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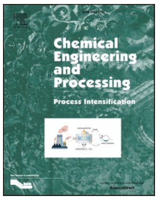

Design and intensification of distillation processes for furfural and co-products purification considering economic, environmental, safety and control issues

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ABSTRACT

Furfural is one of those promising chemicals obtained from biomass that is able to compete with petrochemicals. The purification of furfural is one the most critical stages during its production process, due to it requires a great amount of energy. In this sense, liquid-liquid extraction is one of the most promising alternatives. However, the main disadvantage of this alternative is the losses of co-products, which reduces the profitability of the process. This is work is one of the first to show the separation of coproducts of a purification process of furfural-based liquid-liquid extraction. Different intensified alternatives were tested in order to determine the best separation process for purifiying coproducts. The total annual cost, eco-indicator 99, the individual risk and the condition number were used to evaluate economic, environmental, safety and controllability aspects respectively, of the separation alternatives. The results indicate that the intensified alternatives have a reduction on total annual cost and environmental impact of around 25 %, while the improvements on the risk index is around 4 %. To conclude, an indirect intensified alternative was selected as the best option due to an improvement in cost and environmental impact, important risks reduction and similar control properties than those of conventional schemes.

1. Introduction

One of the most important tendencies nowadays in chemical engineering and technology processes is the Process Intensification (PI). PI, as a branch of chemical engineering was conceived in the United Kingdom by Colin Ramshaw's article published in 1983, which first described the application of centrifugal fields in the distillation processes [1]. PI has been commonly associated to the sector of basic chemical products, and of lately. However, in recent years it has become associated to new areas such as bioprocessing, fermentation [2–4] and fine chemistry [5]. PI offers innovative equipment, processing techniques and the development of new methods which, compared to conventional processes, are substantial improvements in (bio) chemical manufacturing and processing [6].

The philosophy of PI has been traditionally characterized by four characteristics: smaller, cheaper, safer, and environmentally friendly. One of the most important principles for implementing a PI approach is that it can improve the intrinsic safety and environmental impact of a process by considerably reducing the inventory of potentially hazardous chemicals in the processing unit [7]. Although safety and environmental impact can both benefit from PI, they are unlikely to be the driving force in most cases. Implementation of PI usually is based on other factors, such as reductions on energy consumptions and the creation of better-quality products. In some cases, PI will also allow for the commercial production of new and improved products.

The advantages of PI over conventional process improvement strategies are undisputable, and although progress has been made in several aspects and schemes in the design of PI, there is yet more to be done [8]. An important research area in PI is the development of processes for producing renewable chemicals derivate from biomass. The biomass is the most abundant renewable raw material on Earth, for this reason its use for producing renewable products such as chemicals, fuels and energy has been widely promoted in recent years [9]. The biomass can be an ideal substitute to fossil resources as oil for producing different commodities. In this sense, the processes that convert the biomass into high-value products are commonly called biorefineries [10]. Theoretically, a bio-refinery is equivalent to a petroleum refinery which

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Nomenclature

°C	Celsius
BLEVE	Boiling Liquid Expanding Vapor Explosion
CCPS	Center for Chemical Process Safety
DIS	Direct Intensified Scheme
DTC	Direct Thermally Coupled
EI99	Eco-Indicator 99
f_i	Frequency of incident I
GJ	Gigajoule
HAZOP	Hazard and Operability study
IIS	Indirect Intensified Scheme
IR	Individual Risk
ITC	Indirect Thermally Coupled
kg	Kilogram
$K_{i,j}$	Gain matrix
kW	Kilowatt
kWh	Kilowatt-hour
LC50	Lethal median concentration
LFL	Lower flammability limit
LLE	Liquid-Liquid Extractive
NIOSH	National Institute for Occupational Safety and Health
NREL	National Renewable Energy Laboratory
NRTL-HOC	Non-random Two-Liquids Hayden-O'Connell
p°	Overpressure due to explosions
PI	Process Intensification
$P_{x,y}$	Probability
$P_{x,y}$	Probability of affectation
QRA	Quantitative Risk Analysis
SVD	Singular Value Decomposition
TAC	Total Annual Cost
TCED	Thermally Coupled Equivalent Direct
TCEI	Thermally Coupled Equivalent Indirect
t_eE_r	Death with thermal radiation
UFL	Upper flammability limit
UVCE	Unconfined Vapor Cloud Explosion
$x_{i,j}^{Nom}$	Composition in the nominal value
$x_{i,j}^{sp}$	Composition after a perturbation on a manipulated variable
$\alpha_{b,k}$	Damage in category *k* per unit of chemical *b*
β_b	Amount of chemical *b*
γ	Condition Number
σ^*	Maximum singular value
σ_*	Minimum singular value
ω_d	Weighting factor of category *d*

produces fuels and chemicals from oil. In the same manner, effective biomass conversion technologies as well as separation and purification technologies that represent approximately 20–50 % of the total production cost [11], play an important role for a successfully commercial implementation of bio-refineries. Therefore, major improvements in separation and purification technologies can significantly reduce the total cost of production and result in environmentally sustainable and profitable process.

Nowadays the most of the improvements in biorefineries have been focused in the bioethanol production processes from lignocellulose wastes. However, in order to improve biorefineries' benefits, the production of additional products is preferred [12]. In agricultural products, lignocellulosic residues are available. These are made up primarily of cellulose, hemicellulose, and lignin. While cellulose could be used for producing ethanol, levulinic acid, glucaric acid, among others. The hemicellulose can be transformed into important products such as furfural or xylitol. Similarly, lignin can be recovered as a solid fuel for on-site use [13].

In this sense, Furfural has been classified as one of the main biomass-based chemicals by the U.S. National Renewable Energy Laboratory (NREL). Furfural is commonly used as a solvent within the refinement of lubricating oils, as a fungicide, as a nematocide and as raw material in the production of furfural alcohol, which makes up to 60 % of all furfural produced [14,15]. Nowadays, China is the is the leading in the production of furfural, the Chinas' production is based on Quaker Oats process, which was invented in 1922. This process is used to produce the 80 % of the current furfural production and is characterized by an intensive use of energy [16]. However, the Quaker Oats process has not undergone major changes or improvements since the 1920s. Currently, the China's production is based in a number of small producers with a capacity of only a few kilotons per year, while the largest furfural plant which produces 35 kilotons per year is based in the Dominican Republic [17].

The Quaker Oats process, which is the traditional process used to produce furfural, starts from biomass, and it basically consists of three stages which involves conditioning, reaction and separation (distillation) operations. Biomass is milled in the first stage and it is passed to the reaction in the second stage [18]. Hydrolysis reactions occur in the reactor, producing a vapor stream with a composition of about six percent furfural, ninety percent water and four percent by-products (such as acetic acid and methanol) (15). After condensing the stream and due to its high-water content, it is usually sent to a series of distillation columns to achieve the separation and purity of the products.

Furfural production technologies have improved. In general, these improvements have been directed to increase the performance of the reaction unit. For example, the Vedernikovs process proposed that the use of salts and acid catalysts can improve the efficiency of the reaction, as well as provide an increase in the performance of furfural [19]. On the other hand, the Suprayield process makes use of a new concept where furfural is removed from the liquid reaction phase [15]. As a result of this, resinification of furfural (furfural-furfural polymerization) cannot occur and furfural yield increases. Similarly, innovative reaction processes have been studied for the production of furfural from raw materials such as straw, using the "Multi Turbine Column" reactor [20]. In this process, raw material is introduced into the upper part of the continuous turbine reactors, and steam which is fed in countercurrent. This allows furfural to be continuously removed, resulting in higher yields and lower energy requirement [20].

Despite the advances in the reaction unit in order to improve the furfural yields, there are not important improvements for the separation stage, thus, the high energy requirements in the distillation unit remain. Jong et al. [21] present a study where only simple heat integration techniques were applied, including steam recompression and preheating. These authors acknowledge the importance of the study that demonstrates the application of advanced PI techniques, such as the use of split-wall columns in the furfural separation process. Consequently, Nhien et al. [18], have also suggested integrated and intensified processes, including an innovative dividing wall column with a decanter configuration to improve the energy and profitability of the furfural production process.

Nevertheless, the main disadvantages in many current furfural production processes is the inclusion of high energy use, low capacity, and the lack of intensified designs. In this work (using PI techniques) a new intensified separation processes are developed in order to achieve the purification of furfural and co-products with better energy consumptions, safety, environmental impact, and control properties. The processes suggested are based on a liquid-liquid extraction process scheme and the use of coupled columns to overcome limitations in the

