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Involving economic, environmental and safety issues in the optimal purification of biobutanol

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ABSTRACT

Traditionally, the design of a separation sequence for the biobutanol production has been based primarily on economic criteria with little or no consideration to the environmental and safety issues. Since biobutanol is produced from acetone–butanol–ethanol (ABE) fermentation, the process involves several substances that may cause fire and explosion and can lead to negative environmental and health impact. Hence, it is desirable to incorporate safety and environmental issues in the design objectives to determine the optimal separation route. This work presents an optimization approach for the biobutanol separation process from the *ABE* fermentation while accounting simultaneously for economic, environmental and safety objectives. The optimization is carried out through a differential evolution with a Tabu search algorithm, where several Pareto solutions are identified and some routes are highlighted to determine the best compensated solutions. In this case, the best economic solution involves elevated values of the *Eco-Indicator 99*, the best environmental solution incurs high costs, and the safest solution features less separation columns. The most compensated solutions include configurations that represent a balance among the economic, environmental and safety objectives.

1. Introduction

Biofuels are positioned to play an important role in the energy mix because of their ability to reduce CO_2 emissions. Although the search for renewable and sustainable biofuel additives that can be blended with gasoline has focused largely on bioethanol, there are merits for considering biobutanol. For instance, the energy density of bio-isobutanol is 26.5 MJ/l while for bioethanol it is 21.1 MJ/l). It should be noted that 8.27 billion of gallons/year of biobutanol can replace 7.55 billion of gallons/yr of gasoline (see Swanaa et al., 2011). In addition, biobutanol has desirable properties for use in internal combustion engines including lower corrosion, flammability and water miscibility compared with bioethanol. While much work has been reported for the design, environmental assessment, and safety enhancement for methanol (e.g., Ehlinger et al., 2014; Julián-Durán et al., 2014) and ethanol (Murillo-Alvarado et al., 2014; Conde-Mejía et al., 2013, 2012;

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Nomenclature

ABE	acetone–butanol–ethanol
AB	administrative building
AIT	auto-ignition temperature
B_{es}	volume of the enclosed space
B_{uv}	ventilation rate
B_{vdel}	ventilation draft direction
BLEVE	oiling liquid expanding vapor explosion
CR	control room
$C_{TM,i}$	capital cost of the plant ($/yr)
$C_{ut,i}$	utility costs ($/yr).
CF_i	fixed costs ($/yr).
d	chemical compound
DALYs	disability adjusted life years
DDE	dynamic data exchange
DE	differential evolution
DETL	differential evolution with Tabu list
Dcn	column diameter
ETSC	evacuated tube solar collector
Frn	distillate fluxes
f_i	frequency of accidents
GAs	genetic algorithms
$G_{x,y}$	total number of exposed workers
HAZOP	hazard and operability
i	process unit
I	investment cost
j	process unit
k	impact category
LLE	liquid–liquid extraction
LCA	life-cycle assessment
LC50	lethal dose
MIE	minimum ignition energy
M_{mbr}	multiplier for material being released
M_{mr}	magnitude of the release
M_{dr}	duration of the release and the number/density
M_{io}	indoors or outdoors.
N	lifetime of the project (yr)
TAC	total annual cost ($/yr)
UVCE	unconfined vapor cloud explosion
$p_{Immignition}$	probability of immediate ignition
$p_{DelayedIgn}$	probability of delayed ignition
$P_{x,y,i}$	probability of affectation due an accident in the location x,y
QRA	quantitative risk analysis
ROI	return on investment
SCRI	safety software to QRA assessment
SR_i	social risk
WH	Warehouse

Greek symbols

$\alpha_{b,k}$	damage caused in impact category k per unit of chemical b
β_b	total amount of chemical released per unit of reference
ω_d	weighting factor for damage in category d
δ_d	normalization factor for damage of category d

Gabriel and El-Halwagi, 2013; Ojeda et al., 2011), much less work has been carried out for butanol production. Butanol can be obtained using two routes, by the Oxo (petro-butanol) and fermentation (biobutanol) processes. The ABE (acetone, biobutanol and ethanol) fermentation process yields a respective proportion of 3:6:1 of the three products, which is rich in biobutanol. Unfortunately, the concentration of products is typically low (Abdehagh et al., 2014). This limitation has motivated the search for efficient fermentation and separation processes. The genetic modification of microorganisms and altered pre-treatment of the raw material are typically considered as the primary alternatives to improve the production efficiency of biobutanol (García et al., 2011; Kumar and Gayen, 2011). The development of an efficient separation system increases the yield and productivity of biobutanol. The separation of biobutanol by pervaporation using polymer inclusion membranes (PIM) including ionic liquids has been reported to be less expensive than distillation (Matsumoto et al., 2010). Previous studies have concluded that solvent extraction, adsorption and membrane pervaporation are the most efficient approaches to separate biobutanol form the products of the *ABE* process (Huanga et al., 2014). The selection of the separation process for biobutanol has been based on economic aspects, considering exclusively the utility costs. With increasing attention to the environmental and safety issues, there is a need to include these objectives in addition to the economic criteria. The selection of the separation method is not the only important task. System configurations have to be generated and screened. Kraemer et al. (2011) presented a flowsheet for the separation of biobutanol from ABE fermentation by a hybrid extraction–distillation process. Recently, Errico et al. (2015) presented a set of separation processes for the biobutanol mixture accounting for economic and environmental objectives. Notwithstanding the value of the previous research efforts, they have not incorporated safety as a goal for generating, screening, and selecting the biobutanol separation configuration. The safety issue is indeed important in biobutanol production because the process involves substances that are prone to fire and explosion. Inherently safer design approaches can be used to reduce the risk (CCPS, 2009). This approach has been applied to different processes, generating new methodologies for the design of safer processes (Palaniappan et al., 2004; Study, 2007; Patel et al., 2010; Saini et al., 2015). The importance of considering safety in process design resides in the prevention of economic and human losses. Moreover, damage to the environment can also be reduced by mitigating releases and accidents. These environmental and safety issues are best considered during the early process synthesis, conceptual design, and integration stages (e.g., Thiruvenkataswamy et al., 2016; Santibañez-Aguilar et al., 2015; Ramadhan et al., 2014; Hamad et al., 2013; El-Halwagi et al., 2013; Kazantzi et al., 2013; Martinez-Gomez et al., 2013a; Suardin et al., 2007).

This paper presents an approach for including safety objectives in the design of separation processes for biobutanol while also accounting for the economic and environmental objectives. The economic objective includes the total annual cost (TAC), the environmental objective is measured through the Eco-Indicator 99 method whereas the safety objective is quantified through the quantitative risk analysis (QRA) accounting for fire and explosion.

