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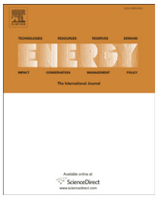

Intensified alternative to purify methyl-Ethyl ketone in a framework of green process

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ABSTRACT

Methyl-Ethyl Ketone (MEK) is a promising bulk chemical due to its several applications. MEK can be produced by hydrogenation of 2, 3-Butanediol, a chemical previously produced by fermentation. As hydrogenation results, the output is composed of water, isobutyraldehyde, 2, 3-Butanediol, and Methyl-ethyl ketone. Because of the thermodynamic interactions, two azeotropes are formed; consequently, the purification of that mixture is challenging. Current needs promote the generation of alternatives with good economic and environmental performance, however, inherent safety and good controllability must also be accomplished. In this study an intensified process is proposed to reduce the energy investment for MEK purification. The alternative is a hybrid process that combines the advantages of using a liquid-liquid extraction column for handling the azeotropes aforementioned. Additionally, this proposal is compared with four alternatives previously proposed based only on distillation. All alternatives were modeled in Aspen Plus and were optimized considering four targets, the total annual cost, the eco-indicator 99, the individual risk, and the condition number as economic, environmental, safety and controllability indexes, respectively. As a result, interesting trends among objectives and design variables were found. Additionally, the intensified design reported an energy investment of 6.78 $\mathrm{MJfuel/kg_{MEK}}$, and the best pure distillation alternative 35.5 $\mathrm{MJ_{fuel}/Kg_{MEK}}$.

1. Introduction

Methyl Ethyl Ketone (MEK) is a colorless liquid that has an acetone-like odor; its odor can be appreciated from approximately 16 ppm [1]. MEK can be found in nature, for example in volcanoes and forest fires. MEK can be found in small amounts in biologically degraded foods and in automobile exhaust [2]. Industrially, MEK is widely used in the manufacture of paints, lacquers, varnishes, glues, resins, gums, nitrocellulose, cellulose acetate, artificial leather, etc. Additionally, it is used in the printing industry, in the production of dyes and waterproofing agents and as an aerosol surface cleaner. For such chemical versatility, the MEK market is estimated to increase to $USD 3.26 billion and its production to 1.754 million tons by 2020 [3]. Mostly of MEK uses are directly related to industrial application, however, recent studies suggest the use of MEK as a possible fuel for spark-ignition engines. In the work presented by Hoppe et al. [4] exhaustive research concluding that MEK offers superior performance over current gasoline, less oil dilution, lower hydrocarbon emissions, and better cold-start properties [4].

On the other side, MEK vapor is heavier than air, it is soluble in water and some other organic solvents. It can form explosive mixtures with oxygen (or air) when they are in concentrations between 1.4 and 11%. It can disperse long distances, consequently it has the possibility of ignition from a distance [1]. Regarding human damage, it has been reported that the amount of MEK at which there are no adverse results (The Threshold Limit Value) is 200 ppm in 8 h, and for short exposures of 15 min, up to 300 ppm. MEK can be rapidly absorbed through the lungs by inhaling it as vapor. It can even be absorbed by contact with the skin. It is known that contact of MEK with a large area of skin can be similar or equivalent to

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increased absorption, increasing an individual's exposure to MEK and causing cytogenic and lung damage. In a study reported by the Center for Occupational Health and Safety it was observed that 143 volunteers exposed to 220 ppm MEK for 4 h, reported headache, sore throat, nausea, and general discomfort. On the other hand, the neurotoxic effects of MEK have been extensively investigated [2,5]. MEK has shown negative results in humans, spontaneous motor decrease and changes in behavior patterns. Other research suggests that MEK can cause peripheral neuropathy when mixed with other organic solvents like n-hexane or methyl butyl ketone, it is even mentioned that it can potentiate the harmful effects of such chemicals [6].

MEK also named 2-butanone is synthesized from C4-raffinates [7]. However, petroleum is a recognized finite resource and is pointed out as a major cause of environmental issues. So, the production of MEK from a renewable resource may be considered as a relief for such problematic. Nevertheless, MEK bio-based production is not yet well based. Currently, several works have proposed biotechnological conversion starting from pure sugar as raw material. This best-case assumption would be considered as the upper limit for MEK production, however, those reported yields differ largely. MEK might be produced by direct fermentation of sugar, however, its production is quite weak with yields of approximately 0.004 $g_{MEK}/g_{glucose}$ [8]. Another bio-based alternative is the production of MEK via decarboxylation of levulinic acid, which might be obtained initially from lignocellulosic material. However, all reported yields are not relevant even if acetic acid and acetone are produced as byproducts [9]. A quite promising alternative to produce MEK is utilizing 2,3- Butanediol (2,3-BD) as intermediate. The interesting picture 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 $g_{2,3\text{-}BD}/g_{glucose}$ [10,11]. Further, the direct dehydration of 2, 3- BD is performed with yields superior to 95% [12].

Notwithstanding the relatively high yields for 2, 3-BD fermentation and further dehydration the downstream process is not well explored so far. Besides, byproducts like isobutyraldehyde (IBA) and 2,3-BD are valuable products, which may increase valorization in a bio-based refinery for MEK production since both have important participation on the food industry and biosynthesis of isobutanol, respectively [13]. 2,3-BD has multiple applications. For example, it can be used as an intermediate for rubber production. Due to its low freezing point, it can be used as an antifreeze compound. Additionally, 2,3-BD has shown its potential in the production of fumigants, perfumes, inks, explosives, and softening agents [14]. On the other hand, Isobutyraldehyde (IBA) is used as an additive for the preparation of fragrances and flavors. Also, it is used as a precursor for the production of plasticizers, isobutyric acid and isobutanol [15]. Note, despite those promising thermodynamic properties aforementioned, the MEK purification stills challenging since two azeotropes are present in the mixture MEK/IBA/2,3-BD/Water (See Fig. 1).

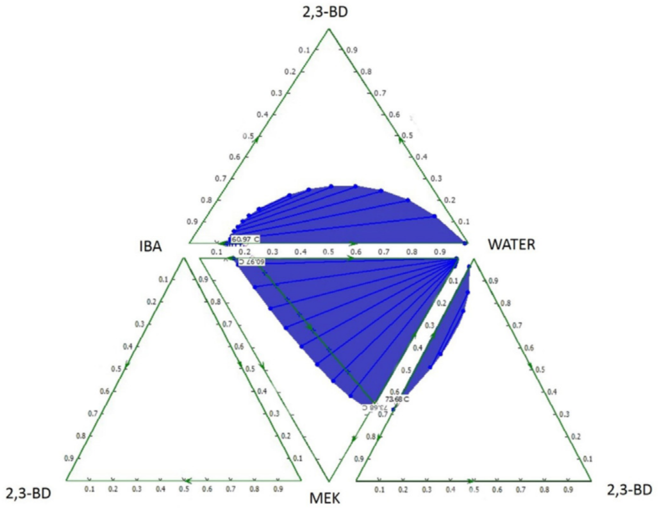

Fig. 1. Heterogeneos azeotropes (mole basis) in the feed mixture.