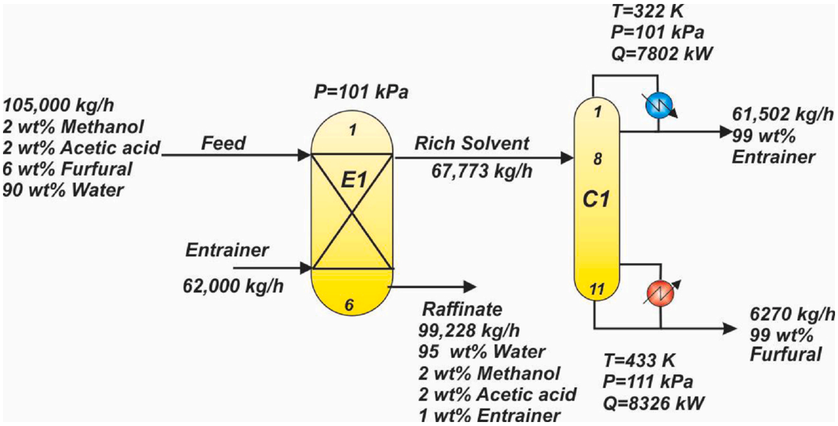
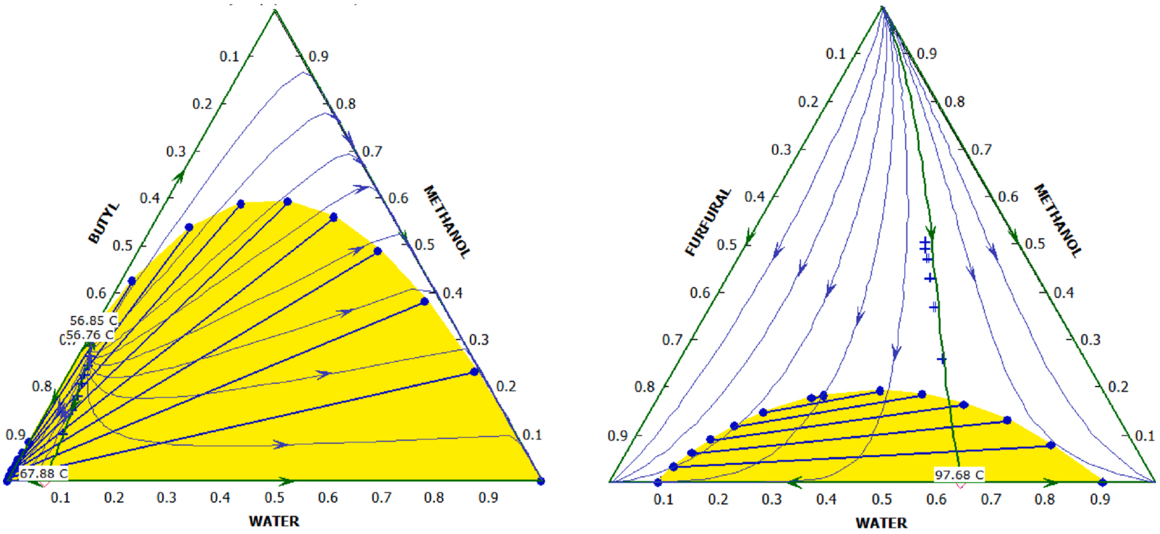


Fig. 1. Case base proposed by Nhien et al. [22].



A)

B)

Fig. 2. Ternary diagrams for mixtures a) water/butyl chloride/methanol B) water/furfural/ methanol.

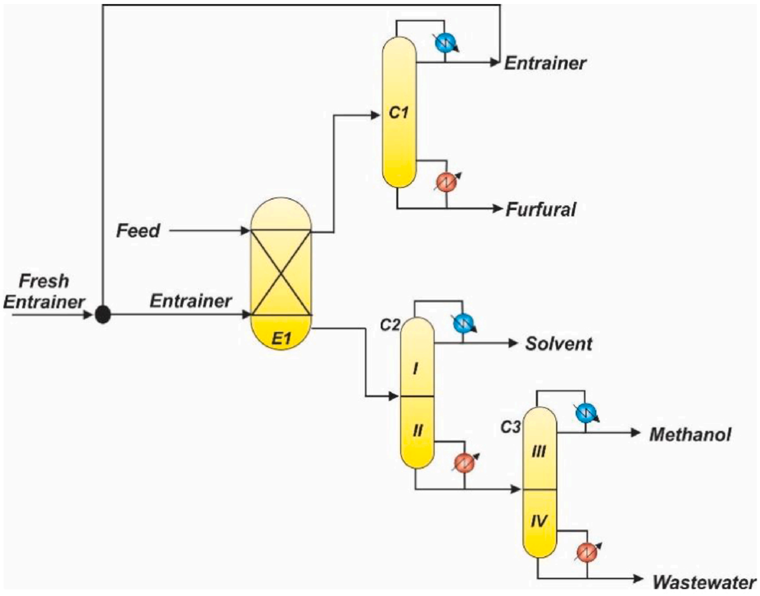
purification of co-products. A comprehensive and systematic study using PI was proposed to generate different intensified alternatives in order to separate furfural from the co-products produced and determine the best processing option. The configurations were rigorously simulated by Aspen Plus, and the furfural production process alternatives were jointly evaluated under economic, environmental, safety and control indexes to generate the most sustainable process separation. These indexes were chosen based on the twelve principles of sustainability in chemical processes proposed by Jiménez-González and Constable [22]. Additionally, Rafiei and Ricardez-Sandoval. [23], proposed that the design of chemical processes should consider a more integrated evaluation where different parameters are evaluated in order to generate a more sustainable process. The consideration of these indexes to evaluate different aspects of the processes during the design phase assists in the selection of the best alternative.

2. Base case and systematic approach for designing schemes

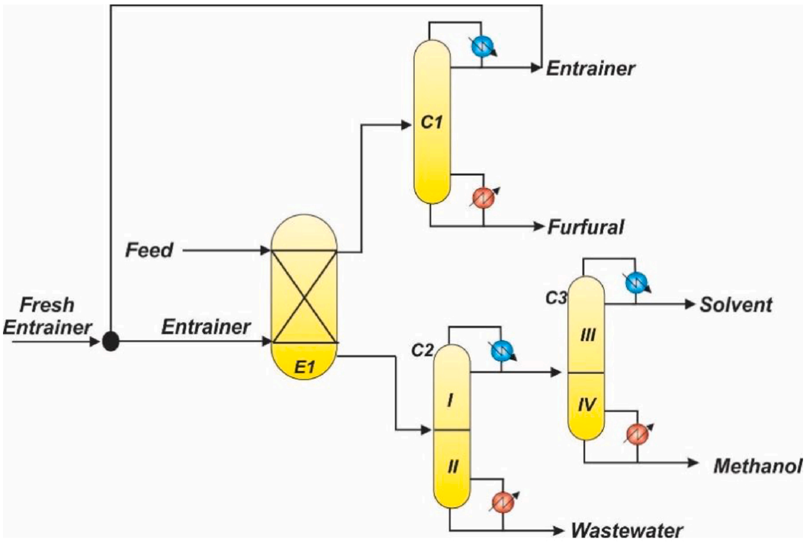
This work uses as its base case the work previously reported by Nhien et al. [24], which proposed an interesting hybrid configuration for purifying furfural. Their proposal consist in a hybrid configuration since two conventional processes are combined: a distillation column and a Liquid-Liquid Extractive column (LLE). Fig. 1 shows the case base proposed by Nhien et al. [24]. It is worth mentioning that in LLE, Butyl chloride was proposed as a solvent. The separation generated in LLE is carried out in such a way that an extract composed of a large portion of furfural is obtained; the extract is then introduced to a conventional distillation column to purify furfural and a considerable portion of the solvent. Otherwise, raffinate from LLE will mainly consist of water, methanol, acetic acid, and Butyl chloride; in Nhien's design, this raffinate stream is considered waste material.

Because the raffinate stream contains a considerable amount of methanol and Butyl chloride, it becomes necessary to convert the stream into a product with greater added value. The proposal of this work is to synthesize and design separation alternatives in order to purify co-products from the raffinate stream, mainly methanol, to achieve a profitable process. However, the separation task is not a trivial issue, Fig. 2 shows the ternary equilibrium diagrams for the mixtures water/ butyl chloride/methanol and water/furfural/ methanol for the second.

Although the presence of azeotropes among the components, the recovery of methanol and the entrainer with conventional distillation can be achieved since the composition of raffinate allows it; hence, improving the profitability of the process. in this work a sensitivity analysis of the process proposed by Nhien et al. [24] is performed in



A)



B)

Fig. 3. Direct (A) and indirect (B) schemes to purify the raffinate stream.

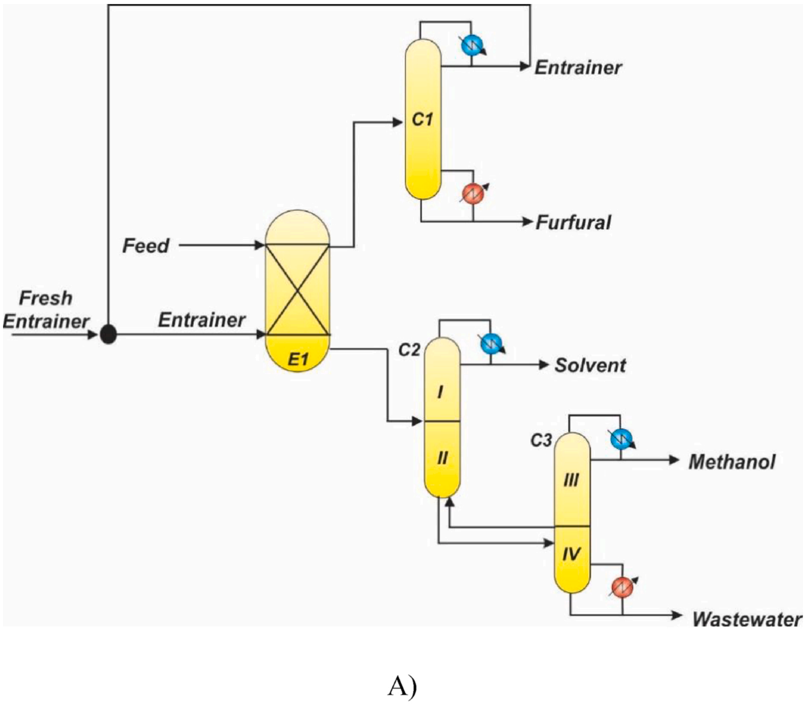
order to reduce the amount of solvent, which reduces the energy consumption, separation costs and improve the recovery of methanol from the raffinate stream. During this sensitivity analysis the amount of solvent and the number of stages for the extractive and column C1 are varied in order to obtain a furfural stream with a purity of 99.9 % wt (the purity required for furfural) with the less amount possible of solvent in the raffinate stream, which helps with the separation of methanol.