2. Problem statement

The problem to be addressed in this paper deals with the inclusion of safety objectives in addition to the economic and environmental objectives in the design and selection of

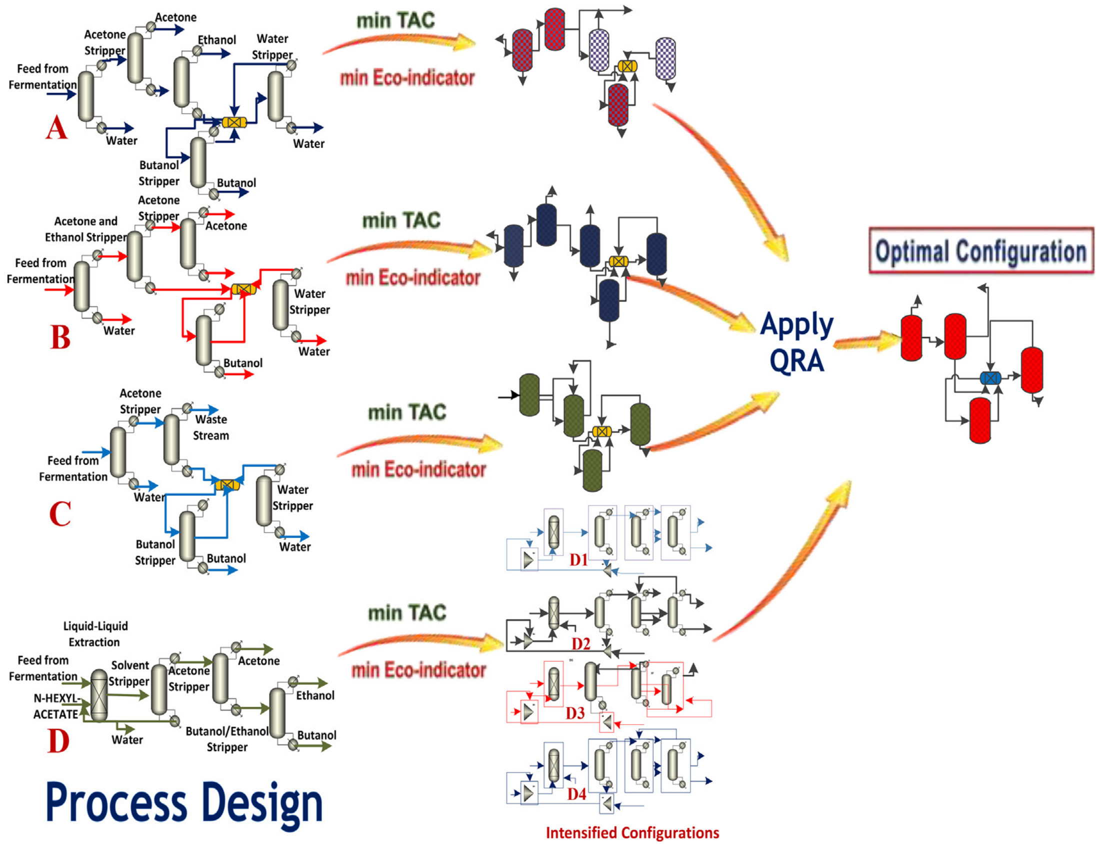

Fig. 1 – Selection of the purification process for biobutanol.

the separation network of a biobutanol process from four commonly used configurations. Fig. 1 shows four separation processes for a biobutanol mixture (see Roffler et al., 1987; Marlatt and Datta, 1986). Processes A, B and C consist of steam stripping distillation and distillation columns, whereas the process D consists of liquid–liquid extraction columns (1D-LL with side stream, 2D-Thermally coupled, 3D-Thermodynamic Equivalent and 4D-Intensified). Each column has different operating conditions and different energy requirements. High temperature and pressure can improve the efficiency of the process. However, these involve extreme operating conditions that may involve hazardous situations, because the process can operate in conditions close to the flash point of the involved substances and it increases the consequence associated with the occurrence of an accident. Moreover, complex processes involve a greater risk, this way it results more convenient to generate simplified processes. It should be noticed that the selection of the optimal process for the purification of biobutanol is not an easy task when it is considered simultaneously the cost, environmental impact and risk. Hence, the purpose of this work is to present a method to find the optimum technology for the purification of biobutanol, considering the cost, environmental impact and risk, and simultaneously optimizing the design and operating conditions of the process (number of stages in each column, feed stage, reflux ratio, distillate fluxes and column diameter). In addition, it was performed a risk analysis to four designs including thermally coupled, thermodynamic equivalent and intensified designs, obtained from the process D. These columns are characterized by the inclusion of an extractive column in order to eliminate both heterogeneous and homogenous azeotrope between butanol/water and ethanol/water respectively using n-hexyl-acetate as extractant agent. Further, in order to diminish the energy requirements, two thermally couplings were introduced in the non-products stream, generating a thermally coupled design. In this case, a thermally coupling at top of first distillation column, and another thermally coupling placed at bottom of second distillation column were introduced. In addition, since some column section can be moved, a thermodynamic equivalent design can be produced expecting similar energy requirements. In this study, the rectifying zone of the first distillation column is moved as rectifying section of the second distillation column, also the stripping zone of the third distillation column is moved as stripping zone of the second distillation column. Finally, by eliminating some column sections and replacing the side stream, an intensified design is generated. Here, the elimination of the condenser in the third distillation column and the transporting section of the same column are considered thereby introducing a side stream in the second distillation column.

3. Optimization formulation

The problem was formulated as a multi-objective optimization problem in order to minimize simultaneously the total annual cost and the environmental impact (*TAC* and *Eco-indicator99*, respectively) and it is represented by the following expression:

$$OF = \{\min TAC, \min Eco\text{-}indicator\ 99\} \quad (1)$$

As third criterion of selection, a quantitative risk analysis (QRA) is applied to the identified solutions to determine the most attractive solution since the economic, environmental and safety points of view. The proposed optimization approach was implemented through a hybrid platform using Matlab, Microsoft Excel and Aspen Plus, whereas the QRA was carried out through the SCRI software. Under this approach, it is difficult to introduce the QRA as an additional objective function, because is impractical to establish a link among Matlab, ASPEN Plus, Microsoft Excel and SCRI. Also, the required CPU time would be impractical. This way, first the economic and environmental criteria are optimized to obtain a set of compensated solutions, and then the QRA was applied to the identified solutions to determine the level of risk for each solution. This approach is very interesting, because it can help to identify the best solution that compensates these tree objectives. The considered objective functions are described as follows:

