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Research article

Synthesis, design and optimization of alternatives to purify 2,3-Butanediol considering economic, environmental and safety issues

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ABSTRACT

2,3-Butanediol is a promising chemical due to its several applications. Nowadays, 2,3-Butanediol is produced by a chemical process. However, it is also produced by microbial production. Several metabolic strategies attempt to enhance the production of 2,3-Butanediol; yet, the recovery of 2,3-Butanediol from the fermentation broth is yet a challenge due to its low concentration. In this manner, a recovery process with cost and energy savings is required. Moreover, a wider point of view is also necessary since current needs involve a process with low environmental impact and high inherent safety. In previous work, the inherent safety was not calculated in early-stage design, which may further lead to misleading risk assessment. In this work, the inherent risk will be approached at early stages at the same time that economic and environmental issues. With this in mind, this paper presents the synthesis and design of some alternatives to purify 2,3-Butanediol based on distillation, those alternatives are synthesized in such way that are obtained as results thermally coupled, thermodynamically equivalent and intensified sequences. Additionally, a dividing wall column scheme was also designed and optimized to compare its performance with the other schemes. The alternatives were designed and optimized considering three objective functions: the total annual cost as an economic index, the eco-indicator 99 as an environmental index, and the inherent risk of the process (analyzed as individual risk). In general terms, the intensified alternative presented 15% reduction of the TAC and 14% of the environmental impact. Moreover, the same alternative presented the lowest inherent risk with a reduction about 50% in comparison with the reference alternative.

1. Introduction

Nowadays, since crude oil reserves have become scarce, some chemicals commonly produced by synthetic routes are gaining more interest if those are produced from a bio-based materials. 2,3-Butanediol (2,3-BD) is a renewable chemical if its production is based on biomass. Several reports pointed out 2,3-BD as a quite interesting bio-based compound since its application covers several industrial sectors. Currently, 2,3-BD has shown its potential for being used in the manufacturing of printing inks, perfumes, explosives, softening agents, fumigants, pharmaceuticals and food (Liu et al., 2016). Moreover, 2,3-BD is also used as ketalized with acetone to produce 2,3-BDO-ketal which can further be used as an octane booster, food additive, polymer formation, etc. (Ji et al., 2011). However, an interesting consideration of this bio-based chemical is its use as potential liquid fuel with a heating value of 27.19 kJ/g (Koutinas et al., 2016); additionally, 2,3-BD is an intermediate to produce methyl–ethyl–ketone (MEK) by means of a dehydrogenation process. As well, MEK could be used as fuel for spark ignition engines with similar efficiency as ethanol.

The 2,3-BD production by fermentation is actually not a new process. There are several reports that are more than a century old. The first report was in 1906 by Harden and Walpole (Magee and Kosaric, 1987). In their work, bacterium Klebsiella pneumonia was used. Further, the industrial production of this compound was performed by Fulmer et al. (1933) because of the high demand of 1,3-butadiene which employs 2,3-BD as a predecessor during the Second World War. However, 2,3-BD production by fermentation decreased because of the huge availability of oil and its further conversion to 1,3-butadiene. Again, in recent years, specifically in the 1970s the interest in producing 2,3-BD by means of biomass fermentation increased in the United States. Currently in order to develop low carbon process in China, this renewable route is relatively appealing (Xu et al., 2014).

Nowadays, a considerable number of microorganism are able to accumulate 2,3-BD. However, only a few do this task in significant quantities. In general terms those species belonging to the genera

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Klebsiella, *Enterobacter*, *Bacillus* and *Serratia* could be considered of industrial application in the production of 2,3-BD, however, only Enterobacter aerogenes and Serratia marcescens are considered promising for industrial application. Recent work has published the yields and concentration of 2,3-BD production produced by fermentation. For example, Ma et al. (2009) reported 150 g/L of 2,3-BD and 10 g/L of acetoin. Ji et al. (2015) informed a concentration of 33.2 g/L and 3.89 g/L of 2,3-BD and acetoin respectively in their research.

Despite that fact that the fermentation process to produce 2,3-BD is relatively a well-known processes has mentioned above, an obstacle of this process is the low concentration of 2,3-BD. The separation and purification stage is challenging. Until now, few alternatives to purify 2,3-BD have been available. An example is a commercial technique that is the simulated moving bed (SMB) which is already installed in a LanzaTech (Xian, 2015). However, this technology represents several drawbacks: during operation the alternating loads of the pumps reduce lifetime and may cause fault during operation, and the material used in SMB is expensive (Harvianto et al., 2018). In the following research for alternatives, some separation options have been also tested; for example the pervaporation process through the use of polydimethylsiloxane (PDMS) and ZSM-5 zeolite particle in PDMS have shown relatively good results in experimental scale. However, some problems must be faced. The activity of the membrane decreases over time, also because of the relative complexity of the fermentation broth, the membrane presents serious disturbs in functionality like membrane swelling (Koutinas et al., 2016). Other alternative, such as reactive extraction has shown impressive results, however the chemicals involved during the operation generate high corrosion and environmental issues. Because of this, it is necessary to use anti-corrosion devices to avoid the corrosive effect. Moreover, the technique is not mature to be implemented on a large scale (Koutinas et al., 2016; Li et al., 2012).

On the other hand, since the boiling point of 2,3-BD is about 180 °C at atmospheric pressure and it does not form azeotrope with water, the use of conventional distillation seems a natural alternative. Although distillation is an old concept, it still dominates the separation technology. Still, today over 90% of the separation operations of multicomponent mixtures are carried out by this operation. While this unit operation has many advantages, one drawback is its significant energy requirement. Therefore, the energy consumption plays a major role in the operational costs of a process. Despite thinking that at first sight the use of distillation might be not profitable, it is possible to implement several synthesis alternatives to reduce both capital and energy cost.

Currently, chemical process design faces the challenge of sustainable technologies for manufacturing fuels, chemicals and various products by extended use of renewable raw materials. New political–social agreements lead several scientific studies, and the process design is not an exception. The application of such agreements implies a radical change in the designer methodologies. Instead of developing a single presumably good flowsheet, the modern process design generates and evaluates several alternatives corresponding to various design decisions and constraints. Then, the most suitable alternative is refined and optimized with respect to high efficiency of materials and energy, ecologic performance and operability (Dimian and Bildea, 2008).

Process optimization is currently a powerful tool to promote alternatives regarding industrial process. So, the union of process design and process optimization has produced interesting approaches where several targets have been pursued. Recently, process optimization and process design have shown their capacities trying to involve several targets in chemical processes. For example Kiss et al. (2012) used the capabilities of process optimization in the synthesis of fatty acid methyl esters (FAMEs) by means of a complex process, of a reactive dividing wall column. The process design and optimization helped to obtain several process warranting the minimal use of energy as reboiler heat duty. This strategy has also been used to purify biofuels. For example Vázquez-Ojeda et al. (2013) designed and optimized process alternatives to purify bioethanol minimizing the cost of utilities. Furthermore, in order to have a wider point of view, Errico et al. (2017) proposed the integration of economic, environmental, and dynamic issues applied to the separation and purification of biobutanol. So it is clear that using process optimization and process design, the alternatives obtained may overcome some of the current social/industrial necessities at early stages.

On the other hand, regarding synthesis and design of separation process, Errico and Rong (2012) have presented an ordered and sequential methodology to generate subspaces of separation alternatives. This kind of methodologies jointly with optimization strategies have shown significant improvements. For example, when biobutanol issue was approached, Errico et al. (2016) claimed a reduction in total annual cost (TAC) values of about 24.5% and 11.8% on the environmental impact in comparison with a reference case which considers only conventional distillation columns. Moreover, when bioethanol purification process was approached, they claimed a reduction of 16% in TAC values (Errico and Rong, 2012). Accordingly, the application of this kind of methodologies will provide energy efficient alternatives to reduce any performance index. Besides, if this robust synthesis methodology is combined with a global optimization process, the results could be promising.