Once the amount of solvent that minimizes the energy consumption and the flow rate of it in the raffinate stream is obtained, the processes to purify the methanol can be proposed. This methodology to generate new alternatives is based on the introduction of thermal couplings and/or transposition/movement of a section, which defines a column section as a portion of any conventional column not shortened by mass or heat streams [25,26]) and process intensification. The orderly and logically structured procedure aspects of this methodology have made it possible to obtain exceptional results in terms of energy, economic and environmental savings [27,28]. In this section, a methodology created to generate different intensified distillation configurations is described in four steps. It is important to emphasize that the intensified schemes are based on thermally coupled configurations and in intensification of the mentioned schemes. The steps to generate the new processes are presented below:

2.1. Detection of conventional schemes

Based on Nhien's proposal, raffinate emerging from LLE can be separated if two conventional options are considered. In Fig. 3, a direct and an indirect topology can be seen and since the raffinate is composed primarily of considerable proportions of three components; only two conventional columns are needed.

In a direct scheme, butyl chloride is purified at the top of first column to then be returned to LLE, and both methanol and water are obtained as



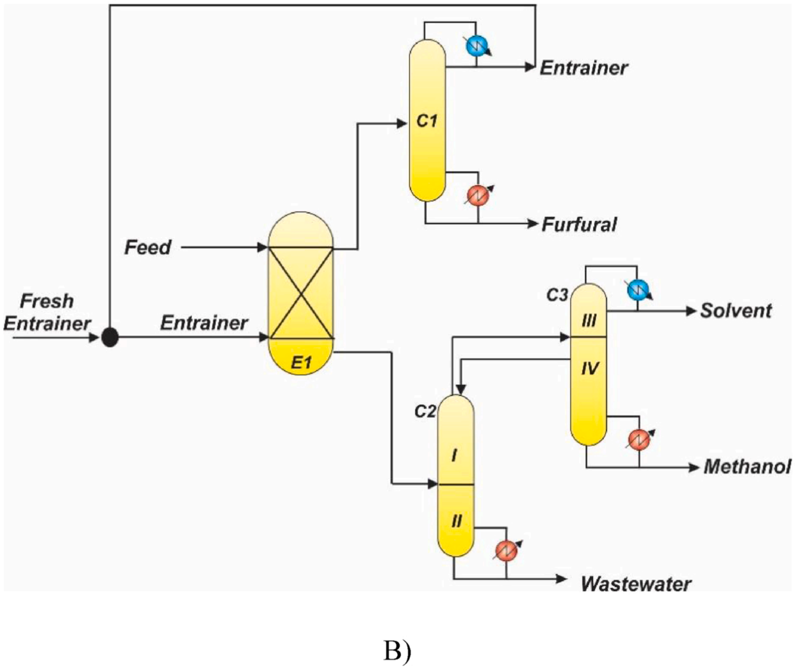


Fig. 4. Thermally coupled schemes to purify the raffinate stream A) Direct scheme (DTC) B) Indirect Scheme (ITC).

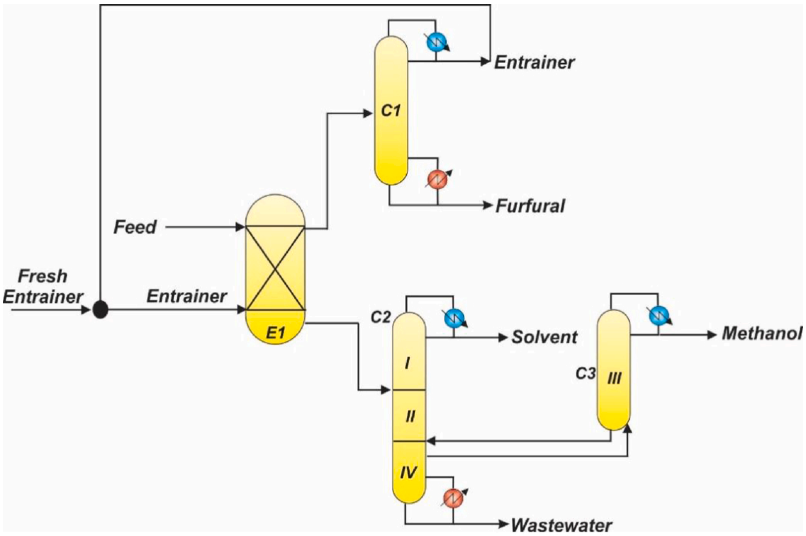
products from the top and bottom of the second column, respectively. In an indirect sequence, water is obtained at the bottom of the first column, and both butyl chloride and methanol are obtained as products from top and bottom, respectively.

2.2. Application of thermal couplings

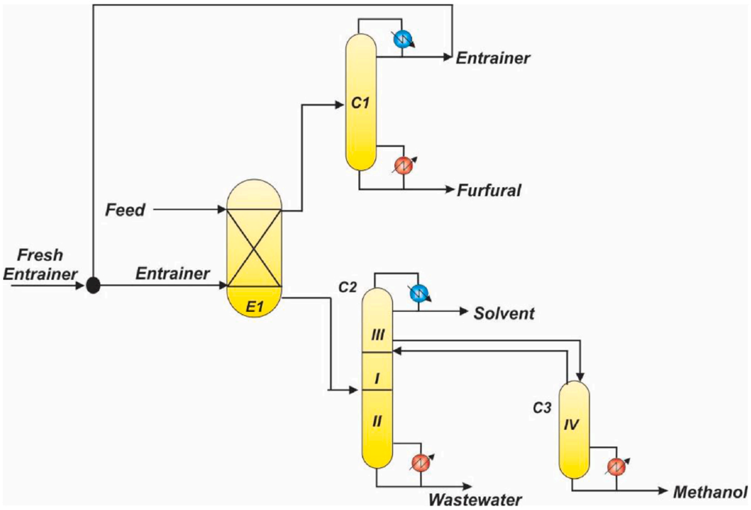
From the topology in cases A and B in Fig. 3, it is possible to generate two modified thermally coupling schemes if a heat exchanger (reboiler or condenser), directly connected to a non-product stream is replaced with a liquid/vapor stream. The scheme in Fig. 4A was obtained by replacing the reboiler of the first column and with a vapor stream emerging from the second column and fed at the bottom of the first column; this scheme is called Direct Thermally Coupled (DTC). On the other hand, the scheme in Fig. 4B was obtained by substituting the condenser of first column and replaced by a liquid stream coming from the second column. It was then fed at the top of first column; this configuration is called Indirect Thermally Coupled (ITC).

2.3. Transposition of column section to generate a thermo equivalent and intensified schemes

Once the thermal couplings have been introduced, it is worthwhile mentioning that there are some column sections where either a condenser or a reboiler provide a common reflux ratio/vapor boil-up between two adjacent columns. Taking this into consideration, it is



A)



B)

Fig. 5. Thermodynamic equivalent schemes. A) Direct thermodynamic equivalent B) Indirect thermodynamic equivalent.

possible to transpose column sections to generate thermally coupled equivalent sequences. Fig. 5A was obtained from the corresponding thermally coupled sequence moving section IV below section II. This option is called Thermally Coupled Equivalent Direct (TCED). In a similar manner, Fig. 5B is generated by moving of section III above section I. This process is called Thermally Coupled Equivalent Indirect (TCEI). These thermally coupled equivalent schemes have similar energy requirements to their respective typical thermally coupled options DTC and ITC. The topology of these new processes provides important differences and new characteristics on important aspects such as safety and control (Fig. 6).

2.4. Elimination of column Section

Once the thermally equivalent schemes have been generated, other strategies can be used in order to further increase the intensification of these configurations. One of the most interesting strategies proposed by Errico et al. [29], consists in the elimination of unnecessary sections, named transport sections, from the thermodynamic equivalent schemes. The methodology used to generate these intensified schemes consists in the elimination of columns or lateral equipment formed by only one section and adding a side liquid stream instead. Because the side stream replaces a thermally coupled, the physical phase of the side stream is determined by the phase state of the stream which connects to the deleted lateral equipment [29]. Fig. 5 shows the Direct Intensified Scheme (DIS), and the Indirect Intensified Scheme (IIS). There is a difference though between the intensified schemes, those being, the location of the methanol stream and the number of stages of each column C2 since each column is formed at different sections.