3.1. *Economic objective function*

The economic objective consists in minimizing the total annual cost and it is expressed as follows:

$$TAC = \sum_{i=1}^{n} C_{TM,i} + \sum_{j=1}^{n} C_{ut,j} \tag{2}$$

where *TAC* is the total annual cost (see Guthrie, 1969; Ulrich, 1984) expressed in \$/yr, and corresponds to the sum of the capital cost of the process (C_{TM}) and the utility cost (C_{ut}), n represents the number of individual units. Additionally, it was assessed the return of investment (*ROI*) as an additional economic measurement. The *ROI* is defined by Eq. (3), where N represents the lifetime of the project (years), I is the investment cost, and CF_i corresponds to the fixed costs.

$$ROI = \frac{\sum_{i=1}^{N} CF_i}{NI} \tag{3}$$

3.2. *Environmental objective function*

The environmental objective function is given by Eq. (4), which is based on the Eco-Indicator 99, β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in category d, and δ_d is the normalization factor for damage. Table 1 shows the impact categories assessed by the *Eco-indicator99* (Geodkoop and Spriensma, 2001).

$$\text{Eco-indicator} = \sum_{b}\sum_{d}\sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \tag{4}$$

In this paper, the *Eco-indicator99* method was implemented (Geodkoop and Spriensma, 2001). The damage categories (i.e., k) are Damage to the resources, Damage to the ecosystem quality, and Damage to the human health. These categories are determined through the following eleven impact categories: surplus energy for future extraction (minerals), surplus energy for future extraction (fossil fuels), regional effect on vascular plant species, local effect on vascular plant species, acidification/eutrophication, ecotoxicity, climate change, ozone layer depletion, ionizing radiation, respiratory effects, carcinogenesis. In the introduced approach, the main contribution to *Eco-indicator99* is associated with the use of external agents such as fossil fuels for heating as well as the use of solvents. For the weighting, we have followed the method of *Eco-indicator99*, separating the impact categories as damages to the human health (expressed in disability adjusted life years "DALYs"), damage to the ecosystem quality (expressed as the loss of species over a certain area), and damage to resources (expressed as the surplus energy needed for future extractions of minerals and fossil fuels). Based on the work by Mettier (1999), the damage to the human health and to the ecosystem quality are considered to be equally important, whereas the damage to the resources is considered to be about half as important. Furthermore, in the presented approach the hierarchical perspective was considered to balance the short- and the long-term effects. The normalization set is based on a damage calculation for all relevant emissions, exactions and land-uses. As there are three damage models, there are also three normalization sets, and in this case the hierarchical perspective was considered to determine δ_d (Geodkoop and Spriensma, 2001).

This work also considers the additional scenario of using solar collectors to supply all the steam needed as heat duty in each distillation column. This scenario was assessed in order to significantly reduce the greenhouse gas emissions that are associated with the use of fossil fuels. Furthermore, considering that each solar collector has its own economic impact, a new Pareto is developed, where the TAC includes the costs for purifying and the number and size of the solar collectors.

3.3. *Risk assessment*

The application of the optimization process through differential evolution and Tabu search yields a set of Pareto solution that compensate the economic and environmental objectives,

Table 1 – Unit Eco-Indicator used.

Impact category	Steel ($\times10^{-3}$ points/kg)	Steam $\times10^{-3}$ (points/kg)	Electricity ($\times10^{-3}$ points/kWh)
Carcinogenics	6.32	0.11	0.43
Climate change	13.10	1.60	0.003
Ionising radiation	0.45	13.13	0.82
Ozone depletion	0.0004	0.002	0.12
Respiratory effects	80.10	0.0007	0.001
Acidification	2.71	12.10	0.28
Ecotoxicity	74.50	2.80	0.16
Land Occupation	3.73	0.08	0.46
Fossil fuels	59.30	12.50	12.00
Mineral extraction	74.20	0.008	0.005

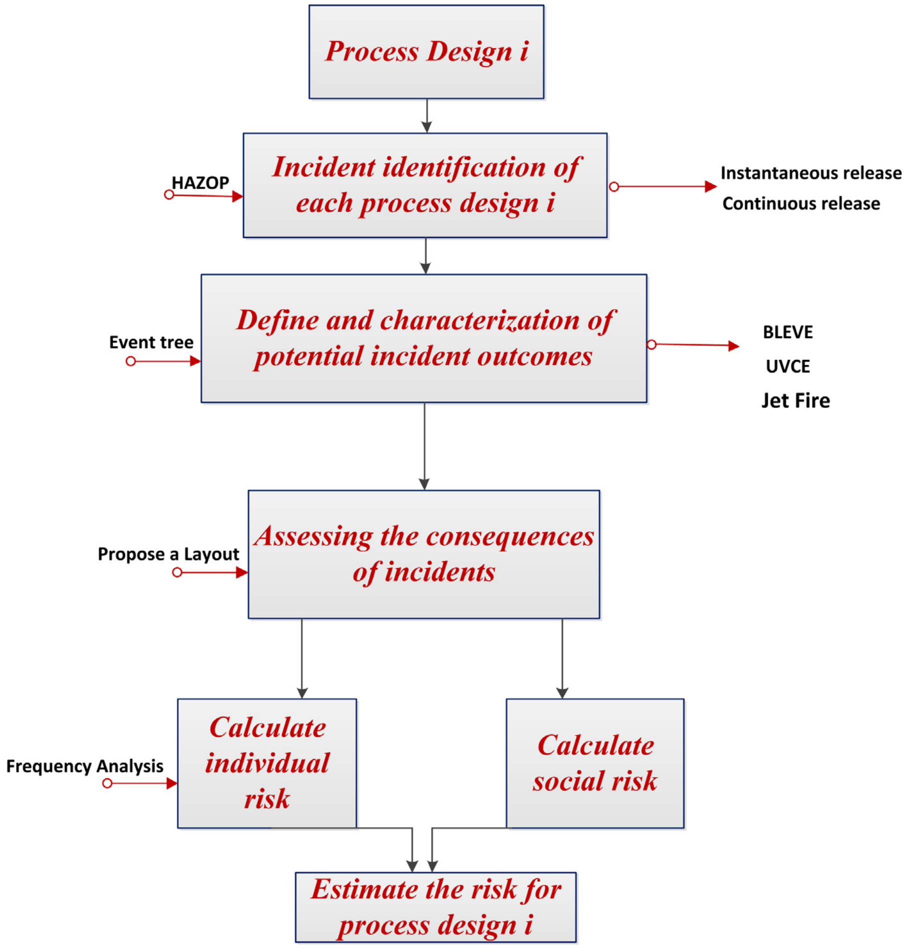

Fig. 2 – Proposed algorithm for the application of a quantitative risk analysis.

and for this set of optimal solutions there are identified the associated risk to determine the best solution. This way, a quantitative risk analysis is implemented for each Pareto solution. Fig. 2 shows the general procedure of QRA applied to each solution obtained.