Despite the usefulness of this approaches, they have focused mostly on the economic issue which is indeed a critical issue. On the other hand, an important issue such as inherent safety has been disregarded or considered as an afterthought following the design (Govasmark et al., 2011; Law et al., 2011). In previous work Khan and Amyotte (2003) reported on the risk evaluation of several chemical processes already designed. Hassima and Hurmea (2010) took into consideration safety for a chemical plant including distillation columns; however, the inherent risk was not calculated as part of the column design. Moreover, Martinez-Gomez et al. (2016, 2017) reported the inherent safety calculation as a secondary task after the design and optimization process for biobutanol and silane production schemes. The separation alternatives could be produced with this traditional approach with a high safety risk related to the handling of high operative pressures, flammable liquids, column sizing, etc. So, not including the risk involved in the downstream process can lead to misleading risk assessment. An effective alternative would be to include inherent safety, economic and environmental issues at early design stages, guaranteeing in this way a process with low economic and environmental impact and it also accounts for the risk assessment on each alternative. In this proposal, the inherent risk will be approached at early stages at the same time as economic and environmental issues.

In this way, with all background research mentioned, this work aims to synthesize, design and optimize some new alternatives to separate and purify an effluent of 2,3-Butanediol coming from fermentation. This approach proposes to produce purification alternatives which consider the balance among several targets. In other words, the optimization procedure will find separation alternatives which consider economic, environmental, and safety issues in order to accomplish the current industrial necessities.

1.1. Problem statement

Although 2,3-butanediol is a useful chemical bio bulk, its microbial production involves a dilute broth which requires further purification. However, according to the state of the art of 2,3-butanediol, this downstream process has not been well explored so far. So, taking advantage of the thermodynamic properties in the fermentation mixture (there is no any azeotrope), distillation process and some energy saving configurations could help in the continuous research of more viable alternatives to purify this compound.

Recently, Penner et al. (2017) proposed a conventional alternative for this task (see Fig. 1). However, it is clear of the necessity for new alternatives which improve performance indexes. With this in mind, the schemes in Fig. 1 will be considered as the reference cases for further synthesis and design methodology.

2. Methodology

In this section, the systematic methodology to synthesize all alternatives to separate 2,3-BD from the fermentation broth is presented. Each step will briefly introduce the specifically intended modifications applied to the reference case in Fig. 1. In general terms, the methodology to predict new alternatives schemes is based on the introduction of thermal couplings, transposition of column section and process intensification. Please note that this methodology has been successfully applied for the purification of bioethanol and biobutanol (Errico and Rong, 2012).

2.1. Step 1: Identification of conventional distillation column

The schemes presented in Fig. 1 were considered as reference cases. Initially, Penner et al. (2017) proposed a direct sequence (see Fig. 1a), and the natural complement for Fig. 1a is the indirect sequence. In the direct sequence, the water in the feed evaporates and is recovered at the top of the first column. 2,3-BD as the heaviest component is separated at the bottom of the second column and at the top is separated acetoin. On the other hand, the indirect sequence separates the heaviest component at the bottom of the first column, and the mixture of water–acetoin is purified at the top and bottom of the second column, respectively. As can be seen in Fig. 1, each section is designated with a corresponding number allowing to identify them. According to Errico et al. (2016), a column section is commonly defined as a portion of the distillation column not interrupted by entering or existing streams or heat flows.

2.2. Step 2: Generation of thermally coupled alternatives

Having both cases of Fig. 1 as a reference, it is possible to generate the subspace of the modified thermally coupled sequences by the substitution of heat exchangers (reboiler and condenser as appropriate) associated to no-product stream with a liquid/vapor interconnection. The scheme showed in Fig. 2a was obtained from Fig. 1a by the substitution of reboiler of the first columns and replaced by a liquid/vapor connection. On the other hand, Fig. 2b was obtained by the substitution of the condenser at the top of the first column by a liquid/vapor connection.

2.3. Step 3: Generation of thermodynamically equivalent alternatives

Now, with the thermal couplings already introduced, there are column sections where the condenser/reboiler provides a common reflux ratio/vapor boil-up between two consecutive columns. With this in mind, it is possible to move this section to generate thermodynamically equivalent alternatives in Fig. 3. Please note that Fig. 3a was obtained from the corresponding thermally coupled sequence moving Section 4 below Section 2. Consequently, water is purified at the top of the first column and 2,3-BD at the bottom, and finally acetoin is purified in Section 3. Following the same procedure, Fig. 3b is obtained from its corresponding thermally coupled sequence moving Section 3 above Section 1.

2.4. Step 4: Generation of intensified alternatives

As a general description, the intensified schemes are those that carry out a separation task with a reduced number of equipment in comparison with its conventional configuration. In this case, any conventional distillation process requires N-1 columns to perform a conventional separation, and consequently the intensified alternatives might perform the same task in less than N-1 columns. Taking this into consideration, the next methodology is simple and consists of the elimination of the side columns which have only one column section. Please consider, for example, the thermodynamically equivalent scheme of Fig. 3a, which eliminated the single rectifying section and added instead a side stream to produce those intensified alternatives with less than N-1 columns of Fig. 4. Another intensified scheme – a ternary DWC (see Fig. 5) scheme – was also designed and optimized to compare its performance with the other schemes.

3. Theory/calculation

In this section the design and simulation of the new schemes for 2,3-BD purification will be approached. For all alternatives considered in this work, the feed stream is that previously proposed by Ma et al. (2009). According to their result in fermentation, the Diol concentration is 150 g/L and 10 g/L of 2,3-Butanediol and Acetoin respectively (see Table 1). All alternatives were modeled by means of Aspen Plus modeler using the NRTL thermodynamic model, which according to Penner et al. (2017), this describes the interactions among all components better. The minimum purities were fixed on a mass base at 99.5% for 2,3-BD and water, and 99.0% for acetoin. For all the columns, the pressure was optimized taking into account the availability of cooling water.

The references cases and the new alternatives were designed and simultaneously optimized having three objective functions: the total annual cost, the environmental impact, and the individual risk. The objective function and the optimization methods are described below.

3.1. Economic index

In this study, the total annual cost (TAC) as an economic index was used. To calculate the TAC, the method initially reported by Guthrie (1969) was implemented . The last version of that equation was presented by Turton (2001). In general terms, the cost estimation of an industrial plant is calculated by separated units as the sum of the annualized capital cost and the operating cost. The cost calculation was measured as follow:

$$TAC = \frac{Capital\ costs}{Payback\ Period} + Operating\ Costs \tag{1}$$

It was considered a payback period of five years in a plant running 8500 h per year. In addition, 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}) (Luyben, 2011).

3.2. Environmental index

In this study, the environmental impact was evaluated by means of the eco-indicator 99 (EI99), which is indeed a model based on life-cycle assessment (LCA). This environmental damage model took into consideration a hierarchical weighting perspective to assess the relative importance of the damage.

By means of this life-cycle assessment method, it was possible to evaluate the overall environmental loads associated with

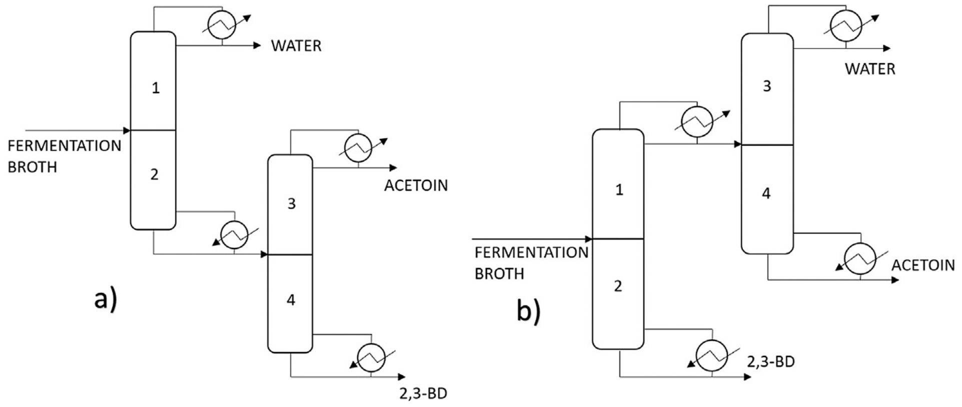

Fig. 1. Pure distillation schemes to separate 2,3-BD.