3. Simulation approach

In this work the mentioned distillation schemes were rigorously designed and simulated using the RADFRAC modulus contained in

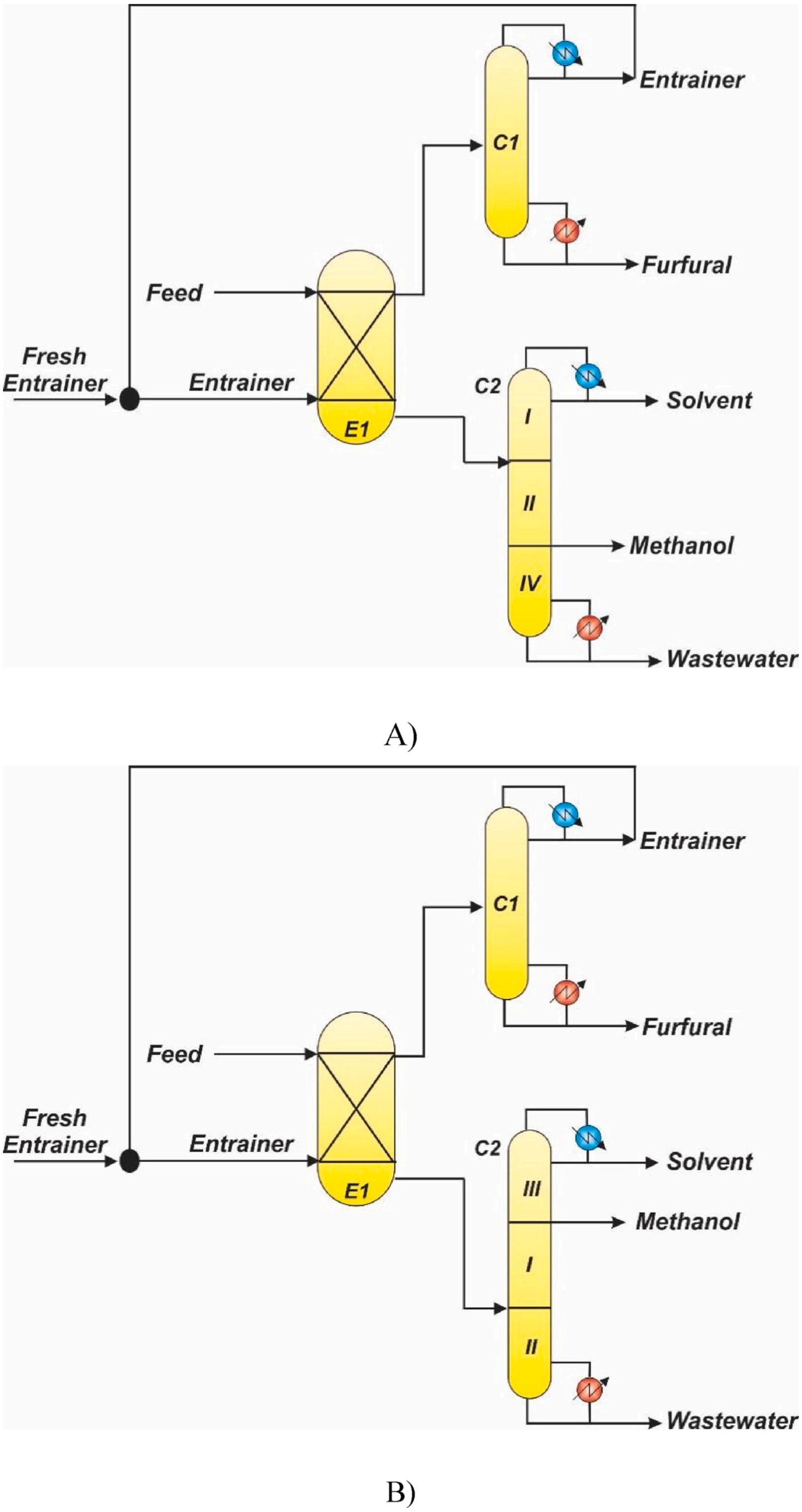


Fig. 6. Intensified distillation schemes A) Direct intensified scheme (DIS) B) Indirect intensified scheme (IIS).

Aspen Plus. This modulus contains the complete set of MESH equations (Mass, energy, and equilibrium equations). In order to perform the design of the separation schemes in the most general and extendible way to the majority of furfural plants, the average composition reported by Zeitsch [15] was used. Zeitsch determined by study of several furfural plants that most hydrolysis furfural reactors produce a vapor stream with a composition of 90 % wt water, 6 % wt furfural, 2 % wt methanol and 2 % wt acetic acid. In the same way Zeitsch found that this stream's thermal conditions are around of 353 K and 2 atm. A production of 6300 kg/h of furfural is considered in order to satisfy the global demand reported by Nhien et al. [18]. This production of furfural corresponds to a feed mass flowrate of 105,000 kg/h. The equilibrium vapor-liquid-liquid in the mixture can be modeled using the thermodynamic package model NRTL-HOC, which contains the Non-random Two-Liquids equations coupled with equation state of Hayden-O'Connell. This thermodynamic model predicts the formation of two liquid phases and azeotropes among different components; as well as takes into account the solvation and dimerization of mixtures that contain carboxylic acids [24,30].

4. Performances criteria

In this section, the metrics used to evaluate the performance of distillation schemes are defined. The total annual cost, eco-indicador 99, individual risk and condition number were selected as criteria to evaluate the plant economy, environmental impact, safety, and control properties, respectively. These criteria were chosen according to the twelve principles of green and sustainable processes proposed by Jiménez-González and Constable [22]. Rafiei and Ricardez-Sandoval [23] have also established that the sustainability of processes can be improved upon employing a more integral approach where different parameters are considered. This integral approach takes into account different design variables that affect some parameters of sustainable process such as process controllability, safety, environmental impact and economy. Hence, a more integral approach where different metrics are considered provides a more extended overview for decision-making procedure in order to select the most sustainable option process. Finally, the four indices are defined as follows:

5. Economic index: total annual cost (TAC)

Total Annual Cost (TAC) is a common metric used to evaluate the economic performance of a set of different chemical processes options. TAC is defined as the sum of annualized capital cost plus the operating cost associated with utilities. Mathematically, TAC can be expressed as follows:

$$TAC = \frac{\text{Capital cost}}{\text{Payback period}} + \text{Operating cost} \tag{1}$$

The capital cost is associated to the construction cost of process equipment, such as condensers, reboilers, distillation columns, trays, process vessels and compressors; whereas the operating cost corresponds to the cost of use of electricity, cooling water, steam and solvents. The Guthrie method is used to calculate the total annual cost. The parameters and equations required to estimate the cost of equipment and utilities were taken from Turton et al. [31]. Carbon steel is the construction material considered, and a payback period of five years is used, which corresponds to an average payback time of a chemical plant. Trays type Sieve with 0.61 m spacing were considered for distillation columns. The utilities costs are calculated considering 8,500 h of operation per year. The utilities used in this work and their respective cost are: low-pressure steam (6 atm, 160 °C, \$14.95/GJ), medium-pressure steam (11 atm, 184 °C, \$14.83/GJ), high-pressure steam (42 atm, 254 °C, \$17.7/GJ), cooling water (\$0.72/GJ) and electricity (\$16.8/GJ) [31].

5.1. Environmental impact index: Eco-Indicator 99 (EI99)

The environmental impact of the distillation schemes is estimated using the eco-Indicator 99 method (EI99), which is based on the life cycle assessment methodology. The EI99 was proposed by Goedkoop and Spriensma [32]. This methodology has been implemented successfully in several chemical processes and biorefineries when estimating their environmental impacts. Piamonte [33], used the EI99 to evaluate the environmental impact of bioethanol and electricity production using wood residues and corn stover as raw materials the results show that a bio-refinery that uses wood is always preferable to a bio-refinery that uses corn stover as it depletes less resources. Grillo Renó et al. [34] implemented the eco-indicator 99 in different biorefineries for producing ethanol from sugarcane, they applied the study to the Brazilian alcohol industry. In this work, the authors were able to identify that stages of cultivation and transportation have a greater environmental impact in the production of bioethanol in Brazil. The authors suggested a different study be implemented based on the effect of depleted land nutrients because of the cultivation of sugarcane during long periods. Silalertruksa et al. [35] used the EI99 to improve the sustainability of biorefineries in Thailand. Their results show that the use of vinasse and cane residue can reduce the environmental impact during the production of bioethanol and sugarcane-based sugars as raw material.

Table 1
Values of EI99 impact categories used for distillation columns. (Goedkoop and Spriensma [32]).

Impact category	Steel (points/kg) × 10^{-3}	Steam (points/kg)	Electricity (points/kWh)
Carcinogenic	1.29×10^{-3}	1.180×10^{-4}	4.360×10^{-4}
Climate change	1.31×10^{-2}	1.27×10^{-3}	4.07×10^{-3}
Ionizing radiation	4.510×10^{-4}	1.91×10^{-6}	8.94×10^{-5}
Ozone depletion	4.550×10^{-6}	7.78×10^{-7}	5.41×10^{-7}
Respiratory effects	8.010×10^{-2}	1.56×10^{-3}	1.01×10^{-5}
Acidification	2.710×10^{-3}	1.21×10^{-4}	9.88×10^{-4}
Ecotoxicity	7.450×10^{-2}	2.85×10^{-4}	2.14×10^{-4}
Land occupation	3.730×10^{-3}	8.60×10^{-5}	4.64×10^{-4}
Fossil fuels	$5.930 \times 10{-}2$	1.24×10^{-2}	1.01×10^{-2}
Mineral extraction	$7.420 \times 10{-}2$	8.87×10^{-6}	5.85×10^{-5}

The EI99 estimates environmental impact based on an evaluation of the following categories: ecosystem quality, resources depletion and human health. These impact categories are divided into eleven subcategories. The subcategory values used in this work are illustrated in Table 1. The eco-points scale shown in Table 1 indicates one point, and each point represents the 1000th part of environmental load of one average European inhabitant per year [32,36]. The steam required to provide energy, the electricity used for pumping cooling water, and the steel required in the construction of the equipment are considered the most important factors in the environmental impact generated by distillation columns according to the previous works reported by Errico et al. [24] and Sanchez- Ramirez et al. [26]. Mathematically the EI99 can be expressed as follows:

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

Where β_b is the amount of chemical *b* released by direct emission per unit of reference, $\alpha_{b,k}$ represents the damage in category *k* per unit of chemical *b* released to the environment, ω_d is the damage weighting factor of category *d*, and δ_d is a normalization factor for damage of category *d*, respectively. The evaluation of EI99 was carried out considering a hierarchical perspective in order to achieve an equilibrium between short- and long-term effects on the environment. The weighting factors considered for major impact categories, which are human health, ecosystem quality, and resources depletion were carried out as reported by Mettier [37] and Goedkoop and Spriensma [32] in a typical hierarchical analysis. Damages to human health and to the ecosystem are given equal importance and they are equally weighted, whereas damage to resources were only given half the importance.