Due to the oil-based methodology used to produce the MEK, the proposals that properly analyze the MEK/IBA/2,3-BD/Water mixture are really scarce. 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. [16] approached the purification of the MEK-water mixture based on a membrane process, the same mixture that Murphy [17] approached, on the other hand, Berg [18] patented the purification of the MEK-Ethyl Acetate mixture.

Recently Penner et al. [19] presented the conceptual design of 4 alternatives for the purification of the MEK/IBA/2,3-BD/Water mixture, however, his proposal is entirely based on distillation columns and decanters. However, it does not propose a robust design strategy with clear objective functions and with recovery and purity restrictions. As usually, distillation is always considered as the first option for this kind of challenging separation. However, the main drawback of using distillation columns is the energy consumption and the thermodynamic efficiency. On the other hand, process intensification (PI) is a promising alternative which support environmental and economic awareness, and represent a more profitable and eco-efficient option [20]. Understanding PI concept as a process that must contain three different kinds of improvements achieved through (1) the integrations of operations, (2) the integration of functions, and (3) the integration of phenomena [21], or even further a process distinguished by five characteristics: reduced size of equipment, increased performance of process, reduced equipment inventory, diminishment in using utilities and raw materials, and increased efficiency of process equipment [22], hybrid processes are a clear example of intensified processes. Hybrid processes based on both liquid-liquid extraction and distillation columns have proven its efficacy in reducing global energy consumption regarding downstream processes. The main reason for reducing energy requirements lies on the fact that a liquid-liquid extraction (LLE) column helps on breaking the thermodynamics interactions among components, consequently the energy requirement is reduced. Additionally, hybrid processes have shown capabilities of improvement in many performance indexes. For example, Errico et al. [23] showed a total annual cost reduction about 25% when a hybrid process of this kind is considered for biobutanol purification. In the same way, Avilés-Martínez et al. [24] also showed the advantages of using LLE to purify bioethanol, reducing energy consumption and TAC. So, with all aforementioned background a hybrid process, based on LLE and distillation columns, could be prospected as a promising alternative.

On the other hand, when the separation process is approached, many studies are focused on reducing, initially, the economic impact and sometimes the environmental impact [25]. The inclusion of at least two objective functions has been considered nowadays from a multi-objective optimization point of view [26]. However, other key objectives are commonly set aside [27—29]. For example, both the control properties and the inherent risk are not considered in the first design stage. This two-step methodology may present several drawbacks for both considerations. Regarding control properties, many separation schemes may present infringement of dynamic restrictions, over-design, and low performance, so a global performance of any proposed design cannot be guaranteed [30]. Further dynamic consequences, may be observed separation alternatives with poor flexibility on operative performance. Regarding the inherent safety, this traditional approach can generate separation alternatives with high risk related to the use of heat duties, explosive liquids, and the size of the column. Note, for example, the purification of methyl-ethyl ketone involves to handling relatively dangerous components such as methyl-ethyl-ketone, 2,3-BD, and isobutiraldehyde which according to the Hazardous Material Information System (HMIS) possess a rating scale of health-flammability-physical hazards of 2-3-0, 2-2-2, and 2-3-0, respectively. In this way, not including risk analysis in the separation processes can generate a misleading assessment of the risk of the global process. Additionally, considering the toxic and physicochemical characteristics of the component of interest, it is quite important that a methodology can be implemented in the initial stages that reduces the risks associated with the treatment of MEK; find the conditions that minimize the risk of continuous and instantaneous leaks of matter and energy. Even that it is able to minimize the risk of catastrophic events associated with the explosive properties of the MEK, for example the inherent risk analysis.

In a broader vision, considering the economic, environmental and security objectives is taking a step forward in the continuous search for sustainable processes. For example, Jimenez et al. [31,32] lists a series of characteristics that a process must have to be evaluated within a green process framework. According to the work of these authors, some metrics in the processes must be jointly evaluated, highlighting the analysis of the life cycle of the process, its controllability, its economic impact as well as the risks associated with this process.

In order to avoid many drawbacks for do not include many performances index in early-design stages, an effective alternative is to include both the control properties and the risk assessment jointly with those considered as critical issues, the economic and environmental impact.

With this in mind, the central idea of this article is to generate a novel and intensified alternative for the separation and purification of MEK. As a fundamental part of the process intensification philosophy, it must be compared with a conventional version to observe its improvement in various performance indices. Currently, the only process to carry out this task is the one reported by Penner et al. [19], So a direct comparison with this work will be attempted. This does not mean that the Penner et al. [19] Proposal will be intensified, the proposal developed in this article is totally new, based on a hybrid process of liquid-liquid extraction and distillation. In other words, the contribution of this work is the proposal of a hybrid and intensified alternative that surpasses the performance of other previously published alternatives to perform the same task. This proposal can generate an intensified alternative that considers a balance between several objective functions, in other words, through a joint design and optimization, alternatives will be obtained considering economic, environmental, controllability and inherent safety aspects according to the current needs of the industry. As far as the authors are aware this is the first work that proposes an intensified alternative for MEK purification and handles those four targets simultaneously and tries to understand the role of the design variables with those four objective functions.

2. Problem statement and case of study

The quaternary mixture involved in this separation is formed by MEK, water, 2,3-BD, and IBA. At first sight, it would look not so complicated, however, there are two binary heterogeneous azeotropes, MEK/water, and IBA/water, both azeotropes at atmospheric pressure (see Fig. 1). In this work, the ratio among all components is 65 wt% MEK, 18 wt% water, 10 wt% 2, 3-BD and 7 wt% IBA (See Table 1) which is indeed a relatively common outlet stream of a dehydration reactor [12,33,34].

Recently Murphy [17], proposed the use of p-Xylene to extract MEK from an aqueous solution. In his work, Murphy studied a set of solvents, highlighting pentane, isopentane and both isomers of xylene. As a result for this task, p-xylene resulted as the best option for this extraction.

With this in mind, this work is proposes a hybrid scheme based on a liquid-liquid extraction column and distillation columns (see Fig. 2).

Note in Fig. 2, the first LLE extractive column aims to facilities the azeotrope separation producing at bottoms a stream with water and 2,3-BD, and at the top a mixture of IBA, MEK, p-Xylane, and traces of water. Furthermore, five columns perform the purification of all components. In the case of IBA and MEK, the purification is developed in tow steps since traces of water avoid to perform it in fewer columns. In order to use MEK for industrial purposes, the product purities in all processes were at least 99.5 wt% MEK, 99.5 wt% 2, 3-BD and 95 wt% IBA [35]. Also in the case of the solvent, p-xylene recovery is obtained above 99.9% wt.

The process was initially simulated employing Aspen Plus 8.8, the thermodynamic properties were estimated with the NRTL-HOC model. The thermodynamic properties package was selected according with the components in the mixture, their physical and chemical properties and process conditions. The NRTL model allows to predict the formation of two liquid phases which is a typical behavior of mixtures that contains organic compound and water. On other hand, the Hayden-O'Connell equation allows determinate the vapor behavior of mixture with no polar and polar compounds

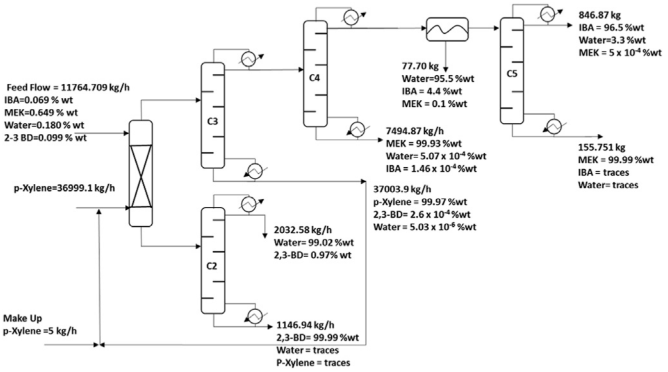

Fig. 2. Intensified alternatives for the MEK purification.