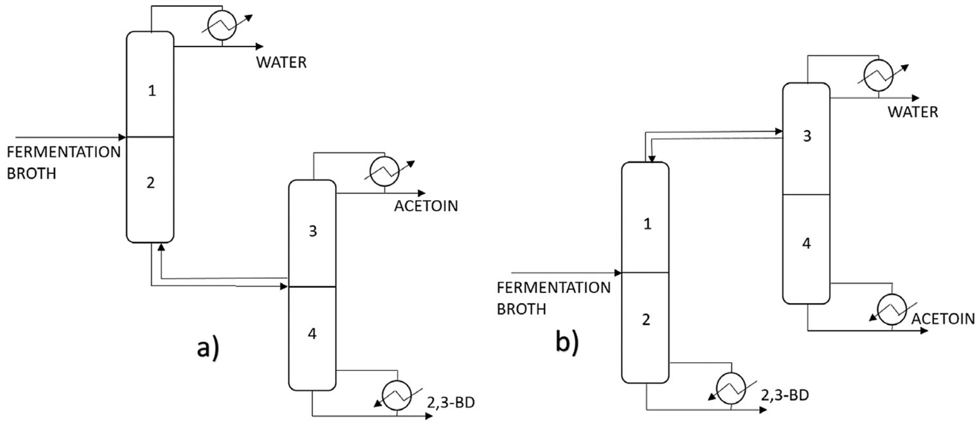

Fig. 2. Thermally coupled schemes to separate 2,3-BD.

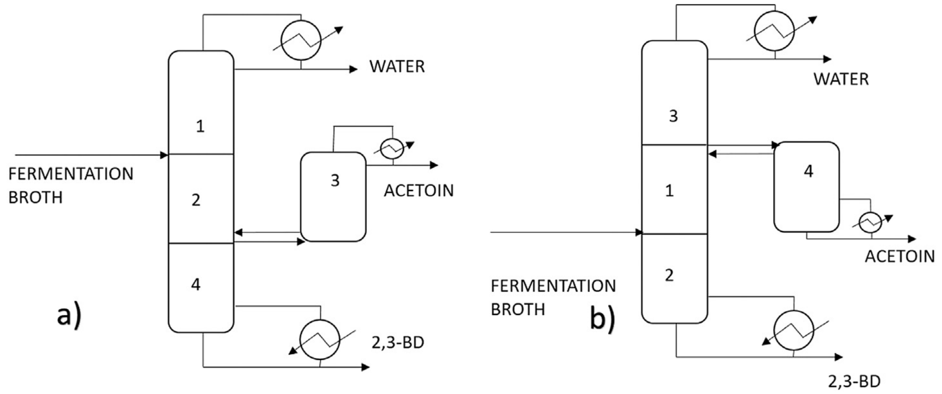

Fig. 3. Thermodynamic equivalent schemes to separate 2,3-BD.

Table 1
Feed characterization.

Mass Fraction			Vapor fraction	Flowrate (kg h^{-1})	Temperature (K)	Reference
Water	Acetoin	2,3- BD				
0.841	0.009	0.149	0	73 170	298	Ma et al. (2009)

a process, product or activity that identified and quantified the material and energy used. Because of the environmental concerns, much work has introduced this kind of methodologies to measure and improve the environmental performances, (Singh et al., 2017; Morosuk et al., 2016).

This eco-indicator 99 (EI99) methodology was made based on the contributions of several LCA experts from the National Institute of Public Health and the Environment (RIVM) (2000) in Switzerland.

In the eco-indicator 99 methodologies, 11 impact categories are considered. These 11 categories are aggregated into three major damage categories: (1) human health, (2) ecosystem quality, and (3) resources depletion. In this case study, for eco-indicator 99 calculation we considered the impact of three factors and we

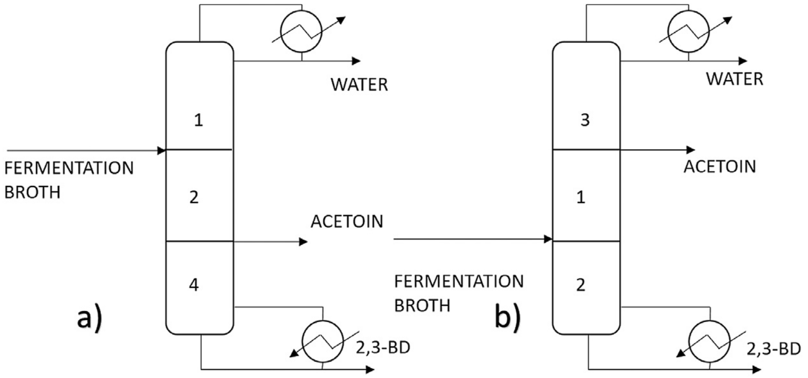

Fig. 4. Intensified schemes to separate 2,3-BD.

assumed them as the most important in this process: the steam used to produce heat duty, electricity for pumping, and steel to build major equipment and accessories. The values for those three factors are summarized in Table 2. The data associated with these upstream activities are generally taken from standard databases (Goedkoop and Spriensma, 2000). 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 (Goedkoop and Spriensma, 2000). 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 and 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. Individual risk index

The quantification of safety is carried out through the individual risk index (IR) which is defined as the risk that a person has based on its position. This risk involves damage as injury or death caused by an accident which has certain frequency occurrence and a likelihood of affectation. The IR does not depend on the number of people exposed. Mathematically the individual risk is defined as multiplication of frequency of the accident (f_i) and 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 affectation can be determined through a quantitative risk analysis (QRA) which is a useful tool that allows to identify the potential incidents and accidents and evaluate their respective consequences and damages. The first step of QRA is the identification of possible incidents. An incident is the release of matter/energy from a process (Medina-Herrera et al., 2014). For distillation columns, there are two potential incidents: a continuous release which is the leak of matter from process equipment due to a rupture in a pipeline, and the instantaneous release that consists in the total loss of matter from the process equipment originated by a catastrophic rupture of the vessel. Those incidents were determined through hazard and operability study (HAZOP). Fig. 6 shows the event trees of possible accidents and their respective frequencies (f_i). The frequencies values were taken according to the American Institute of Chemical Engineers (Kumar, 1996). As can be appreciated on event trees, the possible accidents for instantaneous release are boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), and flash fire and toxic release. While for continuous release, it has been identified as potential accidents jet fire, flash fire, and toxic release.

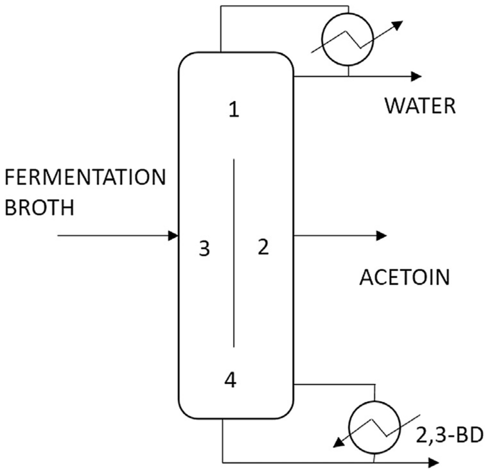

Fig. 5. DWC scheme to separate 2,3-BD.