5.2. Process safety index: Individual risk (IR)

The Individual Risk (IR) is the index selected for safety evaluation. The IR represents the frequency a person is likely to experience or be affected by an accident. The individual risk is independent of the number of people exposed as it quantifies the likelihood of the damage as a function of distance between the accident's epicenter and the location of a victim.

Mathematically, the individual risk (IR) can be expressed according Eq. (3)

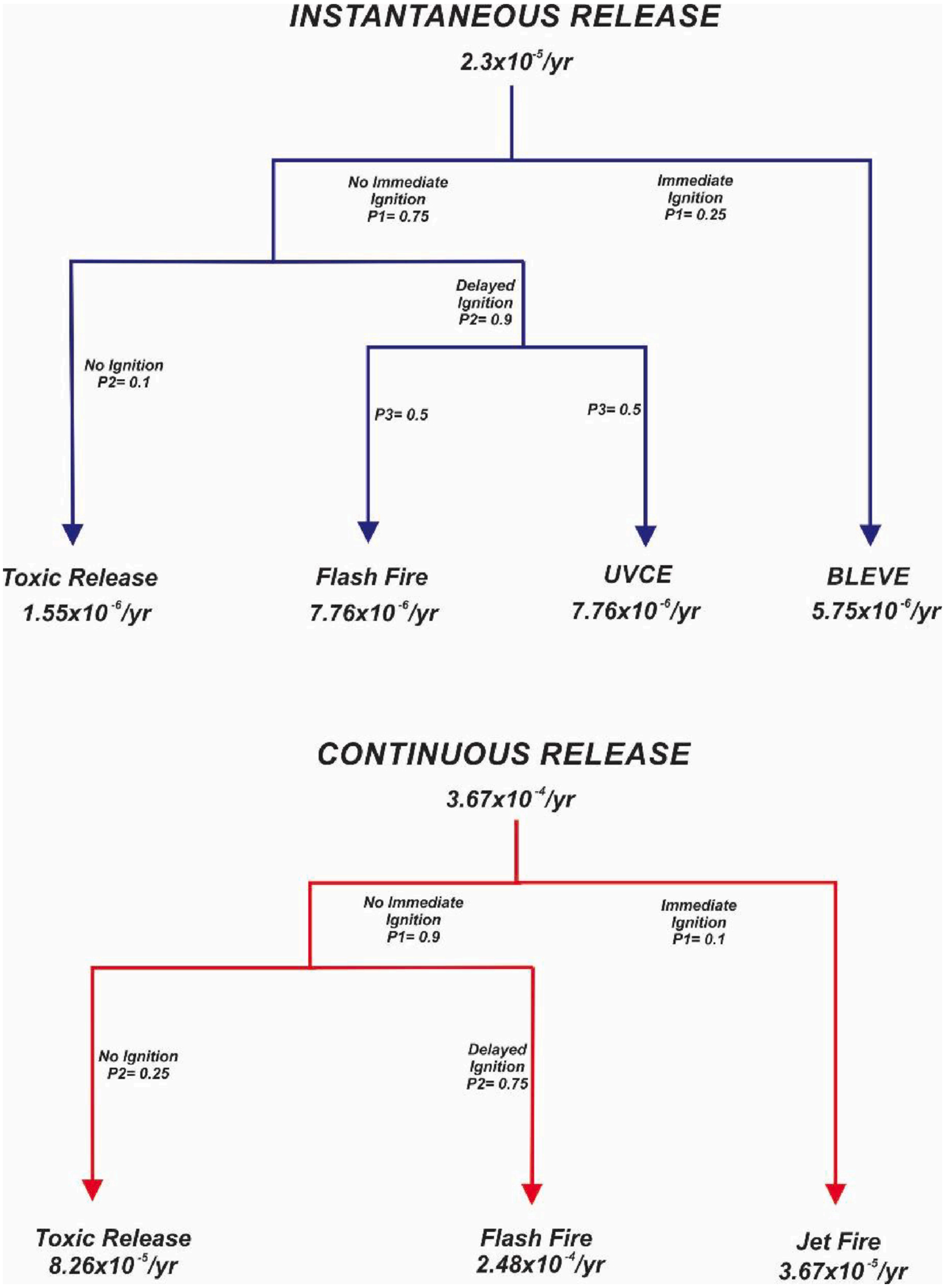


Fig. 7. Event tree diagrams for distillation schemes.

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

where f_i is the occurrence frequency of incident i, and $P_{x,y}$ is the probability of affectation caused by the incident i. The IR is calculated using a Quantitative Risk Analysis (QRA) which is the methodology used for the identification and quantification of possible incidents and their respective consequences. The QRA classifies the incidents in two categories: continuous releases and instantaneous releases. A continuous release is caused by a rupture on a pipeline or a partial rupture on the process equipment causing a leak of matter. On the other hand, an instantaneous release is caused by a catastrophic rupture of the process equipment which may result in the total loss of matter from the vessel. A Hazard and Operability study (HAZOP) is used to identify the possible instantaneous and continuous incidents in distillations columns. This is a common method used in the chemical industry based on deviations of operative conditions. Specific information about this methodology is given by the Center for Chemical Process Safety (CCPS) [38]. Boiling Liquid Expanding Vapor Explosion (BLEVE), Unconfined Vapor Cloud Explosion (UVCE), flash fire and toxic release were all instantaneous release incidents determined during the HAZOP analysis. Jet fire, flash fire and toxic release were identified as continuous release incidents. Fig. 7 shows the tree diagrams for instantaneous and continuous releases identified by the HAZOP method and their respective frequencies (f_i).

The probability of affectation $P_{x,y}$ is computed using a consequence assessment analysis, where the physical variables (e.g. thermal radiation, overpressure and leak concentration) of each incident and their respective damages are calculated. The equations used to calculate the physical variables of each incident are reported by CCPS [38] and Medina-Herrera et al. [39]. A probit model is employed to relate the values of physical variables to damage caused to a person. In this work, the death of a person is the considered damage, which may be caused by

Table 2
Physical properties of components.

Component	Lower flammability limit (LFL)	Upper flammability limit (UFL)	Median lethal concentration (LC50)	Heat Combustion (kJ/mol)
Furfural	2	19	64,000 ppm/4h	2,344
Methanol	6	36	1,037 ppm/1h	726
Butyl Chloride	1.8	10.2	32,000 ppm/1h	2,697
Acetic Acid	6	17	16,000 ppm/4h	876.1

toxics releases, explosions, or fires. The probit equations that correlate the death with thermal radiation ($t_e E_r$) and overpressure due to explosions ($p°$) are provided in Eq. 4 and Eq. 5 respectively.

$$Y = -14.9 + 2.56\ln\left(\frac{t_e E_r^{\frac{4}{3}}}{10^4}\right) \tag{4}$$

$$Y = -77.1 + 6.91\ln(p^{\circ}) \tag{5}$$

Eq.s 4 and 5 were taken from the previous works reported by CCPS [38] and other authors, such as Medina-Herrera et al. [39]. All calculations were made considering 50 m as a representative distance. The probability ($P_{x,y}$) which is computed by the substitution of the Eq. 4 and Eq. 5 into the following equation:

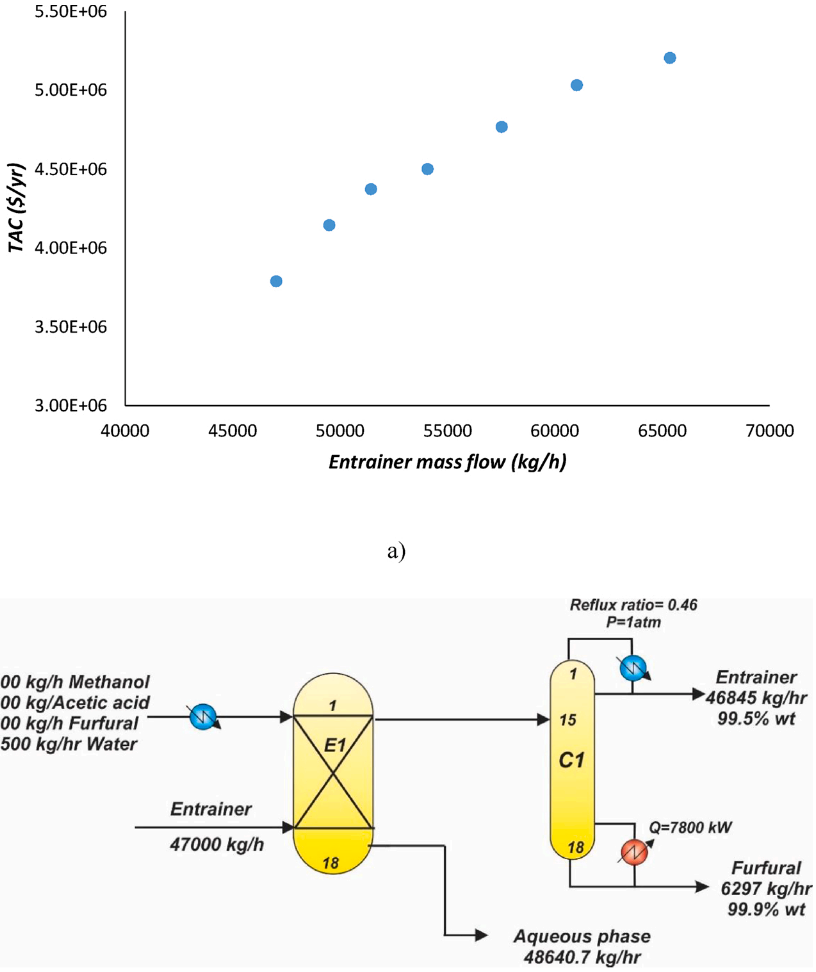
$$P_{x,y} = 0.5\left[1 + erf\left(\frac{Y-5}{\sqrt{2}}\right)\right] \tag{6}$$

In the case of toxic releases, LC50 (Lethal median concentration) is used to determine the probability ($P_{x,y}$) as there exists a lack of probit models for toxic releases of different substances. An atmospheric stability type F with a wind speed of 1.5 m/s is used to calculate the concentrations of the chemical components in the air during a toxic release incident. These conditions correspond to the worst scenarios according to Crowl and Louvar [40].