Table 1
Feed characterization.

Feed Concentration (wt %)				Vapor fraction	Flowrate (kg h-1)	Temperature (K)
Water	IBA	2,3-BD	MEK			
0.18	0.07	0.1	0.65	0	11764.7	298

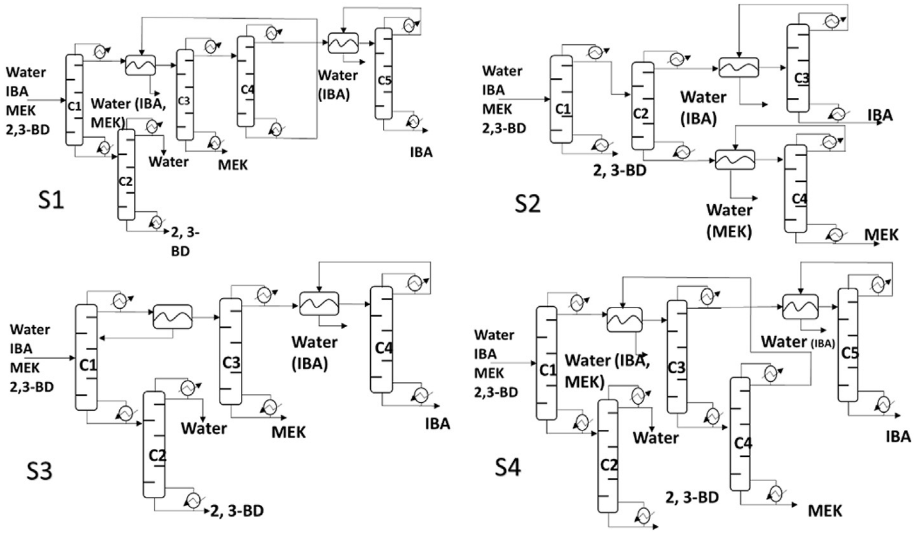

Fig. 3. Pure Distillation Alternatives for MEK purification. Fig. 1a) scheme S1, Fig. 1b) scheme S2, Fig. 1c) scheme S3, Fig. 1d) scheme S4.

at low-medium pressures. In the same time, when the interaction and behavior of mixtures that contains compounds with polar functionals groups are unknown, it is necessary take into consideration a thermodynamic model with the capability to predicts the non-ideal behavior on vapor phase caused the polarity of chemical groups such as alcohol, esters aldehydes, etc. Based on the compounds present in the mixture the Hayden O'Connell equation offers the most reliable completely predictive [19,36–38]. All binary interaction parameters were taken from the same simulator Aspen Plus and they are shown in Table S1 in Supplementary Material.

During this work, this hybrid scheme was rigorously evaluated using a multi-objective optimization considering four objective functions, the total annual cost (TAC), the eco-indicator 99 (EI99), the condition number, and the individual risk as economic, environmental, controllability and safety indexes, respectively. Moreover, the role of the design variables will also be explored.

Just for comparison purposes, the hybrid alternative was compared with four conventional schemes which are based on only distillation columns and decanters (See Fig. 3). Those alternatives were previously reported by Penner et al. [19]. Note for a fair comparison all those four schemes were also optimized considering the same objective functions. As a general description, in the first four schemes, the heaviest component (2, 3-BD) leaves the downstream process either the first or second column, always as a bottoms product. Excluding scheme S2 (Fig. 3b), the distillate stream of the first column is sent to a decanter, with a top phase ok MEK in mixture with IBA and water.

Further, without a remarkable split between water and IBA/water, schemes S1 (Fig. 3a) and S4 (Fig. 3c) demand five conventional columns to separate MEK at high purity, on the other hand, S2 (Fig. 3b) and S3 (Fig. 3c) require only four distillation columns for the same purpose. Note, scheme S3 lacks a distillation column since IBA stream is further mixed with the distillation stream of the first column to break up the distillation boundary. Finally, the last column has the purpose of purifying IBA at the bottom of the column, while the azeotrope at the top is recycled back to the decanter.

3. Evaluation indexes and optimization problem

The optimized operation of MEK purification process is essential to run a bio-based MEK industry, in order to compete effectively with current sources, in future terms, with those oil-derived fuels. Next, the optimization problem is assessed for all separation alternatives, considering the objectives, constraints, and design variables involved. Overall, all design problems in this work are formulated as a constrained global optimization problem.

3.1. Total annual cost calculation

For economic evaluation, in this work, it is used the total annual cost (TAC). Initially, this method was reported by Guthrie [39]. The cost estimation is performed considering separated units; in other words, the method calculates the capital cost as the sum of the annualized cost, plus the operating cost. The cost calculation is carried out with the next equation [40].

$$TAC = \frac{Capital\ costs}{Payback\ Period} + Operating\ Costs \qquad (1)$$

As payback period it is considered 5 years and an operation annual time of 8500 h. Besides, the cost related to heating and cooling water were taken from Luyben et al. [41]. 5 years as payback period is a well accepted time, and has been commonly used in several studies regarding chemical plants [42].

3.2. Environmental index calculation

In order to evaluate the environmental impact, it is used the eco-indicator 99 (EI99), a European model based on Life-cycle assessment (LCA), This methodology was based on the contribution of the experts at National Institute of Public Health and the Environment (RIVM) in Switzerland. Currently, eco-indicator 99 values are available for materials, production processes, transport processes, energy generation processes, and disposal scenarios. The eco-indicator values can be regarded as dimensionless figures. The absolute value of the points is not very relevant as the main purpose is to compare relative differences between products or components. The scale is chosen in such a way that the value of 1 Pt is representative for one-thousandth of the yearly environmental load of one average European inhabitant [43]. In this manner, it is possible to evaluate the overall environmental loads associated with a process, product or activity that identifies and quantifies the material and energy used. So, many works have used this methodology to measure and improve the environmental performances of several processes $^{25\text{-}26}$.

The methodology associated with the calculation of the eco-indicator 99 considers 11 impact categories. These 11 categories are separated into three groups according to the nature of the damage caused: 1) human health, 2) damage to the ecosystem, and 3) damage to natural resources. In this study, for the calculation of the eco-indicator 99, three impact factors were considered: steam for heating, electricity used for pumps and steel used in the construction of main equipment. The values of these three factors are shown in Table 2. The data associated with these factors are commonly taken from standardized databases [43]. The Eco-Indicator 99 (EI99) is defined as follow:

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

Where b_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 by category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in category d, and δ_d is the normalization factor for damage of category *d*.