The first step consists in the identification of incidents, an incident is any loss of matter or energy (AIChE, 2000); the potential incidents associated with these systems are continuous release and instantaneous release. This result is obtained from qualitative methods of risk analysis such as HAZOP (Kletz, 1999). For the assessment of the consequence for each configuration (A, B, C and D), a layout is proposed, which is shown in Fig. 3. In this figure is possible to appreciate the geographic location of the configuration (Process Design, A, B, C and D) as well as other facilities involved in the process: control room (CR), administrative building (AB) and warehouse (WH). The number of persons residing in these facilities is 10, 15 and 7, respectively (based on the typical number of people needed in these facilities, Martinez-Gomez et al., 2013b). The assessment of the consequences consists in finding the probability of damage that these accidents cause to other facilities or personnel. To measure the physical damage caused to the personnel, a vulnerability Probit model is used. The consequence is evaluated as a function of the accidents that can occur. Each incident may involve different accidents. The event tree provides the accidents expected from an incident. According to the event trees, potential accidents that may occur are: BLEVE (boiling liquid expanding vapor explosion), UVCE (unconfined vapor cloud explosion), Jet Fire, Flash Fire, Toxic release and Pool fire for liquid–liquid extraction. Fig. 4 shows the

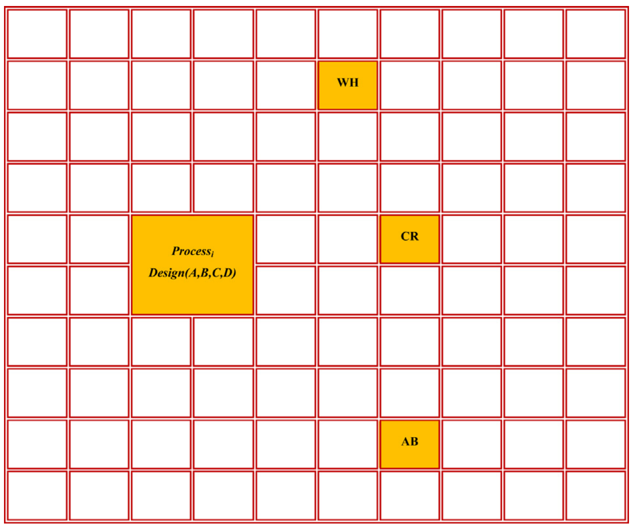

Fig. 3 – Proposed layout for applying the QRA.

algorithm used for quantifying the physical variables that produce these accidents. The calculation of the physical variables (radiation and overpressure) and dispersion was performed with the software SCRI®. The worst scenario was considered for calculating the dispersion, wind speed of 1.5 m/s^2 east direction and atmospheric stability type F were also considered. The toxicity was evaluated considering the lethal concentration (LC50). Table 2 shows the properties of the substances involved in the process, and Fig. 4 shows the general procedure for calculating the consequence as well as the Probit

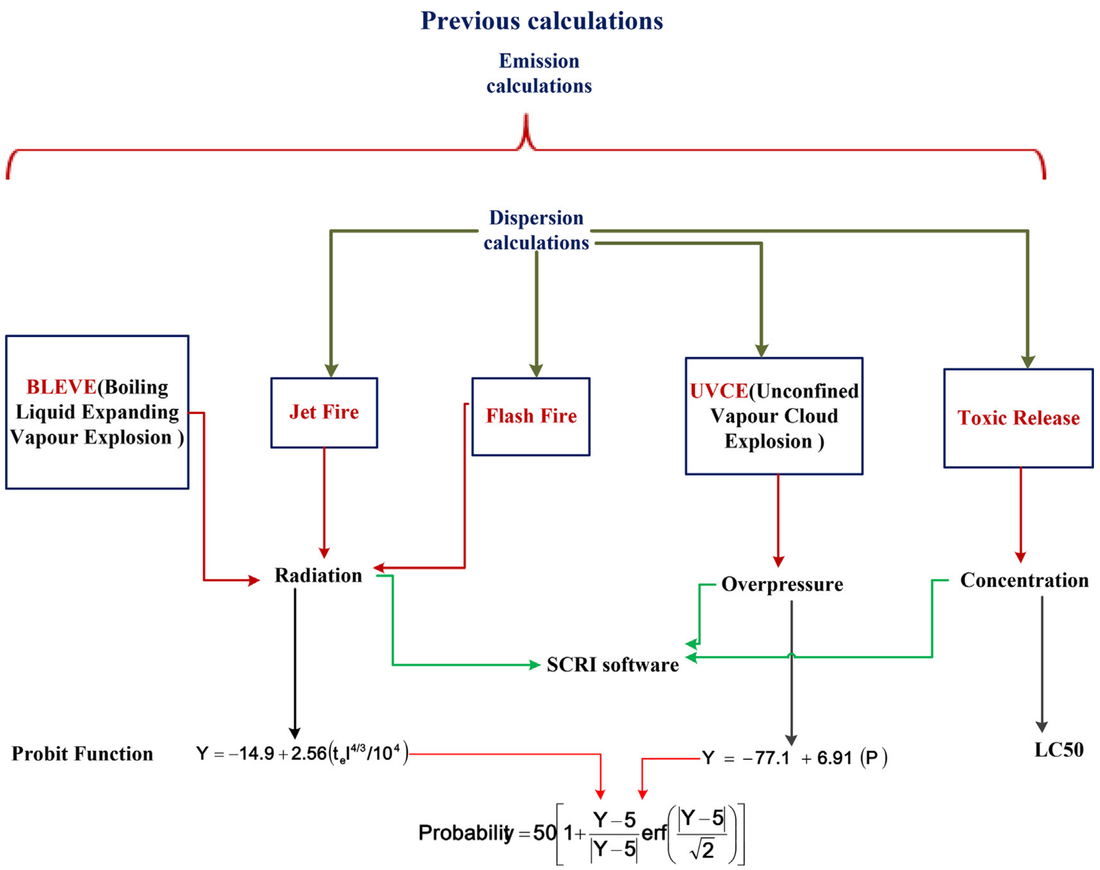

Fig. 4 – Assessment of the consequence.

Table 2 – Physical properties of substances.

Substance	LFL/UFL	LC50	Combustion heat (kJ)	AIT (F)	MIE (MJ)
Acetone	2.60/12.80	50 mg/l/8 h	30,820	1000.40	1.15
Butanol	1.40/11.40	8000 ppm/4 h	36,125	621.86	1.24
Ethanol	3.0/19.00	20,000 ppm/10 h	29,690	1459.40	0.14
Hexyl acetate	–	–	14,400	–	–

functions associated to deaths due to radiation and overpressure, which were taken from Crowl and Louvar (2011).