The physical properties for each substance used in consequence assessment are reported in Table 2. These were taken from the National Institute for Occupational Safety and Health (NIOSH) [41].

5.3. *Controllability index: condition number (γ)*

The condition number is a common index used to determine in a qualitative way the controllability of a specific process. It has proven to be a powerful tool as it analyzes the control properties of a process in order to detect potential operational problems [42,43]. In the case of distillation columns, the condition number has been successfully implemented in several different cases. On the one hand, Gutierrez-Guerra et al. [44] used the condition number to determine the control properties of conventional and intensified extractive distillation



a)

b)

Fig. 8. a) Effect of solvents on TAC b) Final design for extractive and C1 columns.

Table 3
Design specification for distillation sequences.

Design parameters		Distillation sequence						
	Direct	*Indirect*	*DTC*	*ITC*	*TCED*	*TCEI*	*DIS*	*IIS*
	Columns topology							
Stages C2	50	50	50	50	76	61	76	59
Stages C3	50	50	50	50	24	39	–	–
Feed stage C2	27	29	27	29	27	29	27	29
Feed stage C3	9	11	–	–	–	–	–	–
Diameter C2 (m)	1.816	2.82	1.80	2.19	2.28	2.27	3.09	2.16
Diameter C3 (m)	2.48	0.35	2.56	1.73	1.69	0.3	–	–
Vapor stage	–	–	25	10	50	11	–	–
Liquid stage	–	–	24	9	49	10	–	–
Stage Methanol Lateral stream	–	–	–	–	–	–	50	10
	Operation specifications							
Reflux ratio C2	21	21	15.92	–	18	140	200	110
Reflux ratio C3	20.07	4.4	11.55	126.6	8.77	–	–	–
Reboiler duty C2 (kW)	9321	22,162	–	13,922	15,300	14,618	25,000	13,373
Reboiler duty C3 (kW)	10,608	232	15,100	200	–	78	–	–
Top Pressure C2 (atm)	1	1	1	1	1	1	1	1
Top PressureC3 (atm)	1	1	1	1	1	1	1	–
Temperature of Condenser C1 (°C)	56.93	62.84	56.94	–	56.944	56.93	57.80	56.94
Temperature of Condenser C2 (°C)	64.74	56.55	64.37	56.88	64.37	–	–	–
Temperature of Reboiler C1 (°C)	113.29	115.254	–	115.33	115.34	115.34	113.836	115.29
Temperature of Reboiler C2 (°C)	99.63	64.97	99.72	78.40	–	64.18	–	–
	Mass flow of main streams (kg h^{-1})							
Entrainer	254	244	254	250.1367	255.8634	248.623	377	246
Methanol	1870	1880	1914	1952.964	1949.25	1953.74	1899	1914
Wastewater	96,510	96,518	96,429	96437.49	96427.51	96,432	96,332	96480.73
Interconnexion Vapor	–	–	16,700	17,764	11,000	274.94	–	–
Interconnexion Liquid	–	–	115,044	15,561	9043	2234	–	–
Purity of products in main streams (mass fraction)								
Methanol (methanol stream)	99.6	99.6	99.602	99.64	99.602	99.69	23.08	99.63
Solvent (solvent steam)	60.8	60.43	60.01	61.01	60.23	60.76	40.94	60.10
Water (Wastewater stream)	97.9	97.9	97.9848	97.97	97.98	97.98	96.566	97.93

processes and to determine the process with better control capabilities. Furthermore, Segovia-Hernandez et al. [45], implemented the condition number to several intensified distillation schemes to determine which distillation process has better controllability. Mathematically, the condition number is calculated through a singular value decomposition of the gain matrix according to equation [7]:

$$K = W\Sigma V^{T} \tag{7}$$

where W and V^{T} are unitary matrices and Σ is the matrix of singular values. Once the matrix of singular values has been obtained, the minimum singular value (σ_{*}) and the maximum singular value (σ^{*}) need to be identified. The condition number is then calculated using the minimum and maximum condition numbers as follows:

$$\gamma = \frac{\sigma^{*}}{\sigma_{*}} \tag{8}$$

The condition number represents the sensitivity of a system to assimilate a disturbance without process destabilization. High values of condition numbers indicate that the processes could be susceptible to destabilization by small perturbations. Furthermore, low value condition numbers represent a robust process that is resistant to disturbance. For that reason, low values are preferable. In this work, the Singular Value Decomposition (SVD) is performed in an open loop when the gain matrix is obtained considering the nominal state of the compositions of each component and the compositions after the perturbations on manipulated variables of the processes. A negative disturbance of 1 % is considered when this disturbance is applied on nominal values of manipulated variables which are reflux ration and reboiler duty. This magnitude in the disturbance is chosen so that the response of the processes can be approximated to a first order response. Therefore, the gain matrix can be generated as follows:

$$K = K_{i,j} = \frac{1}{2}p\left(x_{i,j}^{Nom} - x_{i,j}^{sp}\right) i = \text{ Component} \\ j = \text{ Manipulate variables} \tag{9}$$

where elements $K_{i,j}$ of the gain matrix K are generated by the subtraction of the composition in the nominal value ($x_{i,j}^{Nom}$) for a specific component minus the composition after a perturbation on a manipulated variable ($x_{i,j}^{sp}$).

6. Results

This section offers the results of all the distillation schemes studied. Four different parameters have been evaluated as performance indexes of the columns. These parameters are the total annual cost, eco-indicator 99, individual risk and condition number. These parameters allow the measurement of the economy of the process, environmental impact, safety, and controllability properties, respectively. Distillation sequences were designed to obtain furfural, methanol, and water with a purity of 99.9 %, 99.6 % and 97.9 % in mass fraction, respectively. The selection of the solvent to purify furfural was taken from Nhien's et al. work [22]. being butyl chloride the entrainer. However, the design of the extraction column was modified in this work in order to reduce the used amount of entrainer and decrease the separation cost. The amount of solvent was varied in a sensitivity analysis to reduce the TAC. Based in the cases presented in section two, the extractive column, and the distillation column C1 are common equipment for all distillation sequences; hence, the results obtained for these two equipment are general in all the cases. Fig. 8 shows the sensitivity analysis and the final specifications for extractive column and distillation column C1. The sensitivity analysis shows how the total annual cost can decrease by reducing the solvent amount. In this Figure each point represents a design for a sequence of extraction of a distillation column. The minimum TAC corresponds to a solvent mass flow rate of 47,000 kg/h. For lower

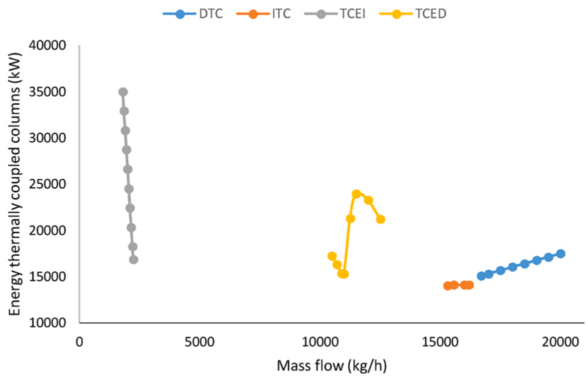


Fig. 9. Sensitivity analysis of interconnexion mass flows.

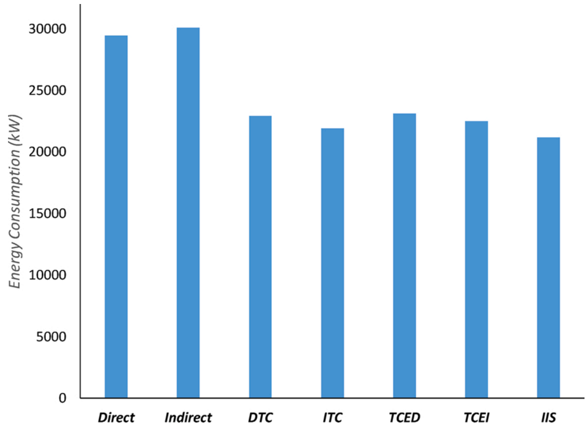


Fig. 10. Energy consumption of distillation sequences.