3.3. Inherent safety index

To quantify the inherent safety associated with the purification schemes, an analysis was made through the individual risk index (IR) which is defined as the risk that a person has considering its position in the process plant. The calculated risk involves damage caused by injury or death, its frequency and probability of affectation. The calculation of IR does not depend on the number of people exposed to risk. Mathematically, the individual risk can be defined as the frequency of an accident (f_i) multiplied by the probability of affectation in a specific position ($P_{x,y}$) according to eq. 3

$$IR = \sum f_i P_{x,y} \tag{3}$$

The frequency and probability of involvement can be determined by quantitative analysis (QRA). This methodology allows to identify potential accidents and evaluate their consequences and damages. Initially, the QRA analysis identifies possible accidents, which is any release of matter or energy [46]. For distillation columns, incidents can be grouped as continuous and instantaneous releases. These incidents were previously determined through a risk and operability analysis (HAZOP). Fig. 4 shows a tree of events that includes the possible accidents associated with a distillation column as well as their respective frequencies (f_i). Similarly, the frequencies were taken by a previous study of the American Institute of Chemical Engineers [46]. The event tree considers the following possible accidents: boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), flash fire, and toxic release. On the other hand continuous releases: jet fire, flash fire and toxic release.

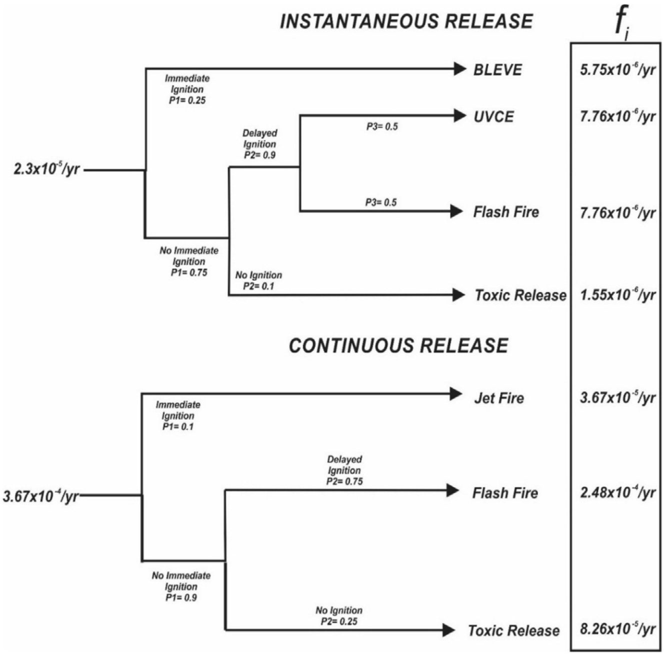

Fig. 4. Events trees diagrams for distillation columns.

Once the possible accidents have been identified, the causative variables must be known as the second step. For example for BLEVE, jet fire and flash fire the causative variable is thermal radiation (E_r), for UVCE it is the overpressure (P_o), and for the toxic release it is the concentration (C). In this work, a distance of 50 m was considered for all the variables The calculations of causative variables to each accident have been shown previously by many authors [47,48].

3.3.1. Probability of affectation (consequences analysis)

As a final stage for the calculation of IR, the probability of affectation must be calculated (probability of injury or death). This probability can be obtained with probit models. A probit model relates a person's response to the dose received from a certain incident, such as heat, pressure or radiation. In this work, a probit function was used to model the probability of death due to overpressure and third-degree burns [46,49,50]. The parameters to Eq. (4) are shown in Table 3. The probability of damage is obtained by replacing probit values in Eq. (5) [50].

$$Y = k_1 + k_2 \ln V \tag{4}$$

Table 2
Unit eco-indicator used to measure the eco-indicator 99 in all cases of study (Geodkoop and Spriensma).

Impact category	Steel (points/kg)	Steam (points/kg)	Electricity (points/kWh)
Carcinogenics	6.32E-03	1.18E-04	4.36E-04
Climate change	1.31E-02	1.60E-03	3.61E-06
Ionising radiation	4.51E-04	1.13E-03	8.24E-04
Ozone depletion	4.55E-06	2.10E-06	1.21E-04
Respiratory effects	8.01E-02	7.87E-07	1.35E-06
Acidification	2.71E-03	1.21E-02	2.81E-04
Ecotoxicity	7.45E-02	2.80E-03	1.67E-04
Land Occupation	3.73E-03	8.58E-05	4.68E-04
Fossil fuels	5.93E-02	1.25E-02	1.20E-03
Mineral extraction	7.42E-02	8.82E-06	5.7EE-6

Table 3
Probit parameters.

	K_1	K_2	V
Thermal radiation	−14.9	2.56	$\frac{\left(t_e E_r^{4/3}\right)}{10^4}$
Overpressure	−77.1	6.91	p^o

$$P_{x,y} = 0.5\left[1 + erf\left(\frac{Y-5}{\sqrt{2}}\right)\right] \tag{5}$$

Finally, the result obtained by Eq. (5) is replaced together with data of LC50, inside the equation Eq. (3) to obtain the individual risk (*IR*).

3.4. Controllability index calculation

Among several alternatives to calculate the control properties of separation schemes, a relatively well-known technique is the calculation of the condition number through the singular value decomposition (SVD) of the relative gain matrix of the evaluated separation scheme at a nominal point, obtained in an open-loop control policy. The application of this techniques is not novel, some authors have used this kind of methodologies for studying conventional distillation columns [51,52], besides, this technique has shown its ability to evaluate also more complex distillation systems [53,54]. However, as has been written those controllability tests were performed as the second task in the design process in contrast with the proposal of this work. Through several studies on separation schemes, SVD has shown that under certain conditions, multivariable model-based techniques result in controllers that can be decomposed into the SVD structure [55]. Sagfors and Waller [56] have shown that in distillation systems SVD is a feasible control structure, even if a quantitative model is lacking. On the other hand [55], claim that even if we had a quite good model and some model-based technique is applied, it is possible to end up with a controller which is indeed very close to the SVD controller anyway.

The decomposition into singular values of a given matrix can be represented as the product of three components:

$$K = U\Sigma V^T \tag{6}$$

Where *K* is an *n* x *m* matrix, *U* is an *n* x *n* orthonormal matrix called the “left singular vector”, *V* is an *m* x *m* diagonal of scalars commonly called "singular values". These values can be organized, according to their value, for example: $\sigma_1 > \sigma_2 > \sigma_3 \ldots \sigma_m > 0$. The product obtained by dividing the maximum singular value by the minimum singular value is known as the condition number of the gain matrix. The condition number is a measure of the relative difficulty that a decoupled multivariable control problem can present [57]. The condition number is calculated as follow.

$$\gamma = \sigma_{max}/\sigma_{min} \tag{7}$$

In terms of the process control, a large condition number may indicates that it will be impractical to satisfy the entire set of control objectives (no matter the control strategy used). In a physical sense, the condition number is the ratio of the maximum and minimum open-loop decoupled gains of system. A large condition number is evidence that relative sensitivity of the case of study in one multivariable direction is very weak [58]. SVD methodology does not predict or solve all the dynamic problems in real chemical plants; however, it is relatively easy to understand and identify basic control difficulties.