When the likely accidents have been identified, the next step is the identification of causative variables for injuries or deceases of each accident. For fires such as BLEVE, jet fires, and flash fires, the causative variable is the thermal radiation (E_r) that a person receives. The overpressure (p^o) is the main reason of deaths for UVCE, while for toxic release the causative variable is the concentration (C). The calculations of causative variables of each accident have been shown previously by Kumar (1996) and Medina-Herrera et al. (2014).

3.4. Causative variables

In this work a distance of 50 m was considered for calculating all causative variables. This distance was fixed due to all the accidents that were considered in Fig. 6 to have important consequences. Note that the continuous releases have higher frequencies. However, we cannot consider only these incidents because a large bias would be created. The instantaneous releases have lower frequencies, but these events commonly represent a greater risk because their greater rank of affectation (more mass/energy is released) provoke more deaths in comparison with the continuous released. This greater affectation to instantaneous releases is considered in the factor $P_{x,y}$ in Eq. (3). Another important point to consider of the instantaneous releases is its ability to provoke chain incidents. If an explosion happens, this explosion can affect other equipment which could provoke other incidents increasing the damage and the risk. Thus the quantification of risk due to

Table 2
Unit eco-indicator used to measure the eco-indicator 99 in both case studies (Goedkoop and Spriensma, 2000).

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
Ionizing 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	$\left(\frac{t_e E_r^{\frac{4}{3}}}{10^4}\right)$
Overpressure	−77.1	6.91	p^o

instantaneous release is important. The calculation of the causative variable starts with the determination of the amount of material released. Medina-Herrera et al. (2014) have previously proposed the models for continuous and instantaneous release to be considered for this work.

3.4.1. BLEVE

The BLEVE is an abrupt release of total mass contained in a vessel to the atmosphere due to overheating of a liquid. The main cause is the contact of external flame with the shell of the vessel weakening the container and causing a rupture below the pressure relief. The thermal radiation in a BLEVE is described and calculated with the model proposed by Kumar (1996).

3.4.2. Unconfined vapor cloud explosions (UVCE)

The UVCE is an explosion caused by a quick release of a large amount of flammable liquid or gas, forming a cloud and disperses in the surrounding air. This explosion occurs mainly in a storage tank process, stirred tanks and pipelines. The main hazard in a UVCE is the blast produced during the explosion, where the overpressure is the cause of injuries. A TNT equivalency model is used to model the vapor cloud explosions, where the magnitude of UVCE is correlated with an equivalent explosion caused by a tantamount mass of TNT. This method has been described and applied for many quantitative risk analysis (Medina-Herrera et al., 2014). Mathematically, the TNT model describes an UVCE event according to Kumar (1996).

3.4.3. Jet fire

A jet fire is produced by the combustion of a flammable material of a continuous pressurized leak that finds immediate ignition. Comparing with other accidents as BLEVE or UVCE, the jet fire has a lower affectation but the probability of occurrence is higher. The thermal radiation (E_r) is the main cause of injuries for jet fires. Klein (1997) provides one of the most used and detailed models for jet fire.

3.4.4. Continuous flash fire and toxic release

A flash fire is the non-explosive burning of flammable material where the main hazard is the thermal radiation. Due to a short duration of flash fire, there is not a model that describes the behavior and the thermal radiation generated during the accident. Thus in this work, the lower flammable limits concentration (LFL) are used to calculate the affectation. If the concentration is equal or higher than LFL, it is considered that thermal radiation generated by flash fire is enough to support a decease. The concentration is calculated through Pasquill–Gifford Model (Crowl and Louvar, 2001), and this equation is also used to calculate the concentration for toxic releases. In the case of toxic release, the concentration obtained by Pasquill–Gifford Model is compared with LC50 (median lethal concentration) in order to determine if the concentration is above what would tolerate an organism. The model used in this work was previously proposed by Pasquill–Gifford to continuous release; the calculations were realized taking into consideration atmospheric conditions type F (stable with a wind velocity of 1.5 m/s), the worst case conditions (Kumar, 1996).

3.4.5. Instantaneous flash fire and toxic release

In the case of Instantaneous flash fire and toxic release, the LFL and LC50 for 2,3-BD and acetoin were considered in the same way that for continuous release. In this work, we used the Pasquill–Gifford model for instantaneous release (Crowl and Louvar, 2001).

3.5. Probability of affectation (consequences analysis)

When the causative variables have been calculated, the next step is to determinate the probability of affectation (probability of injury or decease) which can be found by the consequence assessment using probit models. A probit model is an equation that relates the response that a person would have (probability of injury or decease) with the dose received of a certain exposure like heat, pressure, radiation. In this work, probit models for those deceases due to overpressure and third degree burns are considered (Crowl and Louvar, 2001; De Haag and Ale, 2005; Kumar, 1996). The parameters to Eq. (4) are shown in Table 3. The probability of damage is obtained by replacing probit values in Eq. (5) (Medina-Herrera et al., 2014).

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

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

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

3.6. Multi-objective function problem

Once all performance index are described, the objective function, models, variables and constraints are presented as follow:

Model to solve:

MESH, TAC, EI99 and IR equations

Objective functions:

$$\text{Min}\,(TAC, EI99, IR) = f(N_{tn}, N_{fn}, R_{rn}, F_{rn}, F_{ln}, F_{vn}, D_{cn}, P_{cn}, FC_{cn}) \tag{6}$$

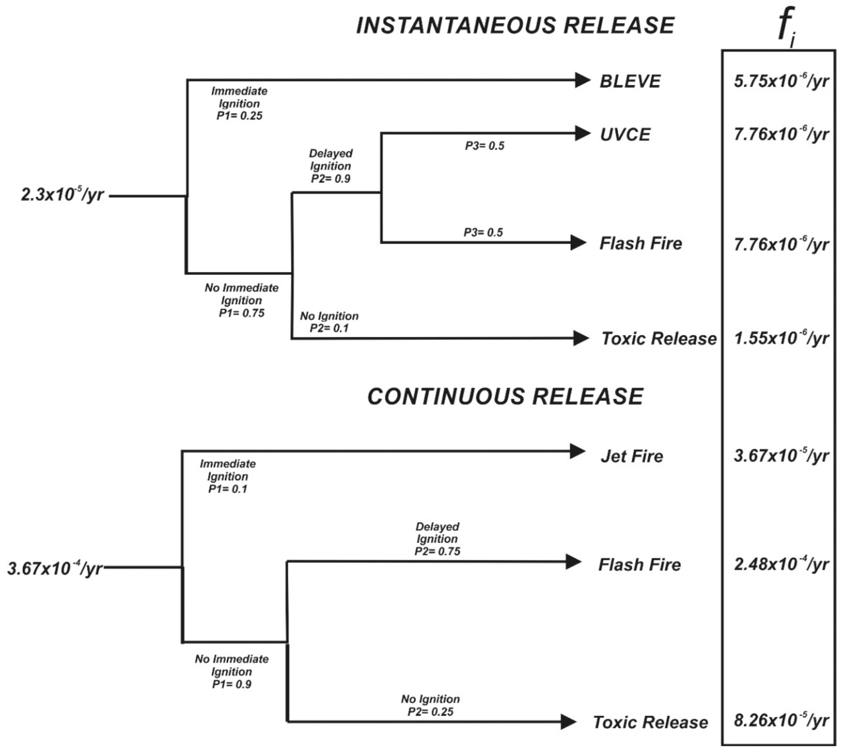

Fig. 6. Events trees diagrams for distillation columns.

where N_{tn} are total number of column stages, N_{fn} is the feed stage in column, R_{rn} is the reflux ratio, F_{rn} is the distillate/bottoms flux, F_{ln} is the interconnection liquid flow, and F_{vn} is the interconnection vapor flow. D_{cn} is the column diameter, while for IR calculation many physicochemical properties are considered, such as molecular weight, heat of combustion, LC_{50} and so on. For the distillation columns, the overall efficiency is calculated according the expression reported by Peters and Timerhaus (1991). Also the physical sizing of the columns was considered within the limits for industrial columns (Douglas, 1988; Górak and Olujic, 2014).

