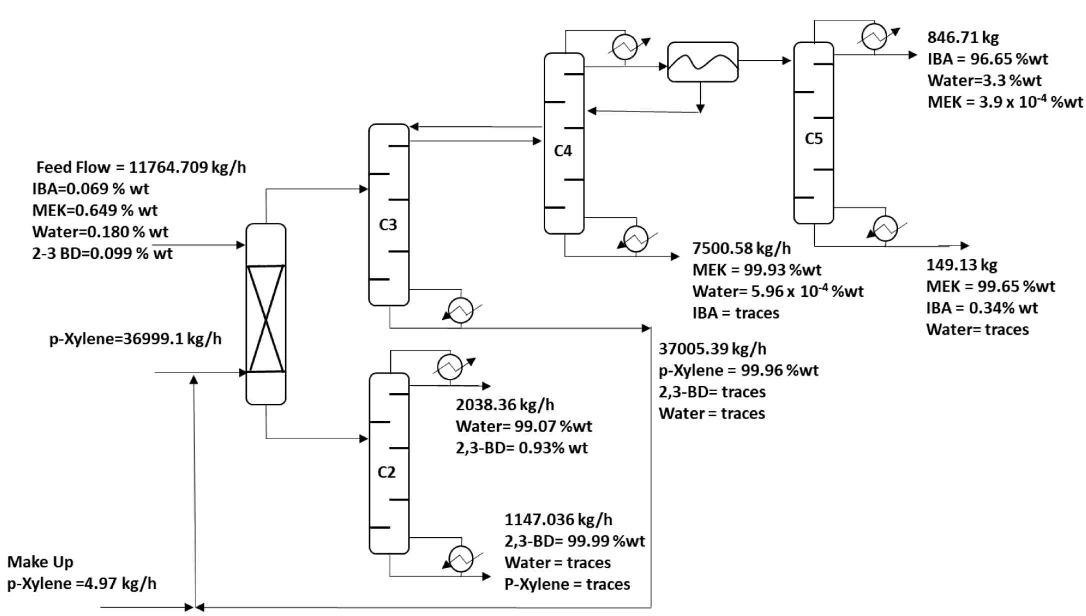


**Fig. 10.** Process flow scheme with flow data of the thermally coupled alternative.

coupling considerably increases all the indicators and the sustainability of this separation process. Once a topological movement is made to the separation scheme, some items are favored in a small percentage, but there is a negative impact on the controllability of the process. The elimination of column sections is not favorable in light of a process with sustainability characteristics; on the contrary, detrimental effects on the sustainability of the separation process were observed. Note in Fig. 9 the variation of the objective function of all alternatives.

Although it is the designer's job to choose the appropriate alternative, according to what has been observed in this work, the alternative with thermal coupling would be the most balanced alternative among those shown in this work. Tables 5-7 shows the general characteristics of thermally coupled, DWC, and intensified schemes. Fig. 10 shows a mass balance of the thermally coupled sequence.

Note in Fig. 10 that, the feed contains a considerable amount of water which generates the intermolecular interactions. By using p-Xylene, it is possible to obtain at the bottom of the LLX column a mixture consisting mainly of 2,3-BD and water which is subsequently purified in column C2. On the other hand, in the LLX column dome, the total solvent and a mixture formed by MEK and IBA to a greater extent is obtained. This mixture is further purified using a thermally coupled column, an azeotropic column and a conventional column.

## 6. Conclusions

In this work, a synthesis, design, and optimization of separation alternatives for the purification of MEK were carried out considering four objective functions, the total annual cost, the environmental impact, the controllability of the process, and the inherent safety, were evaluated in the early design stages.

Considering the capital cost and inherent safety, as a higher degree of intensification is acquired, these indicators improve. However, energy consumption increases, which generates a penalty in terms of the cost of services and the environmental indicator. In the case of controllability, as the process acquires a higher degree of intensification, for this particular case, controllability suffers a considerable decrease. The bottom line after results showed that a thermal coupling is layered to promote the improvement of all four objective functions, and to promote overall process sustainability.

In this case study, the inclusion of a thermal coupling improved by 11% the economic impact, by 12% the environmental impact, and also improved controllability. Not to mention that there was no real penalty in terms of safety compared to the baseline design.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cep.2021.108522.

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