For the control analysis, each purification alternative provides a relative gain matrix in its nominal state. To obtain this matrix, the schemes are subjected to a disturbance in a manipulable variable (reflux ratio, reboiler duty, etc.) The magnitude of the disturbance is small enough (0.5%) that a first-order behavior can be assumed according to many previous work [54,59]. To avoid the SVD dependence of system unit used (variables limited between 0 and 1, and high values for reflux ratio and reboiler heat duties) the approach of the proposal used in here is to limit the variables described. Since the maximum opening of the control valves can be twice the nominal value, the valves are theoretically open by 50%. In this way, to generate the relative gain matrix, a step change must be applied in the manipulated variable, and subsequently, this change must be divided by two. With this consideration, you get the same range of variation when opening and closing the control valves. The consequence of this consideration is to relate both the amount of change and the magnitude of change in a range of 0 and 100%. Moreover, with this form of scaling, and with the term 1/2P in equation 15, the manipulated variables are simultaneously dimensionless standardized. For example, a relative gain matrix for the purification of three components could be stated as:

$$\begin{bmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{bmatrix} = \begin{bmatrix} \dfrac{x_{C1}^{v_1} - x_{C1}^{sp}}{\frac{1}{2}P} & \dfrac{x_{C1}^{v_2} - x_{C1}^{sp}}{\frac{1}{2}P} & \dfrac{x_{C1}^{v_3} - x_{C1}^{sp}}{\frac{1}{2}P} \\ \dfrac{x_{C2}^{v_1} - x_{C2}^{sp}}{\frac{1}{2}P} & \dfrac{x_{C2}^{v_2} - x_{C2}^{sp}}{\frac{1}{2}P} & \dfrac{x_{C2}^{v_3} - x_{C2}^{sp}}{\frac{1}{2}P} \\ \dfrac{x_{C3}^{v_1} - x_{C3}^{sp}}{\frac{1}{2}P} & \dfrac{x_{C3}^{v_2} - x_{C3}^{sp}}{\frac{1}{2}P} & \dfrac{x_{C3}^{v_2} - x_{C3}^{sp}}{\frac{1}{2}P} \end{bmatrix} \tag{8}$$

Where all elements K_{ij}, are the relative gain matrix. The elements of the first row in the right side correspond to the differences among the mass purity of component A in the nominal state x_A^{sp}, and the mass purities after disturbance p.$x_A^{V_1}$ is the mass purity of a chemical compound after a disturbance in manipulated variable 1,$x_A^{V_2}$ is the mass purity of a chemical compound after a disturbance in manipulated variable 2, $x_A^{V_3}$ is the mass purity of a chemical compound after a disturbance in manipulated variable 3. In this work, the relative gain matrix was built as N x N, according to the N output streams of the separation scheme.

3.5. Thermodynamic efficiency

Even thermodynamic efficiency was not considered as an objective function; it was computed as a complementary metric in order to differentiate all process presented in Figs. 2–3. When continuous-flow and steady-state-flow schemes are analyzed (such as those separation process in Figs. 2–3) are analyzed under the laws of thermodynamics, thermodynamic efficiencies can be computed through standard expression as explained in the work of Seader and Henley [60].

$$\eta = \frac{W_{min}}{LW + W_{min}}$$

Where W_{min} is the minimum work for separation and $LW = T_0 \Delta S_{irr}$, is the waste of work in the system and η the thermodynamic efficiency.

3.6. Multi-objective optimization problem

The objective function would take into account those four targets already mentioned. So the objective function is described as:

$$\mathrm{Min}(TAC,\ EI99,\ IR,\ \gamma)=f\left(N_{tn}, N_{fn}, R_{rn}, F_{rn},\ P_{cn},\ FC_{cn}\right) \tag{9}$$

Subject to. $\vec{x_m} > \vec{y_m}$ Where TAC is the total annual cost, EI99 is the eco-indicator 99, IR is the individual risk, γ is the condition number and Rec the recovery for all chemical compounds. N_{tn} are column stages, N_{fn} is the feed stage, R_{rn} is the reflux ratio, F_{rn} is either distillate or bottoms flux, moreover for IR calculation many physicochemical properties are considered such as molecular weight combustion heat of combustion, LC_{50} and so on; y_m and x_m are the vectors of obtained and required purities for the m_{th} components, respectively. In this multi-objective optimization exercise, about 25 variables, continuous or discrete, were considered. The flows of the compounds of interest and their respective purities were considered as constraints. Table 4 shows the type of variables used and the search range in the optimization process.

The variables related to a physical aspect of the distillation columns considered average limits of industrial distillation columns [61]. For the control study, the variables to be controlled were the purities of 2,3-BD, IBA, MEK, and water. Additionally, as manipulable variables were considered the distillate flows, and heat duties associated with the output currents of said products. Since Penner et al. [19] in their work commented on a problem regarding components recovery, when the pure distillation schemes were evaluated, an additional objective function was included, the maximization of recoveries.

4. Global optimization methodology

Once the objective functions are modeled, the optimization procedure was carried out. To optimize the case of study, this work employs a hybrid stochastic optimization algorithm, Differential Evolution with Tabu List (DETL). Differential evolution (DE) was proposed by Storn [62] considering a single objective. Further, the method was adapted by Ref. [63] to solve multi-objective problems. This evolutionary method employs the classical Differential Evolution steps, however; its seek action is improved through the Tabu List (TL) concept. In general terms, the combination of DE and TL avoids revisiting points already evaluated [64]. A comprehensive description of this DETL algorithm is provided by Sharma and Rangaiah [65].

The application of the method was performed by means of a hybrid platform, which involves the interaction among Microsoft Excel, Aspen Plus, and Visual Basic. As a brief description, the vector of decision variables (initially proposed by the algorithm) is sent to Microsoft Excel, which attributes those values to the process variables in Aspen Plus to simulate the model. After the simulation it is completed, Aspen Plus returns Microsoft Excel the results in the form of a vector. Finally, with those data, Microsoft Excel evaluates the objective function and proposes new values of the decision variables in concordance with the stochastic optimization method. For the optimization task, the following parameters were used in the DETL method: 200 individuals, 1000 generations, a tabu list of 50% of total individuals, a tabu radius of 2.5*10−6, 0.80 and 0.6 for crossover and mutation fractions, respectively. These parameters were obtained from the literature and previous tuning process [66].

Table 4
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})

5. Results

In this section, all results obtained after robust optimization are presented. Note, even though four objective functions are jointly the results shown in Figs. 5–7 are presented in a conventional 2D Figure for better understanding. All Pareto fronts were obtained after 200,000 evaluations. Subsequently, no substantial improvement was observed, so it was considered that under the evaluation criteria, the DETL method reached convergence. Thus the results reported here correspond to the best solution obtained. The product purities in all processes are 99.5 wt% MEK, 99.5 wt% 2, 3-BD and 95 wt% IBA.

Regarding the correlation between TAC and IR, Fig. 5 shows the tendency between both objectives. It was possible to obtain safer alternatives; however, as long as IR becomes lower the TAC increase notably. Note, many designs accomplish the task of being a safer process, however, the difference between the lower TAC zone and the upper TAC zone is almost three times bigger. So, the best solution for this optimization process is the highlighted point, which was selected from the zone where both objective functions reach its minimum. During the optimization process, the role of some design variables was observed; a clear trend was observed between the diameter and the IR value. For example, the lowest values of IR were obtained while the reflux ratio was low as well.