Problem constraints:

Subject to $x_{\vec{m}} > y_{\vec{m}}$

Respectively, y_m and x_m are the vectors of both obtained and required purities for the m_{th} components. The minimum purity targets were fixed as 99.5% for 2,3-BD and water, and 99.0% for acetoin. The recoveries were set as 98% as a minimum.

Variables to optimize:

This multi-objective minimization considered 25 continuous and discrete variables. Note that the product streams flows are manipulated and the recoveries of the key components in each product stream must be included as a constraint for the optimization problem. Table 4 shows all the decision variables used in the optimization process.

3.7. Global optimization methodology

In order to carry out the global optimization, we used a stochastic hybrid optimization method, differential evolution with tabu list (DETL). In general terms, the stochastic methods have proven capable of solving complex optimization problems, highly nonlinear and potentially non-convex. Examples of this work is by Errico et al. (2016) and Gutiérrez-Antonio (2016). DETL has its basis in natural selection theory. Differential evolution (DE) was proposed by Storn (1997) considering a single objective function. Furthermore, the method was adapted by Madavan and Field (2002) to solve multi-objective problems. The DE algorithm is summarized in four steps: initialization, mutation, crossover, evaluation, and selection. In the initialization step, the algorithm search in a D-dimensional space $\Re^D$ starts randomly as:

$$X_{\overrightarrow{i,G}} = \left[X_{1,i,G}, X_{2,i,G}, X_{3,i,G}, \ldots, X_{D,i,G}\right] \tag{7}$$

Regarding the mutation step, which has indeed a similar biological meaning, mutation can be described as a change or disturbance with a random element. Starting from a parent vector (named target vector), this parent vector is further muted to generate a donor vector. Finally, the trial vector is obtained recombining both the donor and target vector. We can write the process as:

$$V_{\overrightarrow{i,G}} = X_{\overrightarrow{r^i_{1,G}}} + F.\left(X_{\overrightarrow{r^i_{2,G}}} - X_{\overrightarrow{r^i_{3,G}}}\right) \tag{8}$$

Following with the crossover step, the target vector exchanges its components with the target vector under this operation to form the trial vector $U_{\overrightarrow{i,G}} = [u_{1,iG}, u_{2,iG}, u_{3,iG}, \ldots, u_{D,iG}]$. So, the trial vector is obtained as:

$$\begin{aligned} u_{j,i,G} &= v_{j,i,G} \quad \text{for } j = \langle n\rangle_D \qquad \langle n+1\rangle_D, \ldots, \langle n+L-1\rangle_D \\ &\quad x_{j,i,G} \text{ for all other } j \in [1, D] \end{aligned} \tag{9}$$

Regarding the selection step, and to keep the population size as a constant number, the selection step determines if the target or the trial vector survives from the generation G to the next generation $G+1$. The selection operation is described as following:

$$\begin{aligned} X_{\overrightarrow{i,G+1}} &= U_{\overrightarrow{i,G}} \qquad iff \ \left(U_{\overrightarrow{i,G}}\right) \le f\left(X_{\overrightarrow{i,G}}\right) \\ X_{\overrightarrow{i,G+1}} &= X_{\overrightarrow{i,G}} \qquad iff \ \left(U_{\overrightarrow{i,G}}\right) > f\left(X_{\overrightarrow{i,G}}\right) \end{aligned} \tag{10}$$

It should be mentioned that $f(\vec{X})$ is the objective function to be minimized/maximized.

Regarding tabu concepts, both the tabu list concept (TL) and taboo search (TS) previously proposed by Glover (1989) allow avoiding revisit the search space by keeping a record of visited

Table 4
Decision variables used in the global optimization process.

Type of Variable		Search Range
Number of stages	Discrete	5–100
Feed stages	Discrete	4–99
Side stream stage	Discrete	4–99
Side stream flow	Continuous	8–9 (kmol h^{-1})
Reflux ratio	Continuous	0.1–75
Liquid and vapor interconnection flow	Continuous	10–4500 (kmol h^{-1})
Distillate rate	Continuous	3400–3450/7–9 (kmol h^{-1})
Diameter	Continuous	0.9–5 (m)

points. TL is randomly initialized at an initial population and continuously updated with the newly generated trial individuals. This taboo check is carried out in the generation step to the trial vector, and the new trial individual is generated repeatedly until it is not near any individual in the TL. The total trial individuals NP are generated by the repetition of the above steps. The newly generated NP trial vectors are combined with the parent population to form a combined population with total 2NP individuals.

To optimize the case of study, this work employs a hybrid stochastic optimization algorithm, differential evolution with tabu list (DETL). This evolutionary method employs the classical differential evolution steps, however, its actions are improved by means of the tabu list concept. Initially, this hybrid optimization algorithm was proposed by Srinivas and Rangaiah (2007) improving the computational efficiency of DE by means of testing challenging phase equilibrium calculations followed by parameter estimation problems in dynamic systems known to have multiple minima. Later, Sharma and Rangaiah (2013) adapted and improved DETL algorithm to solve constrained multi-objective optimization problems, and the resulting algorithm is referred to as integrated multi-objective differential evolution.

The global optimization process is performed by a hybrid platform linking Aspen Plus and Microsoft Excel, previously implemented by Zhang and Rangaiah (2011). In Microsoft Excel, the DETL algorithm is written by means of visual basic and the model of the separation scheme is solved in Aspen Plus. Initially, the vector of decision variables is sent from Microsoft Excel to Aspen Plus by means of dynamic data exchange (DDE). Those values are assigned to process variables in Aspen Plus modeler. After simulation, Aspen Plus returns the output data to Microsoft Excel as resulting vector containing output data (flow streams, purities, reboiler heat duty, etc.). Finally, Microsoft Excel analyzes the objective function values and proposes new values of decision variables according to DETL methodology. The parameters used for the optimization process were: 200 individuals, 1000 maximum number of generations, a taboo list of 50% of total individuals, a taboo radius of 1×10^{-6} , 0.8 and 0.6 for crossover probability and mutation factor, respectively. These parameters were obtained from the literature and tuning process via preliminary calculations (Srinivas and Rangaiah, 2007).

4. Results and discussion

In this section, the results obtained after the optimization of all alternatives are reported and also compared in order to select the scheme with the best objective function values. Moreover, despite three objective functions are evaluated, the obtained results are shown in Table 7. All Pareto fronts were obtained after 200,000 evaluations, as afterward, the vector of decision variables did not produce any meaningful improvement. It was assumed that the DETL algorithm achieved the convergence at the tested numerical terms and thus the results reported here correspond to the best solution obtained. The product purities specified in all processes are water and 2,3-BD >99.5 wt% and acetoin >99 and over 98 wt% recovery of all components.

After the optimization process, some trends among objective function were observed. It should be pointed out that in Fig. 8, when the TAC is evaluated jointly IR, it is clear the competitive connection between both targets, as long as the TAC increase, the individual risk decreases and vice versa. On the other hand, Fig. 7 shows the relation between the total annual cost and the eco-indicator 99. As Sánchez-Ramírez et al. (2015) have previously reported both functions show an antagonist behavior, as same as individual risk, as long the TAC increase the environmental impact decrease. To finalize, Fig. 9 shows the antagonist behavior between the environmental impact and the individual risk associated with the conventional downstream process. It is possible to obtain process with low environmental impact, however, the probability of individual accident increase and vice versa.

Regarding pure distillation schemes (see Table 7), it is easy to figure out that between direct and indirect sequence, there is a small difference regarding the individual risk values. However, the difference associated with the TAC values is about 32%. The high difference in TAC is high enough to select as the best option the direct sequence between both conventional alternatives.

