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Design and optimization of an inherently safe and sustainable process for the separation of anisole

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ABSTRACT

Sustainable process design problems are multi-faceted approaches that pose challenges in terms of the evaluation of indicators to optimize inherent safety, economics, and control. In recent years, chemical engineering has taken advantage of recent advances in process systems engineering more notably considering intensification to generate green and more sustainable processes. This work presents the design and optimization of the anisole separation process under three intensified and one conventional schemes using a systematized methodology to find optimal designs of purification processes where the interactions between the different sustainability indicators are balanced to obtain optimal configurations. The indeces chosen in the course of process optimization (inherent safety, economic, and control) aim at generating green and more sustainable process alternatives. The results indicate that the most intensified processes, as is the case of the Dividing Wall Column (DWC), is the one with the best sustainability indicators, with better inherent safety and better operability despite it being an intensified process with fewer operational degrees of freedom. In addition, the environmental impact after the optimization of each of the processes were evaluated. Separation through DWC resulted in 2.43% savings in economic terms, 0.31% in inherent safety, improved controllability performance, and a 3.35% reduction in environmental impact, in comparison with the conventional sequence used as baseline. This indicates that in the case of anisole separation, process intensification can yield a more sustainable process design.

1. Introduction

Anisole (or methoxybenzene with the chemical formula $CH_3OC_6H_5$ and molecular weight of 108.14 g/mol) is an ether in which an oxygen atom is attached to an alkyl and aryl group, smells similar to anise seeds. It exhibits good solubility in most organic solvents including diethyl ether, ethanol, benzene, chloroform, toluene, etc. Anisole is utilized mainly for the manufacturing of perfumes, dyes, drugs, fabric softeners, pesticides, analytical reagents, water treatment and photographic chemicals, besides its application in food ingredients (Vani et al., 2021). The global anisole market was valued at US$ 77.5 million in 2019 and is estimated to reach US$ 115.89 million by 2027 growing at a compound annual growth rate (CAGR) of 5.16% (Maximize market research, 2019). Anisole has a vapor pressure of 3.54 mmHg at 25 °C and therefore shows potential insecticidal effects both as a contact insecticide and as a fumigant to control postharvest pests.

1.1. Anisole production within a sustainable framework

Sustainable, green, and efficient processes are amongst the top priorities needed to be fulfilled in the chemical industry to address the grand challenges of resource depletion, energy consumption, and climate change. Therefore, the identification, design, and development of appropriate processes are important for the industry to remain competitive, along with obtaining more sustainable and efficient processes that are safe to operate as a primary objective (García-Serna et al., 2007). Sustainability, in its broader context, is defined as satisfying the needs of the present without jeopardizing those of future generations. Sustainability must contain three central pillars: economic, social, and environmental. Although increasing efforts are being made to develop more sustainable processes with a green chemistry profile, there remains

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Nomenclature

C^0_{BM}	Cost of the bare module
$C_{TM,i}$	Cost of capital of the plant
$C_{ut,j}$	Cost of services
F^0_{BM}	Cost factor of the bare module
$\alpha_{b,k}$	The damage caused in category k per unit of chemical product b released to the environment
β_b	The total amount of chemical product *b* released per unit of reference flow due to direct emissions
δ_d	Normalization factor for damage of category *d*
ω_d	Weighting factor for the damage of category *d*
°C	Celsius degrees
BLEVE	Boiling Liquid Expanding Vapor Explosion
C–I	Column one
C-II	Column two
C-III	Column three
CN	Condition Number
Cr	Crossover factor
CS	Conventional Sequence
DE	Differential Evolution
DETL	Differential Evolution Algorithm with Tabu List
DWC	Divided Wall Column
EI99	Eco-indicator 99
F	Mutation factor
f_i	Harm or disease caused by event I
F_M	Material factor
F_P	Pressure factor
HAZOP	Hazard and Operability
HP	High-pressure
IR	Individual Risk
LC50	Lethal Concentration 50
LP	Low-Pressure
MP	Medium-Pressure
$N_{Feeding}$	Feeding Stage
NIOSH	National Institute for Occupational Safety and Health
Np	Population number
$N_{Solvent}$	Feeding Solvent Stage
N_T	Total Stage
PI	Process Intensification
P_o	Overpressure
$P_{x,y}$	Probability of injury or disease induced by incident i
QR	Reboiler Duty
QRA	Quantitative risk analysis
TAC	Total Annual Cost
TCS1	Thermal Coupled Sequence 1
TCS2	Thermal coupled sequence 2
t_eE_r	Thermal radiation
TR	Tabu Radius
TS	Tabu Search
UVCE	Unconfined Vapor Cloud Explosion
X_I	Concentration
α	Relative volatility