Fig. 5A shows the dispersion profiles for the first column of route A, where it is possible to appreciate the distances at which the upper and lower flammable limit is reached, for continuous release of biobutanol. Moreover, Fig. 5B shows the distance which reaches the LC50. If the two profiles of the layout are overlapping, it will be appreciated the scope that accidents like UVCE, Flash Fire as well as the toxic release, on the people of the affected facilities. Although the toxic release only affects the control room, Flash Fire and UVCE have a significant effect to other facilities. The variation of these profiles is linked to the operating conditions of the columns. Similarly, Fig. 5C, D and E shows profiles of radiation from BLEVE, Jet Fire and the overpressure generated by UVCE. For Jet fire, it is noted that the values of significant radiation are within a short distance (max 4.64 m). This is because the behavior of Jet fire is governed greatly by the pressure (see Haag and Ale, 2005), being this similar to the atmospheric conditions for all the considered configurations for the distillation columns. For BLEVE and UVCE, radiation profiles and overpressure are also presented. To analyze frequencies and probabilities, an event tree was used. The probability of immediate ignition, $p_{\mathrm{Immignition}}$, was calculated according to the conditions of release of the material, which depends on the operating conditions of the process; this is obtained by Eq. (5), where *AIT* is the auto-ignition temperature, *MIE* represents the minimum ignition energy, P and T are the pressure and temperature of the process, respectively. The probability of delayed ignition, $p_{DelayedIgn}$, was computed from Eq. (6) (see Moosemiller, 2011). Here, M_i corresponds to the product of the multipliers M_{mbr}, M_{mr}, M_{dr} and M_{io}. M_{mbr} is related to the multiplier for material being released as shown by Eq. (7). M_{mr} is the magnitude of the release. It is calculated through Eq. (8), where FR is the flow rate from the hole in lb/sec. The duration of the release and the number/density and strength of ignition source is given by M_{dr}, which is obtained through Eq. (9), where t is the time in seconds and S is an adjustment factor that depends on the type of source. Finally, M_{io} depends on the location of the operation and whether it is indoors or outdoors (see Eq. (10), where B_{es} is the volume of the enclosed space, B_{uv} is the ventilation rate and B_{vdel} is the ventilation draft direction). Fig. 6 shows the frequency analysis (i.e., the event trees) for a distillation column.

$$p_{\mathrm{Immignition}} = \left(1 - 5000e^{(T/AIT)}\right) + \left(\frac{0.0024P^{1/3}}{MIE^{1/3}}\right) \quad (5)$$

$$p_{DelayedIgn} = 0.3\prod M_i \quad (6)$$

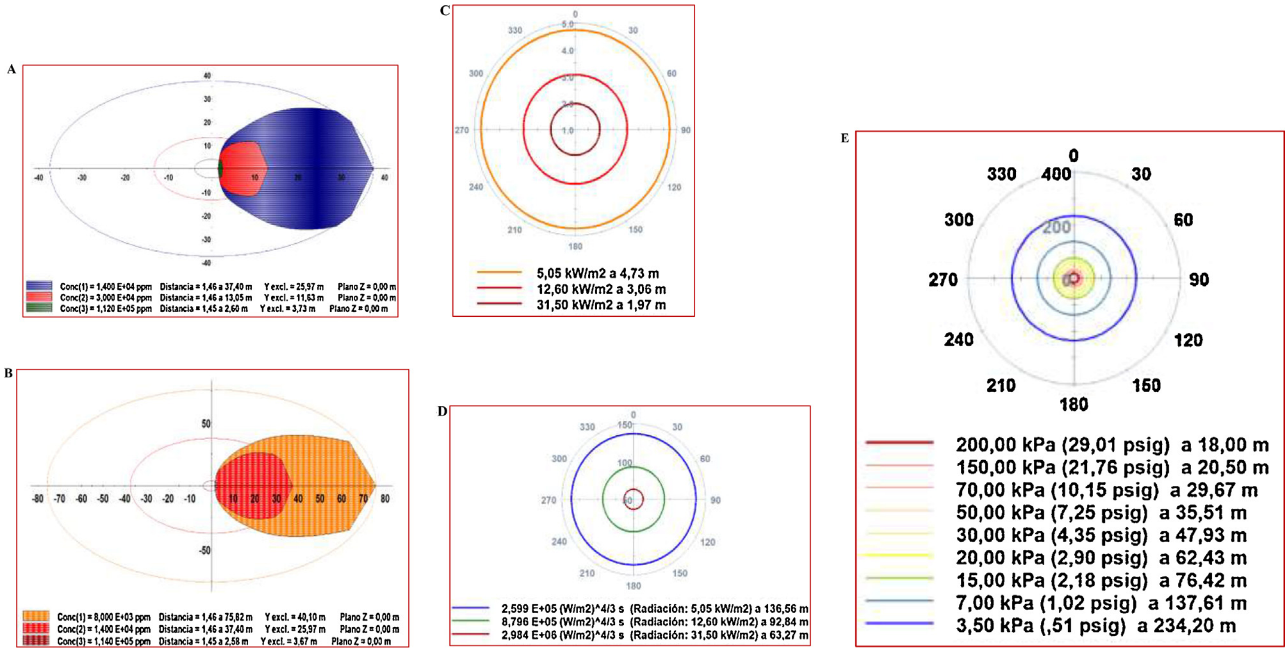

Fig. 5 – (A) Dispersion profiles for the first column of the route A (1.4%LFL-11.2UFL). (B) Distance which reaches the LC50 (800 ppm). (C) Radiation profile due to Jet Fire. (D) Radiation profile due to BLEVE. (E) Overpressure profile due to UVCE.

$$M_{mbr} = 0.6 - 0.85 \log MIE \quad (7)$$

$$M_{mr} = 7e^{0642 \ln(FR) - 4.67} \quad (8)$$

$$M_{dr} = \frac{\left[1 - \left(1 - s^2\right) e^{-(0.015\,S)t}\right]}{0.3} \quad (9)$$

$$M_{io} = 2\,B_{es}\,B_{uv}\,B_{vdel} \quad (10)$$

The risk quantification is done in terms of social and individual risks. The individual risk is the risk that a person has based on its position, which involves a damage of a certain magnitude and with certain frequency due to the effects of physical variables caused by the occurrence of an accident. This risk is independent of the number of people exposed. According to Eq. (11), the individual risk at geographical location x,y is determined by multiplying the probability of affectation caused by an accident ($P_{x,y,i}$) and the frequency