It was extensively proved that there is a correspondence among the alternatives included in the different subspaces (Errico et al., 2016; Errico and Rong, 2012). It means that once the best structure is identified in a specific subspace of alternatives, only the configurations derived from that structure are expected to be promising. For such reason, since the direct alternative has been identified, only the schemes derived for that configuration are considered for optimization procedure. The general characteristics of both selected conventional alternatives are shown in Table 5.

With this in mind, the alternatives presented in Figs. 1a, 2a, 3a, 4a, and 5 were further optimized, and all results are presented in Table 7. Focusing the analysis only on the TAC values, the evolution of TAC jointly with the synthesis procedure is clear. Initially, when the thermal coupling is introduced at the bottom of the direct sequence, the thermally coupling alternative is able to save about 11% in comparison with the direct sequence. Furthermore, when the corresponding section is moved to obtain the thermodynamic equivalent alternative, the TAC values are similar, only with a slight difference about 0.5%. This similarity is due to that separation is performed with exactly the same theoretical stages and similar heat duty.

Finally, the intensified alternative reaches TAC savings about 14% in comparison with conventional direct alternatives. Please notice the Pareto fronts for intensified schemes in Figs. 7–9. On the other hand, in comparison with the conventional indirect alternative, the TAC savings are 32%, 38%, 38.5% and 40% for the direct, thermally coupling sequence and intensified alternative respectively.

Regarding the eco-indicator 99, the data in Table 7 show a similar tendency than TAC values for each scheme analyzed. Since this environmental measure is carried out considering the steam for heating, the electricity for pumping and the steel for building, and considering the impact for each category in Table 2, the tendency is clear. In general terms, the indirect scheme shows

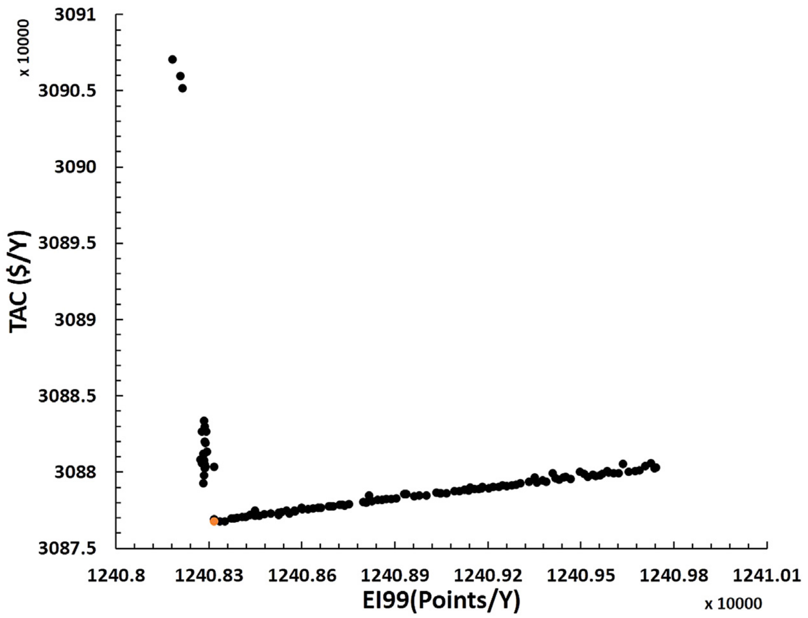

Fig. 7. Pareto front between EI99 and TAC for the intensified scheme.

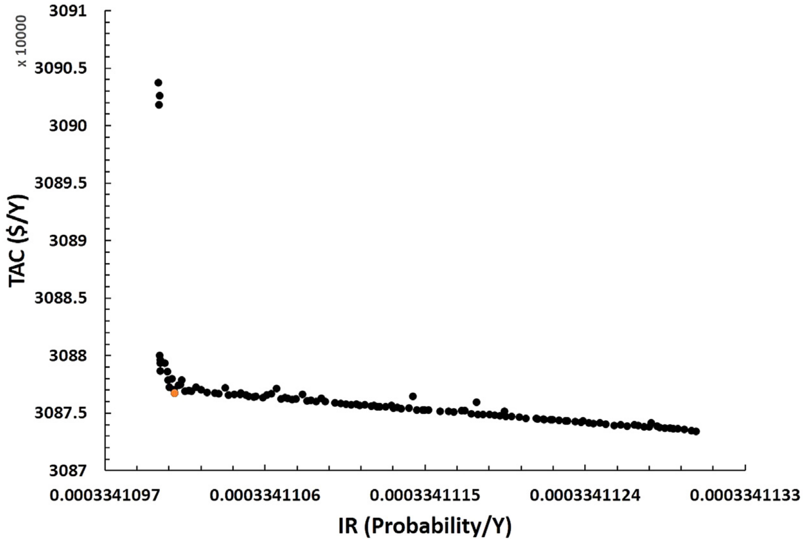

Fig. 8. Pareto front between IR and EI99 for the intensified scheme.

Table 5
Design parameters and performance indexes for conventional schemes.

	Direct		Indirect Sequence	
	C1	C2	C1	C2
Number of Theoretical Stages	49	50	120	50
Reflux ratio	0.3	15.672	0.226	15.67
Feed stage	42	12	105	12
Column diameter (m)	0.575	0.502	0.933	0.502
Column height (m)	28.7	29.3	71.9	29.3
Overall efficiency	0.7534	0.7738	0.7222	0.7485
Operative pressure (kPa)	101.35	101.35	101.4	101.4
Distillate flowrate (kmol h^{-1})	3416	8.089	3424	8.089
Condenser duty (kW)	50 197	1615	47 487	1615
Reboiler duty (kW)	60 044	1622	57 328	1622
TAC ($ y^{-1})	35 032 419		51 155 609	
Eco-Ind (points y^{-1})	14 328 558		22 627 903	
IR (points y^{-1})	0.0006686		0.0006663	

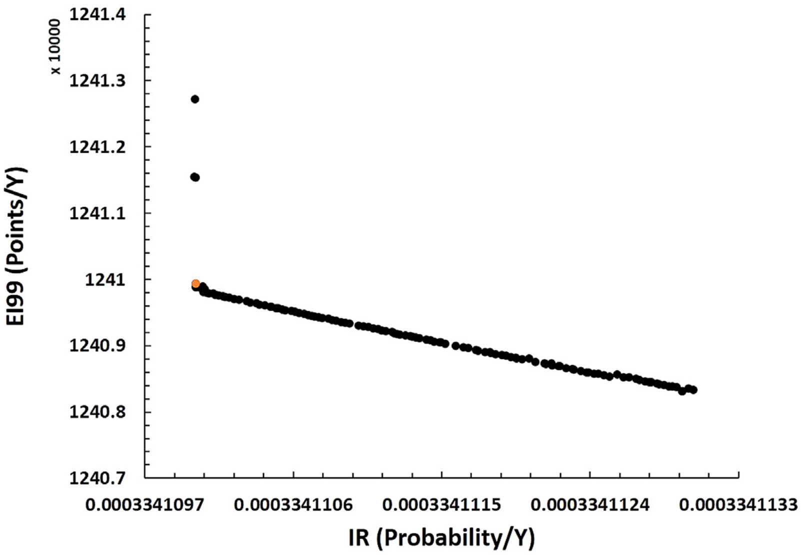

Fig. 9. Pareto front between TAC and EI99 for the intensified scheme.

the highest environmental impact as equal as the economic analysis shown. For comparison purposes, it seems wise to consider only the direct scheme. With this in mind, both the thermally coupling and the thermodynamic equivalent schemes showed a reduction about 13%, and the intensified scheme a reduction on environmental impact about 14% of this environmental index. On the other hand, regarding the Individual risk, in general terms the direct sequence, the thermally coupling and the thermodynamic equivalent presents a similar individual risk. However, the intensified alternative reduces the individual risk about 50%, which is understandable since the intensified scheme considers only a single column to perform the separation. Considering this data, the intensified alternative may be considered as the best option to purify the 2,3-BD.