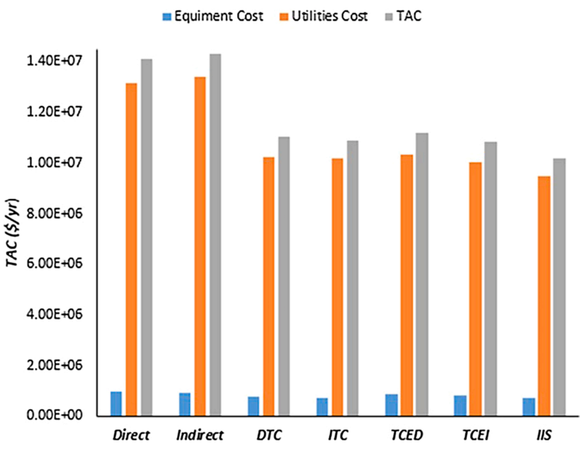


Fig. 11. Comparison of total annual cost.

solvent amounts, the separation of mixture is infeasible; thus, these values are not considered. In the referred work of Nhien's et al. [22], the amount of solvent used is 62,000 kg/h. Therefore, the design obtained in this work has a 25 % of solvent saving. The energy consumption required to purify furfural is 7800 kW compared to the 8326 kW reported by Nhien et al. [22], whose energy savings are around 7 %. Here, energy saving is not proportional to solvent saving since a reduction in the solvent implies more energy stages as well as greater energy use to achieve separation.

Once the extractive and distillation column C1 have been designed, the purification of methanol from the aqueous phase can be worked. The purification of methanol is commonly considered in the purification of furfural, as it is a high value co-product generated during its production, and its recovery generates profit improvements in the furfural process [15,46]. In order to provide a fair comparison between the extractive process and the conventional purification process, the purification of methanol must be included. The purification of acetic acid is not considered, as it is not economically feasible, and the wastewater it generates, rich in acetic acid, is sent away to treatment plants [15,17]. The design specifications of all distillation alternatives used to recover methanol and the solvent are shown in Table 3.

It is important to mention, that in order to quantify the improvements of intensified schemes, the conventional direct and indirect schemes are considered as benchmarks since all intensified alternatives are generated from these two processes. A sensitivity analysis on the interconnection streams was carried out. This procedure consists in manipulating the interconnection mass flowrate (vapor or liquid according to the case) up to reduce the energy consumption of intensified alternatives. The sensitivity analysis of interconnection mass flows was carried out in Aspen Plus, it is important to mention that this is a typical procedure used to reduce the energy consumption in columns with thermally couplings [23,45]. Therefore, the thermally coupled schemes are compared in the point with minimum energy consumption. Fig. 9 shows the results for the sensitivity analysis of the interconnexion mass flowrate for all thermally coupled schemes. In this sense, a comparison of energy consumption of sequences is shown in Fig. 10. The results indicate that conventional schemes have energy consumptions of around 3000 kW; yet the direct scheme has a lower energy consumption than the indirect scheme. This difference, being only of 400 kW, makes it not much of an important difference. However, the thermally coupled schemes (DTC and ITC) have important energy savings in contrast to their respective conventional configurations. In this work, the thermo-equivalent configurations of Direct Thermally Coupled (DTC) and Indirect Thermally Coupled (ITC) have been considered.

These thermo-equivalents, direct and indirect schemes are TCED and TCEI processes, respectively. The energy requirements for TCED and TCEI are almost equal in their respective thermally coupled schemes. The results were expected since the only difference between these schemes is the moving sections of columns used to promote the thermally coupled. Although the different thermally coupled alternatives have similar energy consumptions, the structure and configuration of the column in the different alternatives provide special safety and control properties specific of each process. The energy savings of thermally coupled schemes are close to 22 % to DTC and TCED schemes and 25 % to ITC and TCEI with respect to their respective conventional processes. Theses energy savings are generated as thermally coupled schemes avoid the formation of remixing phenomena, which is one of the main causes of thermodynamic inefficiencies in multicomponent distillation [47]. In the case of intensified processes, only the Indirect Intensified Process (IIS) is considered, because the Direct Intensified Scheme (DIS)

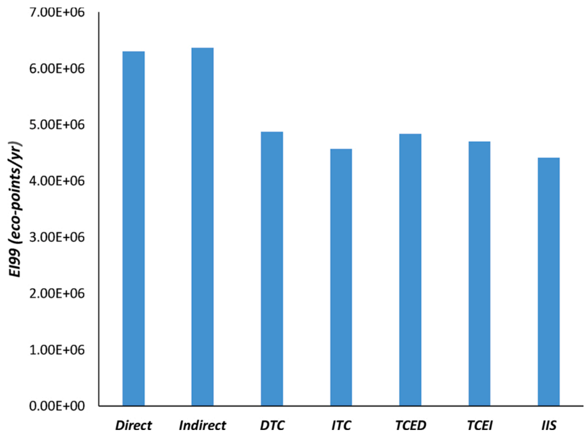


Fig. 12. Comparison of eco-indicator 99.

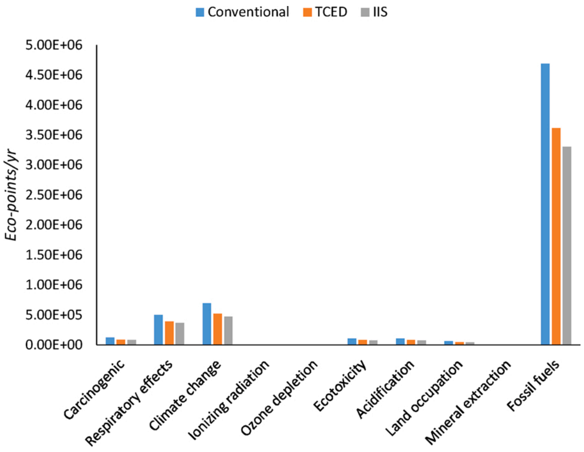


Fig. 13. Contribution of impact categories to EI99.

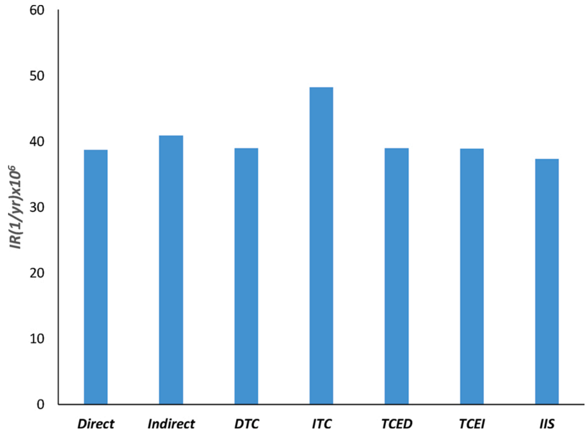


Fig. 14. Comparison of individual risk.

Table 4
Comparison of condition number for the different distillation processes.

Configuration	Condition number (γ)
Direct	18.21
Indirect	40.46
DTC	48,403
ITC	546.49
TCDE	148.60
TCEI	1351
IIS	79.99

does not reach the purity mass flows of methanol on methanol stream. The topology of DIS option does not allow for an appropriate concentration of methanol as it is a volatile compound which tends to concentrate near the top of the column. The location of the side stream generated by the intensified method concentrates near the bottoms of columns, thus making it not adequate in the purification of methanol. In order to provide better analysis, the design parameters of DIS option are reported in Table 3. In the case of IIS option, this process shows the lowest energy consumption as it promotes the concentration of methanol and it incorporates the separation of methanol in a single shell, which reduces the cost and energy consumption. During this intensification option a reboiler is eliminated, thus further decreasing energy consumption.

The results of TAC and EI99 are illustrated in Figs. 11 and 12, respectively. In these cases, the results indicate that cost and environmental impact are directly associated with energy requirements; for this reason, these indexes follow the same tendency respect to the energy consumption previously mentioned in Fig. 10. Fig. 11 shows the contribution of annualized equipment cost and utilities cost to TAC. In all cases, equipment cost represents a small part of the total annual cost, which is around 5–10 % for a payback period of 5 years. The mixture from the bottom of the extractive column is mostly water with small amounts of methanol, this large amount of water causes the distillations columns to require big reflux ratios and large energy requirements in order to achieve the separation of methanol. This extensive use of energy demonstrates that the need to implement more efficient alternatives is relevant. In Figs. 10 and 11, it is clear how the thermally coupled schemes and the intensified option have important energy reduction, which impacts TAC. The alternative with the lowest environmental impact and lowest total annual cost is the intensified option. This alternative performs the purification of methanol and solvent in a single shell without the extra columns, saving on energy consumption and construction cost. Contreras-Zarazúa et al. [48] and Nhien et al. [18] studied the purification of furfural and methanol using different azeotropic distillation alternatives. Their studies, as well as our work, take into consideration the same feed flow and composition. Their results show processes with a total annual cost of around 9.3 million USD/yr. The processes studied in this work have TAC of 10–13 million USD/yr. The difference of cost is not as significant, thus indicating that the processes obtained here could be competitive with conventional furfural purification processes.In order to delve into the study of eco-indicator 99, Fig. 13 shows the contribution of different impact categories on EI99. As mentioned beforehand, energy consumption has a strong influence on EI99, however this contribution is divided into 11 impact categories. The results show that the categories of fossil fuel, respiratory effect and climate change have the stronger influence over EI99. These impact categories are directly associated with the use of energy in the processes as it can be assumed that energy is generated by the combustion of natural gas which is one of the most common fuels used in chemical plants. Harmful effects, both on respiratory problems and climate change are due to the combustion of fuels which emit large amounts of carbon dioxide and carbon monoxide. Based on Fig. 12, it becomes clear that the thermally coupled and intensified schemes can reduce the damaging effects of excessive fossil fuel combustion compared with conventional optionsBased on the results of TAC and EI99, it seems clear that intensified processes are a better option due to their reduction on energy consumption, lower cost and environmental impact. However, when other parameters such as security or control are analyzed, the options become less clear. Fig. 14 shows the individual risk results for all alternatives. The objective of distillation sequences is to separate methanol and solvent fractions with high purity in order to reuse them. Since these components are volatile and flammable, high concentrations of these compounds are prone to generate accidents (most of which may be caused by ruptured equipment or pipeline). Thus, quantification of a safety index is of great importance. The result shows that thermally coupled and intensified alternatives do not have important improvements on security aspects, and other alternatives such as ITC demonstrate to have a worse security index than its respective conventional process. The individual risk which quantifies the probability of affectation (injury or death) caused by an accident in a chemical process is directly related to the topology, size, and operating condition of the process equipment. In this sense, processes with extreme operation conditions, larger equipment or topologies that benefit the concentration of volatile and flammable components are classified as higher risk processes. All operative conditions are similar because all the distillation sequences make the separation of the same components, thus the individual risk is influenced by the size of the equipment and topology of the process. However, the indirect and ITC schemes have higher values of IR because they concentrate the methanol and solvent in column C3. The ITC process has a similar equipment size to its respective conventional process (indirect scheme), which indicates that the topology of ITC process promotes larger amounts and higher