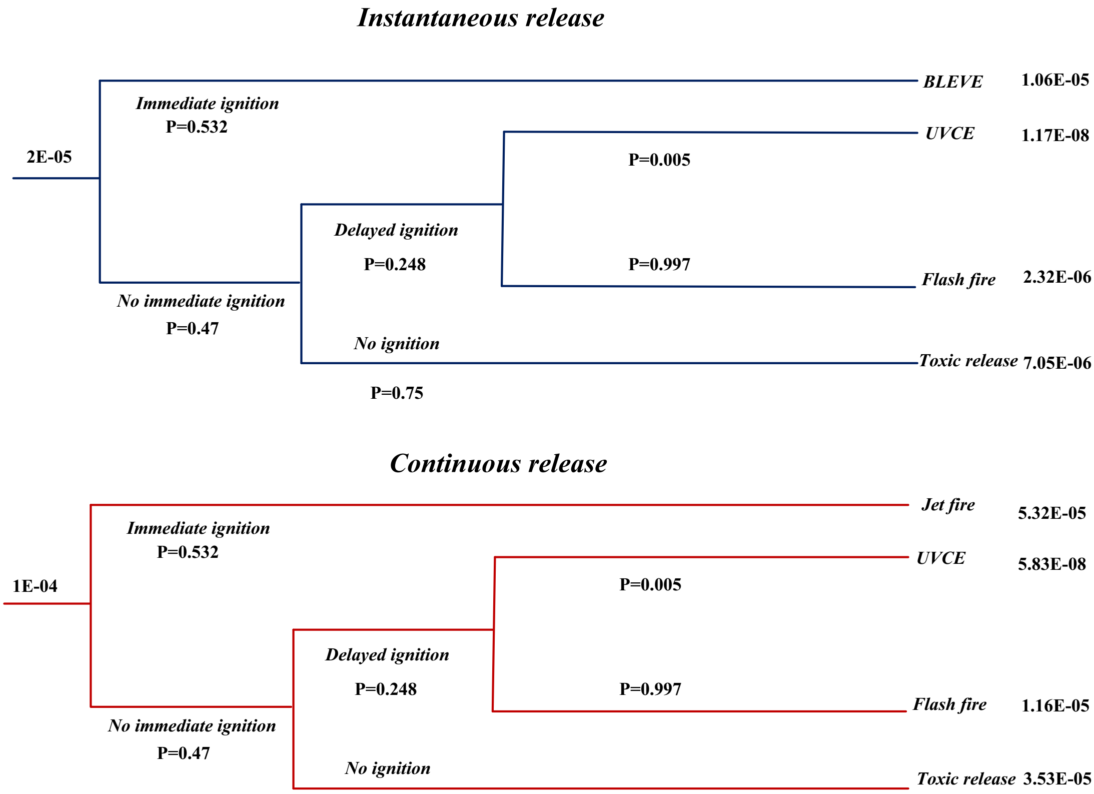

Fig. 6 – Event trees for the considered distillation columns.

of accidents, f_i. The sum of individual risks provides the total individual risk of an incident.

$$IR_{x,y} = \sum_{i=1}^{n} f_i P_{x,y,i} \tag{11}$$

The social risk (*SR*) is determined by Eq. (12), which indicates the multiplication between the probability of affectation, $P_{x,y,i}$, and the total number of workers exposed to the physical variables of an accident.

$$SR_i = \sum_{x,y}^{n} G_{x,y} P_{x,y,i} \tag{12}$$

4. Solution strategy

The number of stages, feed stage, reflux ratio and flow of distillate are optimizing variables in the considered columns, this optimization problem is significantly complex for which the Differential Evolution with Tabu List (DETL) method (Srinivas and Rangaiah, 2007) is applied. The implementation of this optimization approach was made using a hybrid platform through Microsoft Excel and Aspen Plus. The vectors of decision variables (i.e., the design variables) are sent from Microsoft Excel to Aspen Plus using a DDE (Dynamic Data Exchange) technique through a COM technology. In Microsoft Excel, these values are assigned to the design variables that Aspen Plus needs. After the simulation, Aspen Plus returns to Microsoft Excel the resulting vector of variables. Finally, Microsoft Excel analyzes the values of the objective function and proposes new values for decision variables according to the used stochastic optimization method. For the optimization of the analyzed process routes, the following parameters are used for the DETL method: 200 individuals, 500 generations, a Tabu list of 50% of total individuals, a Tabu radius of 0.0000025, and 0.80 and 0.6 for crossover and mutation fractions, respectively. These parameters were obtained through a tuning process via preliminary calculations. The tuning process consists of performing several runs with different number of individuals and generations, in order to detect the best parameters that allow obtaining the better convergence performance of the DETL method. For determining the used parameters for the heuristic search algorithm, a tuning approach based on previous experiences for this type of problems was implemented.

5. Results

Fig. 7 shows four Pareto curves obtained from the optimization process, in each curve are identified the points p1, p2 and p3, each one represents an attractive solution. Point p1 represents the best economic option and at the same time the worst environmental solution. Point p3 also represents an unbalanced solution between cost and environmental impact, because this favors by the environmental aspect, but this design has high costs. On the other hand, point p2 represents a balanced solution between two objectives, this solution is interesting because it has a significant slope change that produces a small cost. In other words, the point p2 is located in a zone where the minimum values of both objective targets (*TAC* and *Eco-indicator-99* values) were obtained through the optimization process. Furthermore, point p2 represents a non-dominated solution in the Pareto front. This behavior is observed in the four graphs which show evidence the contradiction between the two objectives, so that configurations with a high *TAC* have a small environmental impact. On the other hand, for a configuration with high environmental impacts, the cost decreases. The above trend is due to the higher number of stages and larger diameter of the column but the minor heat duty. These combinations produce the largest *TAC* but the smallest *Eco-indicator-99*. In Table 3, a comparison of the solutions obtained for the four routes is shown. In this table, the values for the *Eco-indicator-99* and *TAC* are compared. Process route D has much more economic potential compared with process routes A, B and C. This is due to the replacement of some columns by columns of liquid–liquid extraction. The process C is the one with less environmental impact. An additional evaluation by the *ROI* (see Fig. 8) shows the same conclusion, where the process D is the most viable from the economic point of view. Four design taking as a base design the process route D were proposed generating thermal coupling with an intensified designs. Our results showed that since the hybrid L-L configuration is considered, a decrement in the *TAC* values is also observed in comparison with those schemes that only account for conventional distillation columns in the separation of the ABE mixture. For example, after the optimization process, point 1 of process route C shows a *TAC* value of $172,191/year and the point p1 of the hybrid L-L configuration shows a *TAC* value of $127,803/year. This represents about 25% savings in *TAC*. A similar situation is observed when all process routes are compared with the hybrid L-L configuration (see Table 3). Furthermore, the inclusion of any thermal coupling diminishes the energy requirements which is a normal and well a reported behavior (Triantafyllou and Smith, 1992). In this case, the *TAC* and the *Eco-indicator99* are 24.5% and 11.8% lower compared with respect to the base hybrid design. When some column sections (rectifying and stripping zones) are moved, no improvement in the *TAC* and *Eco-indicator99* values are observed. However, when the intensified design was studied, there were obtained savings by 15% in the *TAC* with a 25% of penalty in the *Eco-indicator99* with respect to the thermally coupled design. The reduction in *TAC* values is normal since this design performs the same purification with only two distillation columns instead of three columns as the thermally coupled design. The penalty in *Eco-indicator99* is because of the slightly increase in the heat reboiler duty, which impacts drastically the *Eco-indicator99*.