The interesting approach for both objective functions is the antagonist behavior in Pareto front of all schemes. For example, the behavior of TAC evaluated with EI99 is shown in Fig. 7. It can be seen that the upper zone in the Pareto front is produced by designs which preferably include bigger columns, and the largest diameter of the column but the lowest heat duty. These combinations produced the highest TAC value but the smallest eco-indicator 99. The lower zone of the Pareto front includes smaller columns, the smallest column diameter, but the largest heat duty — which produced the lowest TAC but the highest eco-indicator 99. In the middle of both zones, it can be assumed that the minimum values of both objective functions coexist. Moreover, some variables may directly affect the increase/decrease of both functions. For example, the reflux ratio plays a major role in this kind of objective function. The increase of this variable will consequently increase the reboiler duty, cost of services and the corresponding section of the EI99. In this manner to find a correct value of this variable is mandatory in order to find a balanced behavior among those objective functions.

Regarding the evaluation of TAC and IR, it is interesting the reason for such reduction on this incident probability. Fig. 8 shows the evaluation of TAC and IR in the intensified scheme. Since IR calculation considers continuous and instantaneous chemical releases, it is clear that as long as internal flows increase, IR will increase because of the quantity of inventory inside the column increase. This will provoke that if an accident happens the affectation and duration of the events, or probability of death will be greater because there is more mass that is source to fires, explosion and toxic releases. This is the general tendency. However, note that for IR calculations several physicochemical properties are involved, such as heat of combustion, flammability limits and so on. With this in mind, it is of interest that the feed stream to be separated is mainly composed of water, which obviously for its physicochemical properties generates a contrary behavior. In other words, the IR increases with high internal flows (caused by high reflux o high diameters), however in this case of the study for almost all sequences, the first columns separate mainly water, consequently, the internal flows are enriched with water. This amount of water solubilizes the other component to separate and its flammability and toxicity decrease. Furthermore, at second column acetoin and 2,3-BD are separated, but at this instance, the internal flows follow the common IR behavior because of the quantity of water is fewer in comparison with the first column. In this manner, the IR calculation does not generates a proportional behavior with TAC because of this associated conflict.

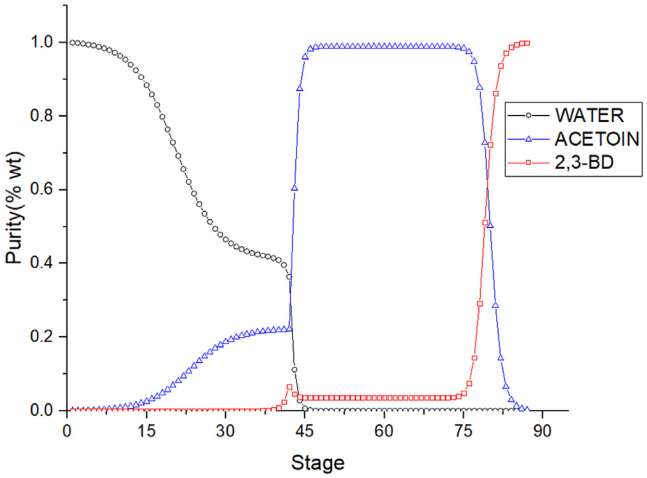

Fig. 10. Concentration profile for the intensified scheme.

Regarding the TAC values, please notice that the TAC calculation involves the cost associated with both the equipment and the services. In this case, as mentioned, high internal flows do not always produce high IR values. However, a great amount of internal flows is associated with a larger reboiler duty/reflux ratio which consequently increases the TAC. The same tendency is observed with the size of the column, as long as increase the size TAC values also increase.

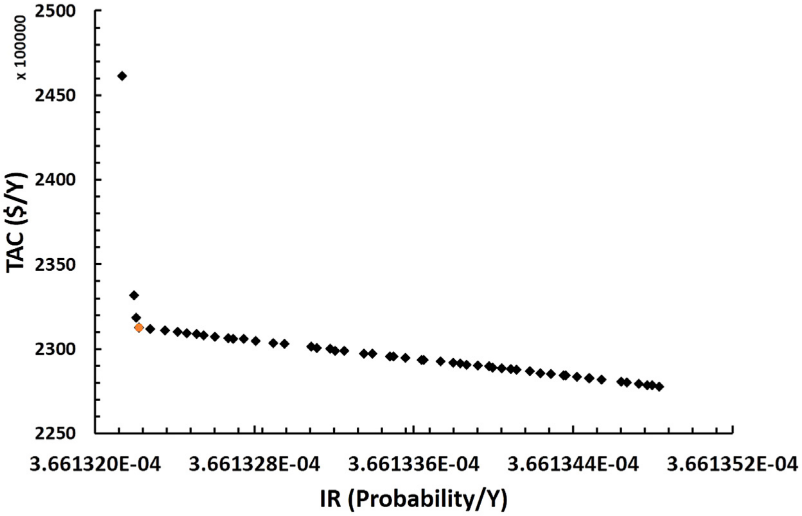

Fig. 11. Pareto front between TAC and IR for the DWC.

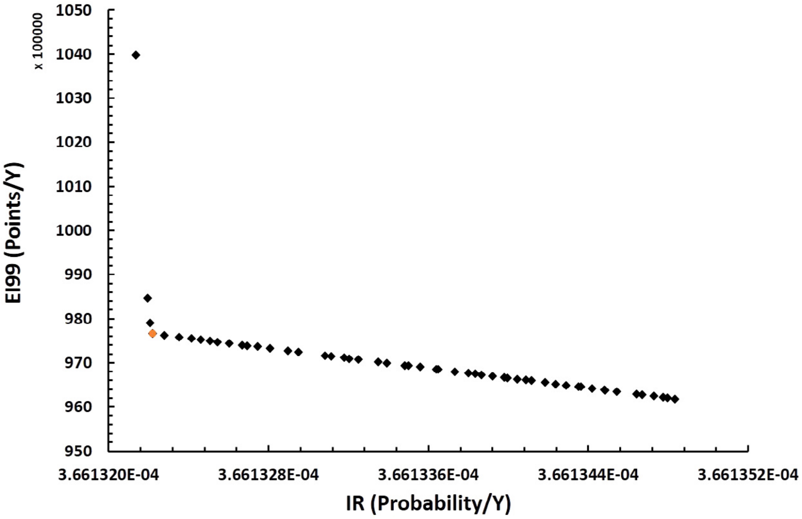

Fig. 12. Pareto front between EI99 and IR for the DWC.

Furthermore, this brief description can explain the differences in IR values between thermally coupling and thermodynamic equivalent alternatives. Despite that the general architecture for both alternatives is similar and the use of services is relatively similar, the IR value is not equal. This difference is totally related in the previous paragraphs. One can observe that in the thermally coupled sequence it is necessary to carry out the separation in two columns. On the other hand, the thermodynamic equivalent scheme performs the same operation with a single column and a side rectifier. Consequently, the amount of water increases in the first column in comparison with the rectifier, where the internal flows are composed mainly by acetoin.

Similar to this, the reduction on IR values for the intensified column can be explained mainly in two directions. Reduction in equipment will generate a reduction on IR values. Moreover, the presence of water through the column also may decrease the IR values.

Finally, when the tendency of EI99 is evaluated and observed jointly with IR in Pareto front in Fig. 9, a similar behavior is observed. In Table 2, one can observe that the category which impacts mostly on EI99 calculation is the use of steam for heating. With this consideration, it is expected a similar tendency as TAC-IR. The internal flows play an interesting role already mentioned. However, those flows must be heated. So, in almost all alternatives, the first column separates the water and implies a great amount of steam, impacting directly on EI99 value, however, the concentration of flammable compounds decrease. On the other hand, the last column, in order to reduce both IR and TAC values, is composed mainly by small columns, which indeed needs fewer services than the first column. In this sense, the conflict is generated for both targets calculation.