In the same way, the lowest IR values was obtained with

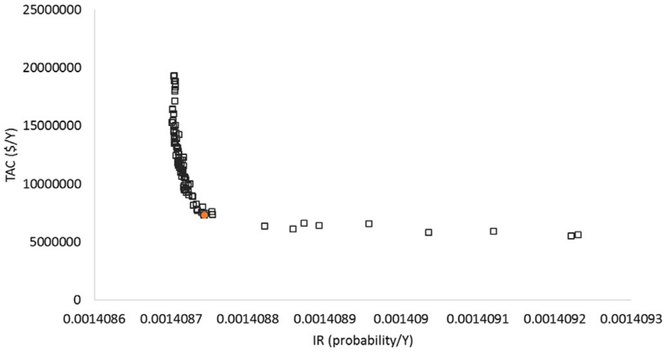

Fig. 5. Pareto front between TAC and IR for the intensified alternative.

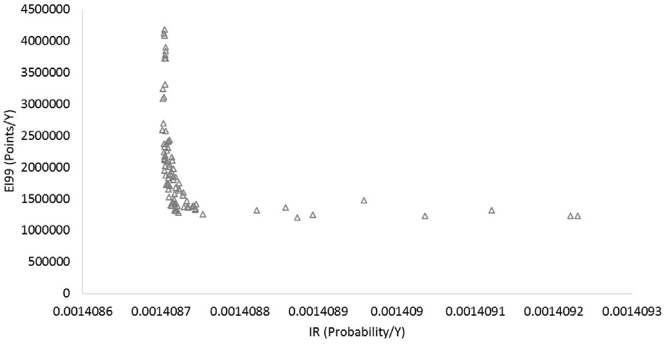

Fig. 6. Pareto front between IR and EI99 for the intensified alternative.

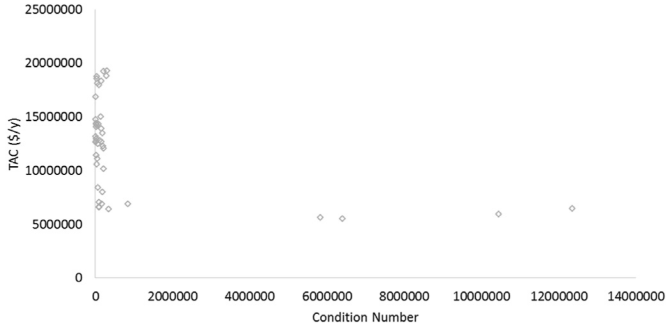

Fig. 7. Pareto front between TAC and CN for the intensified alternative.

columns of small size (short diameter). Going deep on those trends it is quite interesting the behavior aforementioned; both trends have its impact in TAC. For example, as long as reflux ratio decrease the reboiler heat duty decrease as well; however, the number of stages increase to compensate the energy invested and reach a high purity. This preliminary conclusion connects immediately with Fig. 6 where IR and EI99 are studied. Note that a similar trend is observed, low IR values correspond directly with high EI99 values, and remember the EI99 is strongly connected with the use of steam and steel. So, low IR values were obtained with low reflux ratio/ reboiler duty. However, the increase in EI99 in Fig. 6 is not due to the diminishment of reboiler duty is due to the increase in stages which are associated with the amount of steel used in each column.

Regarding the evaluation of TAC and condition number, Fig. 7 shows the Pareto front for both objective functions. The condition number can let us know the expected controllability properties of those analyzed schemes. Even though the sizing of the columns is one of the design variables that use to correlate with the condition number [67], during the optimization test the design variable that shows tendency was the reflux ratio. As long as reflux increase the condition number decrease, so high TAC values are related to low condition number values (meaning that built-in controllability has its cost). Please observe in Table 5 the main parameters to reproduce the best solution obtained of the intensified alternative.

Regarding the evaluation of TAC and EI99 values, the antagonist behavior observed was according to the work previously reported by Sánchez-Ramírez et al. [68]. In the upper zone of the Pareto front, commonly, there are designs with columns of large size but relatively low heat duties. This combination produces high TAC values in conjunction with small values of EI99. The lower zone, on the other hand, is mainly composed of columns of reduced size but large heat duties. Finally, in the middle of both zones, the objective functions reach their minimum values. Some variables affect the increase/decrease in both functions. For example, the reflux ratio plays a major role in this kind of objective functions; the increase of this variable will consequently increase the reboiler duty, cost of services and the corresponding section of the EI99.

On the other hand, Table 6 shows the objective functions obtained after the optimization process of the pure distillation schemes. At first sight, it would be easy to select the best alternative among those four schemes. The cheapest alternative is the S4, and the most expensive is the S3. Moreover, the TAC difference is high by several magnitude orders. However, having into consideration the amount of MEK recovered in the separation process, the view change completely. In other words, despite within the objective function is included to accomplish certain recovery of all components, after optimization, the recoveries were not completely equal. After the optimization process, the MEK recoveries obtained after optimization, for such purities already mentioned were, 99.9 wt%, 65.4 wt%, 56.6 wt% and 44.9 wt% for S2, S1, S3, and S4 respectively. For the byproducts 2, 3-BD/IBA the recoveries were 99.9/61.3 wt%, 99.9/74.4 wt%, 99.9/99.7 wt%, and 99/98.8 wt% for S2, S1, S3, and S4 respectively. Evidently, not all recoveries accomplish the constraint previously considered; a relatively simple way to understand such behavior is to place in the quaternary diagram (Fig. 1) the mixture before entering decanter which would be posteriorly purified into MEK. Note that, such streams, in schemes S1, S2 and S4, are relatively far from the ax of the binary mixture water-MEK, consequently it is quite complex to separate such mixture in single equipment. This is the reason why, in some cases a leaving stream from the decanter is returned back to a separation column, trying to decrease waste material.

At first sight, schemes seem similar; however, a key difference is

Table 5
Design parameters and performance indexes for the intensified scheme.

	LLE	C2	C3	C4	C5
Number of stages	10	33	45	45	54
Reflux ratio		3.483	0.529	16.636	5.01
Feed stage	1, 10	4	27	5	23
Column diameter (m)	1.455	1.285	1.407	1.544	1.098
Operative pressure (kPa)	101.353	101.353	101.353	101.353	101.353
Distillate flowrate (kmol h^{-1})		111.997	123.297	19.193	12.9292
Condenser duty (kW)		5776	1693	3191	694
Reboiler duty (kW)		6354	4125	3202	727
η (%)	32.56				
TAC ($ y^{-1})	7903251				
Eco-Ind (points y^{-1})	1338593				
Condition Number	88121				
IR (Probability y-1)	0.0014087				

Table 6
Objective function for pure distillation schemes.