Fig. 9 shows the results of the scenario in which the use of a solar collector was proposed, the results show a significant reduction in the values of the *Eco-indicator99*, because this is calculated considering zero emissions. However, the costs are higher compared with the first stage.

The results of the risk analysis show that the riskiest configuration is route A. This is mainly due to the inventories that are processed in this route A, which are superior to the rest of the routes. The inventories and the number of technologies used for the purification process of biobutanol play an important role in the magnitude of risk. The routes C and D are the less hazardous configurations, these configurations have fewer columns and also lower inventories. Table 4 presents the obtained individual risk (*IR*) and total individual (*TIR*), from the quantitative risk analysis to the routes A, B, C and D as well as for intensified routes obtained from process D, in the same way that the social risk (see Table 5), the C configuration is the one with the lowest individual risk. From the viewpoint of inherent safety, the configurations C and D represent proper solutions.

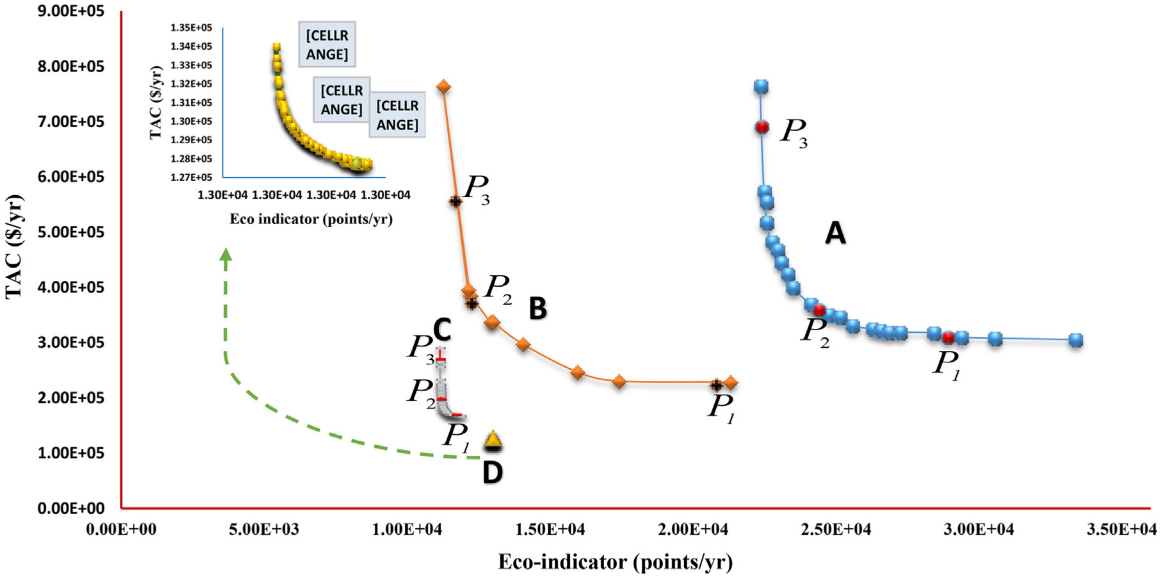

Fig. 7 – Pareto fronts for the analyzed process routes.

Table 3 – Economic and environmental comparison of the routes to purify biobutanol.

Design	Point	TAC ($/yr)	Eco-Indicator 99 (points/yr)
	1	310,269	28,894
A	2	360,054	24,377
	3	692,193	22,378
	1	224,799	20,783
B	2	385,390	12,198
	3	558,065	11,465
	1	172,191	11,850
C	2	211,478	11,165
	3	271,205	11,144
	1	127,803	12,976
D	2	129,773	12,972
	3	133,418	12,971
1D-LL with side stream	128,785	13,016	
2D-Thermally coupled	103,083	11,641	
3D-Thermodynamic Equivalent	104,215	11,570	
4D-Intensified	99,110	15,594	

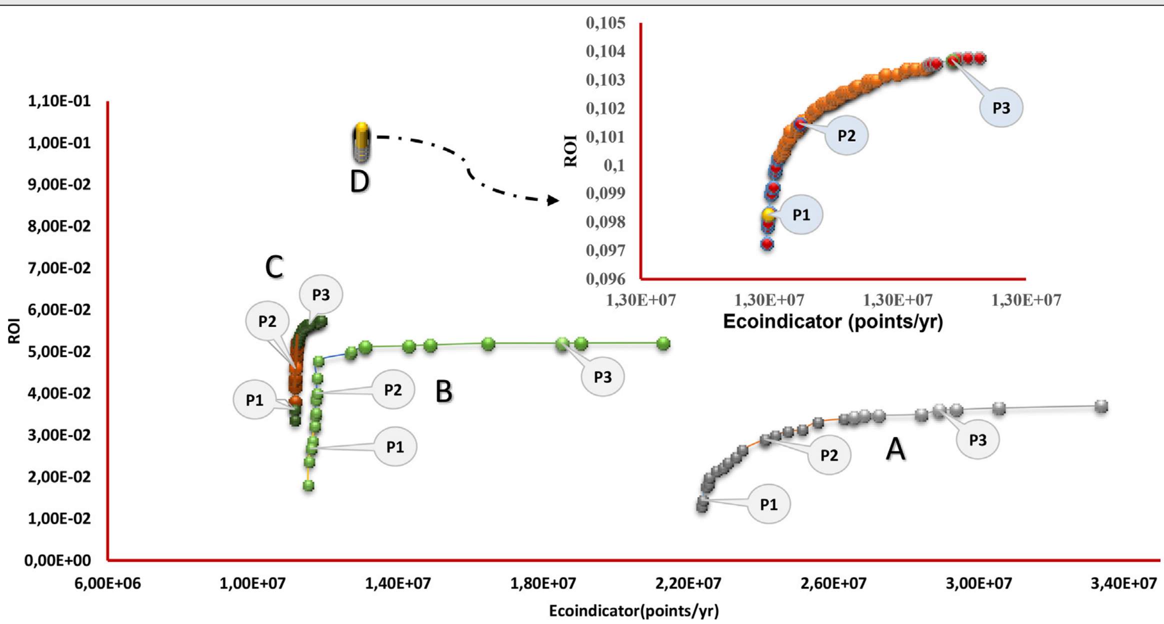

Fig. 8 – Pareto fronts for evaluating the ROI.