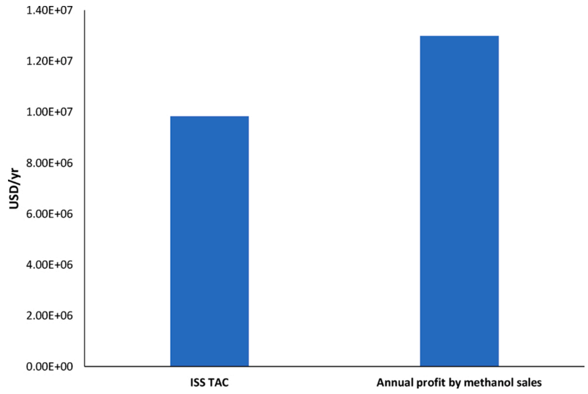


Fig. 15. Comparison of Costs for ISS process and methanol sales.

concentrations of methanol and solvent through column C3. This higher concentration and large amounts of volatile compounds are caused by the interconnection flow required in this process. The individual risk for the other thermally coupled schemes is similar with respect to the conventional processes. In these schemes the solvent is recovered in the same wastewater column, which causes a dilution of the solvent across the column; hence, a risk reduction is generated in comparison to the ITC and indirect schemes. The intensified option presents the lowest IR because of two main reasons. First, the intensified alternative makes the separation of the solvent, methanol, and water in a single column, thus the probability of failure or accident is reduced by using less equipment, which reduces the individual risk. The second reason is directly related to the first one, in this case the separation of methanol and solvent in a column with large amounts of water reduces the probability of explosion, toxic release and fires; improving the IR. The last index studied in this work is the condition number, a comparison of the condition number at zero frequency, for the different configurations is presented in Table 4. Due to the difference in the orders of magnitude between the different processes, the results are not shown in a figure. The condition number represents the sensitivity of a system when it is perturbed. Values close to 1 indicate that the process easily assimilates the perturbation, a condition number of 1 represents an ideal case where the process is not altered by the perturbation. The results show that the conventional sequences have better control properties than the intensified schemes. Usually, the interconnection streams provide stability to the thermally distillation columns because the perturbation is distributed and mitigated into two columns. However, the concentration of methanol and solvent are so low that a small perturbation induces a strong alteration of the compositions. In this case, the interconnection flows cannot mitigate the perturbation and a snowball effect is generated which affects the control properties of thermally coupled schemes. The intensified option offers the most similar controllability with respect to conventional alternatives since the separation is carried out in a single shell, in this case the perturbation could be cushioned by large amounts of water. The quantity of water inside the IIS scheme is so that the variation on the composition of solvent and methanol is not so appreciable in contrast to the thermally coupled schemes.

Based on the results, the intensified option is chosen as the best alternative to recover methanol and solvent, this alternative has the best environmental impact, cost, and safety properties. On the other hand, the control properties of intensified schemes are better than the thermally coupled and they are likely the control properties of conventional cases. The intensified scheme is a competitive option due to it having similar costs, environmental impact, and even better safety properties than other alternatives reported by Contreras-Zarazúa et al. [48] and

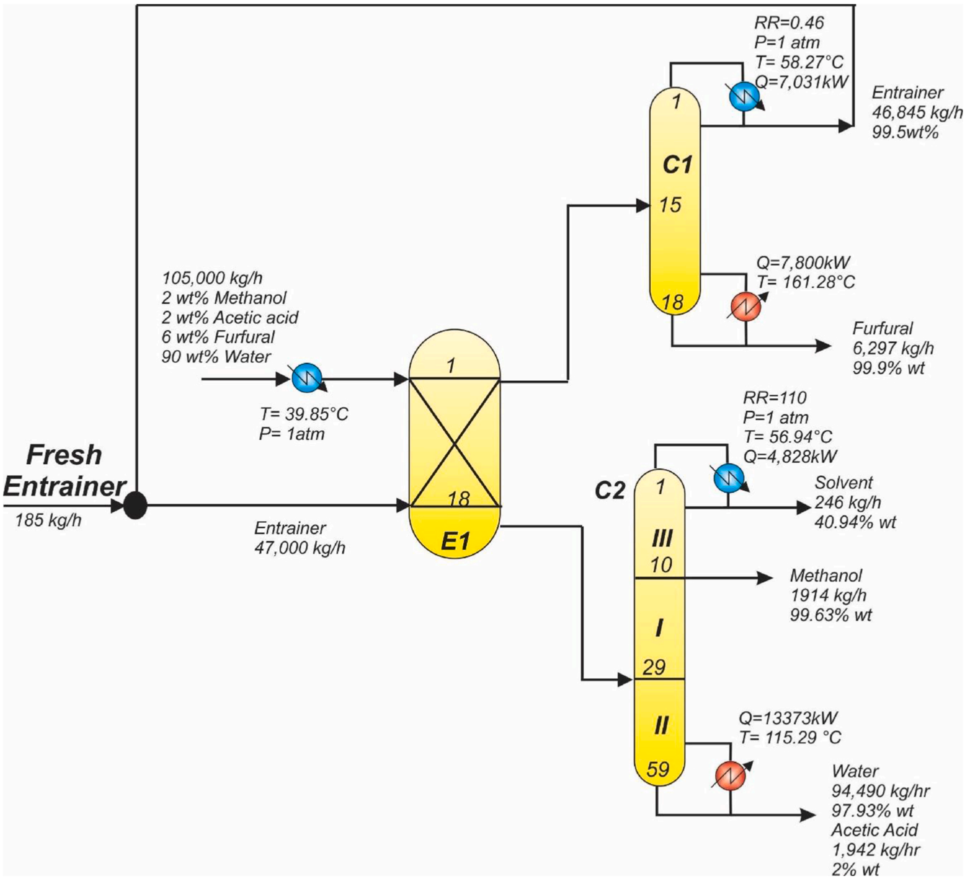


Fig. 16. Mass flows and energy requirements for ISS process.

Nhien et al. [18]. Finally, in order to determine the feasibility of methanol recovery, a comparation of the profits generated owing to methanol sales and the purification cost for ISS scheme which is considered the best option is presented in Fig. 15. The IIS is selected as the best option and consequently as representative case due to it has the lowest cost and environmental impacts, the costs for IIS include the purification cost for furfural and methanol. The methanol's sale price corresponds to 850 USD/ton, this price was obtained from Alibaba web [49]. Please note, that the profits due to methanol sales exceed the purification cost, for this reason, it is possible to finance the process separation for methanol and furfural using the methanol sales. Therefore, the profits due to furfural's sales are considered net profits, for those reasons the methanol recovery is economically feasible. Finally, the Fig. 16 shows the mass flows and energy requirements for the ISS process, which is considered the best option for purifying methanol. The mass flows and energy requirements for the other processes are shown in the supplementary material

7. Conclusions

This work has designed different alternatives to purify furfural and co-products based on extractive distillation with butyl chloride as a solvent. Because of the topology of the process, different intensified alternatives are proposed in the recovery of the solvent and methanol. The intensified processes were contrasted with their respective conventional options. The results indicate that an important reduction of 25 % in the amount of solvent can be achieved by an increment in the number of stages required to purify furfural and the entrainer in column C1, compared to previous work of Nhien et al. [18]. At the same time, this reduction in the entrainer quantity causes an energy saving of 7 % compared to the previous work reported by Nhien. On the other hand, important reductions on cost and improvements on separation are achieved by the reduction of solvent used. Additionally, the intensified schemes for the recovery of methanol and solvent show important energy savings of around 22–27 %, where the IIS schemes is the process with lowest energy requirement. It is important to highlight this since the complexity and composition of raffinate mixture and the conventional direct and indirect schemes have similar energy consumption. Because of this complexity and composition of the mixture, the factor with the strongest contribution of TAC and EI99 is the energy required for the separation. For this reason, the tendency of results for TAC and EI99 is the same than energy tendency. In these cases, the Indirect Intensified Scheme (IIS) is the option with lowest environmental and cost issues. On the other hand, important improvements on the intensified are not observed because high amounts of water mitigate the improvements. In the same way, because of the quantity of water and the topology of intensified options, the control properties are degraded in order to achieve methanol with high purity with the exception of an ISS alternative. Based on the results, the indirect intensified scheme (ISS) is selected as the best option to purify methanol and solvent because of its better cost, environmental impact, safety issues and similar control properties compared to conventional options. The authors propose for a future work, the search of new solvents or the implementation of optimization technique to improve the process and its results.

CRediT authorship contribution statement

Gabriel Contreras-Zarazúa: Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Miriam E. Jasso-Villegas:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **César Ramírez-Márquez:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Eduardo Sánchez-Ramírez:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **José Antonio Vázquez-Castillo:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Juan Gabriel Segovia-Hernandez:** Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

None

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cep.2020.108218.

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