	S1	S2	S3	S4	S5 (Intensified)
TAC ($ y^{-1})	104719750	31011553	153136510	4435273	7903251
Eco-Ind (points y^{-1})	2993581413	14669116	16200579	891801275	1338593
Condition Number	3.8	3.99	4.78	147.5	88121
IR (Probability y-1)	0.00167156	0.0013323	0.00133414	0.00166587	0.0014087

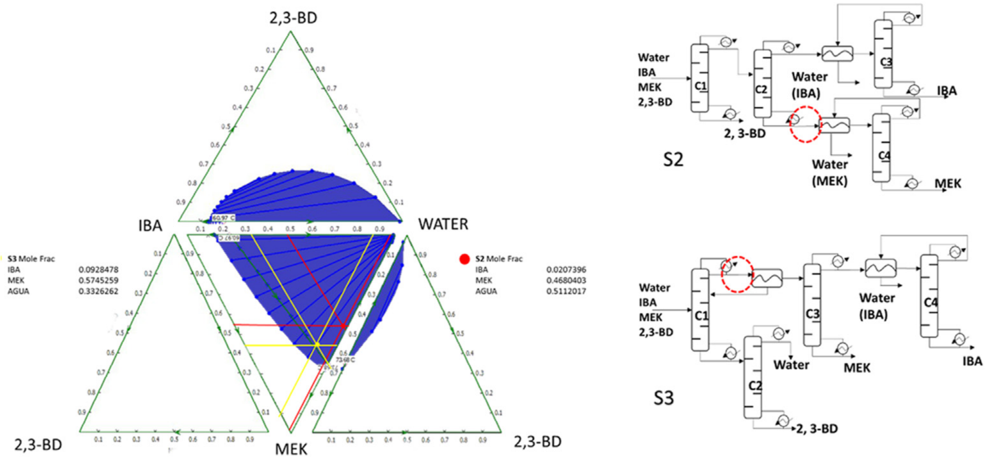

Fig. 8. Thermodynamic analysis of the decanter feed mixture in schemes S2 and S3.

the location of decanters. The role of the decanter is to promote the separation when three phases are present. However, the decanter is not always capable to separate entirely those three phases due to the ratio among components. Observe Fig. 8, we take the mixture before entering the decanter as examples to subsequently purify MEK. Please note in the quaternary diagram, mixture of scheme S2 is the closest one to the binary mixture MEK-WATER (binary ax MEK-WATER). On the other hand, the mixture S3 is the farthest one, note also because of the performance of decanter, a leaving stream of decanter must be returned to column C1 to avoid wasted MEK; contrarily, in scheme S2 the leaving stream from decanter contains only water and few MEK traces.

A similar situation happens with the other schemes, beacause of the decanter location, is not possible to recover a considerable amount of MEK.

Additionally, it is easy to see that the main difference between the S2 design and the rest, is the separation that is performed in column C1 in all the schemes in Fig. 3. That is, in scheme S2, in the bottom of C1 is purified/obtained 2,3-BD, while in schemes S1, S3 and S4, the bottom of C1 is fed to column C2 in order to purify 2,3- BD and water.

In other words, the column C1 has a key role in separating the mixture. Schemes S1, S3, and S4 try to remove as much water towards the bottom of the column trying to get as far away from the azeotropic zone as possible, while in S2 only 2,3-BD is sent to the bottom of the column.

With this in mind, Fig. 9 shows the difference and why it is not possible to obtain high recoveries in schemes S1, S3 and S4.

Fig. 9 shows a sensitivity analysis by varying the bottoms rate of column C1 and observing what happens to the flow (kg/h) of each component. The vertical green line shows the point where column C1 of scheme S2 is operating. Under that bottoms rate, notice that it is possible to purify the 2,3-BD in the first column. On the other hand, schemes S1, S3, and S4 must be designed with a larger bottom rate to obtain 2, -3 BD, and water to subsequently both be purified. Note then, by continually increasing the bottoms rate to obtain the greatest amount of water, you reach an infeasible design area due to the presence of the various azeotropes already known. Once the azeotropic zone has been crossed, it is possible to return to operating with bottom rates above 3290 kg/h. However, a considerable amount of MEK is already present in that feasible area, evidently decreasing the overall recovery of MEK. The greater the amount of water obtained at the bottom of the column, the greater the amount of MEK entrained and the overall recovery is decreased.

Possibly, it may seems feasible to design the column C1 before reaching that non-feasible area and not drag MEK to the bottom of the column. However, consider that before reaching the infeasible zone, the amount of water sent to the bottom is approximately 1050 kg/h, which would cause that approximately 1065 kg/h would be sent to the column dome. That large amount of water would make MEK recovery even more difficult.

On the other hand, a sensitivity analysis was performed to represent various operating temperature conditions of the first decanter in S1, S3 and S4. This sensitivity analysis was made considering the stream at the top of the best point obtained in S1. Fig. 9 also shows the analysis.

Please note that, even though the operating temperature varies, there is no variation in the separation of the three phases or in the

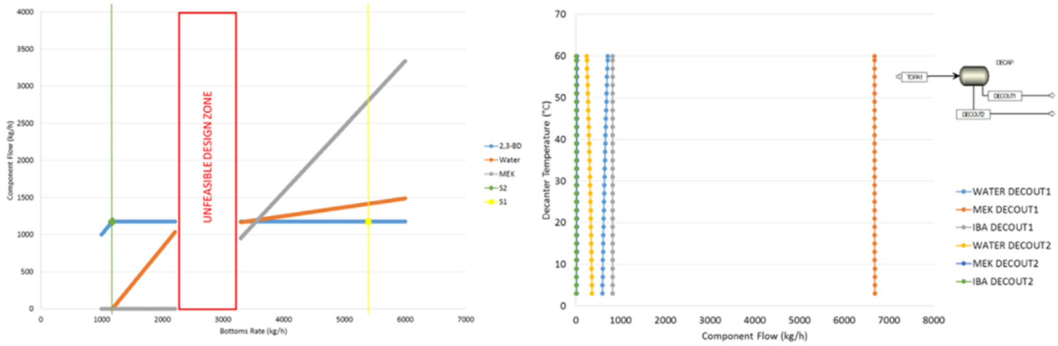

Fig. 9. Sensitivity analysis for C1 and first decanter in schemes S1, S3 and S4.

flows obtained by component. In other words, the decanter cannot completely separate all the water present in the 3 phases, which further complicates the overall recovery of MEK in subsequent equipment.

Therefore, with these analyzes it is clear to us why it is impossible to obtain high recoveries of MEK. That is, the separation schemes S1, S3, and S4 do not perform the same operation. In other words, in the work published by Penner et al. [19] an error was made in the synthesis process, and it is reflected in this work when those schemes are properly designed.

Additionally, as we mentioned in previous paragraphs, schemes S1-S4 were previously proposed by Penner et al. [19]. Those schemes were only conceptually designed, in other words, those schemes were not rigorously evaluated under certain purity and recovery constriction. They do not even show flowstreams or a mass balance. However, we wanted to evaluate those schemes even when we did not know about their capabilities to recover and purify MEK.

On the other hand, note the difference in IR is reflected immediately because of the difference in the number of columns. Since schemes S2 and S3 are designed with only four distillation columns, it is evident that IR decrease is due to a decrease of the number of columns as well.