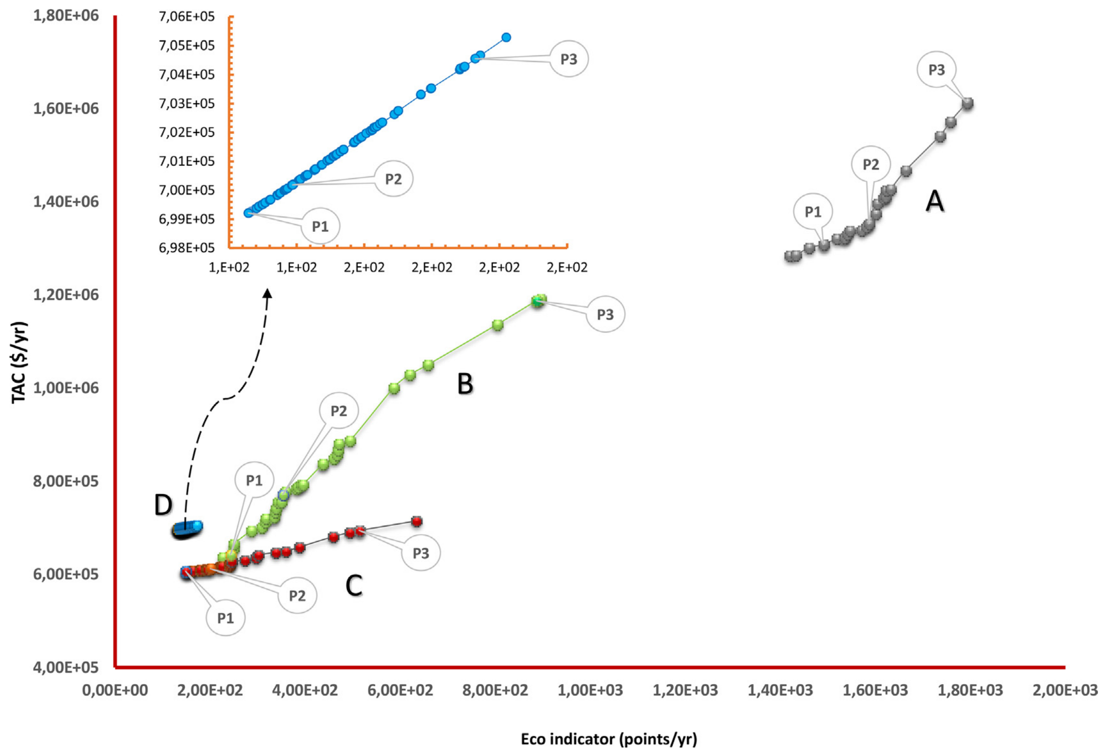

Fig. 9 – Pareto fronts for each process route involving solar collectors.

Table 4 – Individual risk.

Process design	Unit	IR ($\times10^{-5}$/yr)	TIR ($\times10^{-5}$/yr)	Intensified process design	Unit	IR ($\times10^{-5}$/yr)	TIR ($\times10^{-5}$/yr)
A	EA CC WH	4.75 15.50 4.39	24.60	1D	EA CC WH	3.26 5.41 3.06	11.70
B	EA CC WH	4.42 14.90 3.84	23.20	2D	EA CC WH	3.14 5.81 3.06	12.00
C	EA CC WH	3.72 14.30 3.35	21.40	3D	EA CC WH	5.06 5.41 5.06	15.50
D	EA CC WH	4.20 14.00 4.25	22.50	4D	EA CC WH	3.94 4.08 3.44	11.50

Table 5 – Social risk.

Process design	Unit	Social risk (fatalities)	Total social risk (fatalities)	Intensified process design	Unit	Social risk (fatalities)	Total social risk (fatalities)
A	EA CC WH	31 72 62	165	1D	EA CC WH	30 60 14	104
B	EA CC WH	41 52 62	155	2D	EA CC WH	30 66 15	111
C	EA CC WH	41 52 62	127	3D	EA CC WH	60 77 21	158
D	EA CC WH	28 61 60	149	4D	EA CC WH	51 41 14	80

For the intensified configurations obtained from the configuration D, the results regarding to the individual risk show that the route 3D is the riskiest route, obtaining a value of 15.5E−05 yr^{-1} (see Table 4). In the same way, the results show that the configuration 4D is the less risky route presenting an overall individual risk of 11.5E−05 yr^{-1}. The route 3D is the riskiest route because of the quantities of product that are fed to the columns. The operating pressure has no significant impact on the value of the risk, because most of the columns operate at atmospheric conditions. Moreover, the temperature has a significant impact on the level of individual risk because it is greater or equal to the self-ignition temperature, which increases the likelihood of immediate ignition, increasing as well the individual risk. Table 5 shows the social risk for each configuration expressed in terms of fatalities. The value of social risk also indicates that the configuration 3D is the riskiest one, which presents a risk of 158 fatalities. The social and individual risk were calculated considering the failure of all units that conform the configuration, for that reason the number of fatalities is high. It should be noticed that the intensified configurations are safer than routes A, B, C and D. The results show that the intensification strategy (minimization) significantly reduces the risk. This can be observed in Table 5, where the configurations 1D, 2D and 4D present lower risks compared with the conventional designs (reported in column D), which are used as the basis for obtaining the intensified designs. The main reason for this difference in results is due to the minimization of inventories in the intensified designs. Furthermore, there is an attenuation in the operating conditions of the intensified designs, which reduced the affectation area due to physical variables of radiation and overpressure. When the intensified designs are compared with the conventional designs, specifically for the cases A and B, it is possible to note the difference in the number of needed units, where the processes A and B require 5 units, the intensified solutions only require 4 units.

6. Conclusions

This paper has presented an optimization approach and a case study for the technology selection of the biobutanol separation process while accounting for the economic, environmental and safety issues. The optimization approach is based on a differential evolution with Tabu search algorithm, and the economic objective considers the minimization of the total annual cost, whereas the environmental objective includes the minimization of the, and the safety objective considers the minimization of the associated risk, which *Eco-indicator99*was measured through quantitative risk analysis. Several attractive configurations were identified through Pareto curves. Route A (steam stripping distillation and distillation columns) was found to be the worst since the economic and environmental points of view, this route consists of a steam stripping distillation and distillation columns.

The use of solar collectors represents an alternative for replacing fossil fuels, which impacts positively in the environmental objective but has a negative impact in the economic objective (i.e., the *TAC* increases more than 25%).

Route D (where some of the distillation columns were replaced with a liquid–liquid extraction column) was found to be economically viable. It is also the next-to-best option from a safety perspective. This makes it an attractive solution.

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