After analyzing the results obtained after optimization, it is clear that intensified alternatives showed the best performance measured by TAC, EI99, and IR. Moreover, for further dynamic analysis, it could be expected a relatively positive dynamic behavior since the ratio among all components in the feed stream falls within what (Tedder and Rudd, 1978) call region of optimality for this kind of intensified schemes with only a single column with a side stream. One should notice that even though the differences on the TAC, EI99 or IR values in each Pareto front is small, those Pareto fronts were obtained after 200 000 evaluation (200 individuals, 1000 generation). In other words, the exhaustive search procedure allows to find the zone where the objective functions find its minimum values. In previous generations it would be possible to find designs accomplishing all constraints but with higher values of the objective function, so the differences among several designs

Table 6
Design parameters and performance indexes for thermally coupled, thermodynamic equivalent, intensified and DWC schemes.

	Thermally Coupled		Thermodynamic Equivalent		Intensified	DWC	
	C1	C2	C1	C2	C1	Section 4	Sections 1–3
Number of Theoretical stages	49	50	87	12	87	15	71
Reflux ratio	0.3	68.5	0.3	25.023	0.333		10.0938
Feed stage	42	12	42	12	42	12	–
Column diameter (m)	0.675	0.502	0.675	0.502	0.675	0.942	1.493
Column Height (m)	28.7	29.3	51.8	6.1	51.8	7.9	42.1
Overall Efficiency	0.6941	0.7601	0.7258	0.7466	0.6838	0.6845	
Operative pressure (kPa)	101.353	101.353	101.353	101.35	101.353	101.353	
Distillate flowrate (kmol h^{-1})	3417.5	7.62	3416.28	7.14	3416.07	3415.8537	
Interconnection Vapor flow (kmol h^{-1})	–	3859.5	–	24.85	–	–	–
Interconnection Liquid flow (kmol h^{-1})	3986.76	–	32	–	–	–	–
Wall Location	–	–	–	–		–	32-36
Side stage	–	–	–	–	49	–	50
Side flow (kmol h-1)	–	–	–	–	8.155	–	8.084224401
Condenser duty (kW)	49 676	6352	50 201	384	51 507	–	428 343
Reboiler duty (kW)	–	65 861	64 439	–	61 457	–	438 198
TAC ($ y^{-1})	31 360 313		31 055 124		30 536 031	23 1268 638	
Eco-Ind (points y^{-1})	12 559 191		12 757 857		12 407 199	97 659 879	
IR (points y^{-1})	0.0006795		0.0006684		0.00033411	0.0003661	

Table 7
Objective function values for all configurations.

Objective Function	Direct Fig. 1(a)	Indirect Fig. 1(b)	Thermally Coupled Fig. 2(a)	Thermodynamic Equivalent Fig. 3(a)	Intensified Fig. 4(a)	DWCFig. 5
TAC [$ y^{-1}]	35 032 419	51 155 609	31 360 313	313 055 124	30 536 031	231 268 638
EI99 [Points y^{-1}]	14 328 558	22 627 903	12 559 191	12 557 857	12 407 199	97 659 879
IR [Probability y^{-1}]	0.0006686	0.0006663	0.0006795	0.0006684	0.00033411	0.0003661

would be larger. However, we are interested in finding that zone with the minimum objective function values in order to make a fair comparison among the alternatives. Tables 5–7 show the general characteristic of all schemes in case of interest of reproduction, including the design selected as the best intensified scheme, and Fig. 10 shows the concentration profile of the intensified scheme, considered as the best alternative for 2,3-BD purification.

Additionally, another intensified alternative was tested. The ternary dividing wall column was also proved, under the same optimization process and with the same objective functions. Figs. 11–12 show the best values reached after the optimization procedure. In general terms, the DWC is not a suitable alternative to separate this mixture. Even though, the IR value seems competitive in comparison with the intensified scheme (because of the single shell), the TAC and EIR99 values are not. Despite its intensified nature, a critical study for ternary mixtures presented by Tedder and Rudd (1978) allows to intuit and predict that because of the ratio among components in the feed stream, the topology of DWC structures is not a good alternative for this mixture.

5. Conclusions

This work has proposed the evaluation and inclusion of the individual risk and the environmental impact associated with both the total annual cost and the eco-indicator 99 of alternatives to separate and purify 2,3-BD. This approach has been performed by means of a multi-objective optimization problem, finding through Pareto fronts the most balanced solution among all objective function. In other words, it was possible to find a solution where all objective functions reach its minimum values.

Once the optimization test was applied to the proposed alternatives by a synthesis procedure, the initial results showed that between the two conventional alternatives the direct sequence is better than the indirect scheme. Derived from the direct sequence, the intensified alternatives, which separate and purify the feed stream in a single column, showed the best performance index (economic, environmental and safety) in comparison with all alternatives. It was possible to reach economic savings of about 15% in comparison with the direct sequences, a reduction about 14% on the environmental impact and a reduction about 50% regarding the IR. Moreover, because of the ratio between the components on the feed stream, and according to Tedder and Rudd (1978), it could be expected relatively good operability. In general terms, the reduction in TAC values is associated with the reduction in equipment. Regarding IR evaluation, it was evident the high dependence of this index with the size of the equipment, the amount of internal flows, and the kind of chemical to be separated. In other words, since this objective function is directly in competition with the other function, through the optimization process the algorithm sought parameter of reflux ratio, equipment sizing, interconnection flows, etc, to decrease those objective function. On the other hand, for minimizing the environmental index it was necessary to find operative variables which decrease the energy consumption, jointly with both steel and electricity requirements. However, this search had an antagonist behavior with the TAC and IR calculation because of all of the variable involved for all objective function.

Abbreviations

2,3-BD	2,3-Butanediol
MEK	Methyl–Ethyl–Ketone
TAC	Total annual cost
SMB	Simulated moving bed
PDMS	Polydimethylsiloxane
LCA	Life-cycle assessment
EI99	Eco-indicator 99
RIVM	National Institute of Public Health and the Environment
QRA	Quantitative risk analysis
IR	Individual risk
HAZOP	Hazard and operability study
BLEVE	Boiling liquid expanding vapor explosion
UVECE	Unconfined vapor cloud explosion
LFL	Lower flammable limits concentration
LC50	Lethal concentration

DETL	Differential evolution with tabu list
DE	Differential evolution
DDE	Dynamic data exchange
kJ	Kilojoule
L	Liters
g	Grams
NRTL	Non-random two-liquid
HP	High-pressure
MP	Medium-pressure
LP	Low-pressure
GJ	Gigajoule
°C	Celsius
Pt	Point
β_b	Total amount of chemical *b* released per unit of reference flow due to direct emissions
$\alpha_{b,k}$	Damage caused by category *k* per unit of chemical *b* released to the environment
ω_d	Weighting factor for damage in category *d*
δ_d	Normalization factor for damage of category *d*
f_i	Frequency of the accident
$P_{x,y}$	Probability of affectation in a specific position
E_r	Thermal radiation
p^o	Overpressure
C	Concentration
m	Meter
yr	Year
TNT	Trinitrotoluene
s	Second
h	Hour
N_{tn}	Total number of column stages
N_{fn}	Feed stage in column
R_{rn}	Reflux ratio
F_{rn}	Distillate/bottoms flux
F_{ln}	Interconnection liquid flow
F_{vn}	Interconnection vapor flow
D_{cn}	Column diameter
P_{cn}	Column pressure
TL	Tabu list
TS	Taboo search
wt%	Weight percent
kPa	Kilopascal
kW	Kilowatt
kg	Kilogram

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