With the results showed so far, scheme S2 can be considered as the most balanced purification process among S1−S4 in Fig. 3. Fig. 10 shows a complete mass balance for scheme S2. However, a quick comparison between scheme S2 and the intensified scheme is revealing. Note the reduction in both TAC and EI99 is huge. Even though the condition number of intensified is higher than the rest of the schemes (S1−S4) it is worth to analyze the role of the mass entrainer in order to reduce the energy requirements in MEK purification. Note, for example the total energy invested in S2 is about 271764 MJ/h, on the other hand, the best point obtained for the hybrid process requires 51580 MJ/h, which represents an energy reduction of 220184 MJ/h. Moreover, considering the MEK production scheme S2 consume 35 MJ/kg_{MEK} and scheme S5 6.78 MJ/kg_{MEk}. The complete comparation between the performance of scheme S2 and the intensified scheme S5 are presented in Table 6.

Moreover, in the hypothetical scenario where all MEK produced as fuel was burned, with 31.45 MJ/kg as energy density, the energy profit of the downstream process for S2 and S5 (intensified) would be −31266 MJ/h (negative) and 188622 MJ/h, respectively. In a complementary calculation between those two schemes, the thermodynamic efficiency was 28.64 and 32.56, for scheme S2 and the intensified scheme respectively. The lower efficiency is directly related to the efficiency of the separation. In other words, the intensified alternative purify in a better way since uses a lower heat duty to perform the separation. In this way, the inclusion of a liquid-liquid column in the downstream process increase the thermodynamic efficiency.

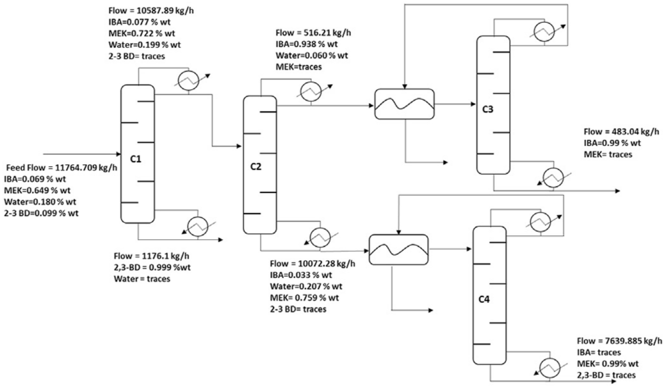

Fig. 10. Complete mass balance for the selected Scheme S2.appsec1

Additionally, the reduction in EI99 is also remarkable. For example, S3 present an environmental impact of 16200579 points/year; however; the intensified S5 scheme presented 1338593 points/year a reduction above 90%. Regarding inherent safety, scheme S2 is safer than the intensified scheme about 5%. Note as aforementioned, the inherent safety is affected by many circumstances, in this case, the increase of IR in the hybrid scheme is initially due to the increase in distillation columns, four columns for scheme S2 and six for S5. Moreover, note in scheme S2 the presence of water in many columns reduces the concentration of dangerous components and consequently the inherent safety. However, in scheme S5, most water was initially removed by the mass agent.

Regarding the condition number. It is clear that the intensified S5 scheme, despite being the best in terms of cost and environmental impact and having a relatively similar impact on inherent safety, does not present the best controllability results. However, it should not be forgotten that the condition number is a qualitative measure of controllability. That is, the intensified scheme is not X times worse than any other between S1−S4. Given the qualitative nature of the condition number, the immediate conclusion is that the intensified scheme is less conditioned than other schemes to possible disturbances. Additionally, the dynamic effort that must be made to control this scheme in a closed-loop operation will be greater.

At this point it is important to highlight that according to the processes intensification the "multifunctional" equipment that couples elementary processes (transfer−reaction−separation) to increase productivity and/or selectivity with respect to the desired product and to facilitate the separation of undesired by-products. Extractive processes involving single units that combine several separation operations have received considerable attention as they offer major advantages over conventional processes due to the interaction of mass and energy transfer. Thermodynamic limitations, such as azeotrope, may be overcome and the yield of reactions increased [69]. The intensified proposal presented in this work (hybrid separation liquid-liquid extraction with distillation), according to the results obtained, shows that the process intensification establishes: reduction in total annual cost and environmental impact and better inherent safety, compared to conventional systems. Similar results when comparing hybrid separations against conventional systems have been reported by: Avilés-Martínez et al. [24], Errico et al. [70], Sánchez-Ramírez et al. [25], Quiroz-Ramírez et al. [71], among others. Therefore, the results obtained are consistent with what was previously reported in the literature for intensified systems. It is also important to note that Torres-Ortega et al. [72] has established that the intensification of processes can affect the control properties compared to conventional systems. In this work this point is also observed and is consistent with what is reported in the literature.

6. Conclusions

This work proposes an intensified alternative to purify MEK to overcome all hurdles in conventional distillation systems. Additionally, also proposes the evaluation and inclusion of the inherent risk and the condition number (jointly with economic and environmental indexes) in early design stages in order to generate separation alternatives which accomplish current global needs. After the optimization process, all separation schemes showed very interesting results. The intensified alternative, a hybrid process based on LLE, resulted as the most promissory since it was the only alternative able to recover and purify the entire feed mixture. Unlike pure distillation schemes, which were not energetically viable, the hybrid process improves energy consumption, energy profit and thermodynamic efficiency in comparison with the scheme based on distillation. Additionally showed huge energy savings which are consequently observed in performances parameters as TAC, EI99, and IR. Considering the qualitative nature of the condition number, it is difficult to establish the percentage of improvement of the other schemes with respect to the intensified one. However, given the good results in economic and environmental terms, it is evident that there is sufficient motivation to design a robust control structure for the intensified system. Moreover, it was possible to know the existing correlation among several design alternatives into the objective functions, highlighting the reflux ratio and heat duties. In other words, it was possible to understand the tendencies and the opportunities zones to design separation alternatives to accomplish current economic, environmental, controllability and safety needs. It is inferred, from the observed thermodynamic behavior, that an alternative to complement a part of the separation process is to use azeotropic distillation with entrainer. However, previous studies have demonstrated the effectiveness of liquid-liquid extraction operation on azeotropic distillation with entrainer [73,74]. Moreover, this kind of research efforts combined with studies from other knowledge areas could lead in future years to a profitable MEK production, which could compete with traditional oil-based components. Finally, process intensification aims to drastically reduce the energy consumption and processing cost of the chemical processes by utilizing the synergy between multifunctional phenomena at different time and spatial scales and enhacing the mass, heat and momentum transfer rates as seen from the results obtained in this work.

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.

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Notation

2,3-BD	2,3-Butanediol
2DS	2 C scenario
BLEVE	Boiling liquid expanding vapor explosion
CN	Condition Number
DETL	Differential Evolution with Tabu List
EI99	Eco-Indicator 99
HAZOP	Hazard and Operability study
IBA	Isobutyraldehyde
IEA	International Energy Agency
IR	Individual Risk
IR	Individual Risk
LC50	Lethal Concentration
LCA	Life-cycle assessment
LFL	Lower Flammable Limits Concentration
MEK	Methyl-Ethyl Ketone
QRA	Quantitative Risk Analysis
RIVM	National Institute of Public Health and the Environment
SVD	Singular Value Decomposition
TAC	Total Annual Cost
TL	Taboo List
TS	Taboo Search
UVECE	Unconfined Vapor Cloud Explosion
γ	Condition Number
σ	Singular Values
Σ	Diagonal Matrix
η	Thermodynamic efficiency

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2020.119641.

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