a need in reduction of emissions, reduction in the use of energy, and ensuring that their physical waste is disposed of properly and with the smallest possible carbon footprint (Arastoopour, 2019). Achieving improvements in a single indicator does not suffice in achieving a more sustainable process. Thereby, Jiménez-González and Constable (2011), suggest that the sphere of action of sustainability and green chemistry is based on aspects such as the economy, operation, and inherent safety of a process. Within Chemical engineering, and particularly process systems engineering (PSE), there have been great attempts to contribute to the development of green and sustainable processes through process intensification (Boodhoo and Harvey, 2013; Gani et al., 2020). Process intensification provides substantive support and capacity-building for the sustainable development goals and their related thematic issues to the downscaling of processes; which represents economic, lower environmental impact, operable and safer processes.

While the economics and operability of a process contribute to the sustainability and green chemistry profile, some works in the literature suggest that inherent safety does even more. Athar et al. (2019), show that risk assessment through inherent safety is a recognized approach used around the world to improve the sustainability of the existing process plant or the design of a new facility. Traditionally, risk assessment has been done sequentially, i.e. after the steady-state design has been obtained. Therefore, it is recommended that in the early stages of the design of any process, the inherent safety concept be evaluated to achieve a more sustainable process design. This is mainly due to conflicting trade-offs between steady-state and dynamic process design objectives.

A case study that fits perfectly into the search for new sustainable and green processes is the anisole separation process. Given its characteristics, anisole is expected to be an environmental friendly chemical as a fumigant (Yang and Liu, 2021). Rajesh et al. (2020) have studied the effect of increasing anisole fraction in the biodiesel extracted from waste cooking oil in a diesel engine. Tests were performed by blending anisole with waste cooking oil methyl ester up to 30% vol. and the results were compared with baseline diesel and biodiesel operation. The results reveal that, increasing the anisole content in biodiesel prolongs the ignition delay period. It is concluded that waste cooking oil methyl ester blended with 10% by vol. of anisole can be effectively utilized in diesel engine applications with lower emissions. Bouoidina et al. (2021) have focused their work on the inhibition of corrosion of steel in 1 M HCl acid medium by three anisole derivatives. In the search for alternative biofuels, conversion of lignocellulosic biomass has spawned interest in aromatic compounds obtained from lignin. Among them, anisole has recently triggered significant interest. In an attempt to clarify the kinetic effect of the addition of anisole to practical fuels, an experimental and kinetic modeling study of anisole co-oxidation with isooctane has been performed by Mergulhao et al. (2021). This study showed that: addition of anisole leads to a pronounced increase in both the first-stage and total ignition de-lays of isooctane; while the ignition delays increase over the whole temperature range, a 60/40 isooctane/anisole blend still shows Negative Temperature Coefficient behavior. Also, amide bond cross-coupling is a powerful transformation that is vital for transforming traditionally inert amide bonds into cross-coupling synthons through the cleavage of N–C bonds under mild and modular transition-metal-catalyzed conditions. The immense potential of the amide bond cross-coupling stems from the inherent presence of amides in biomolecules, polymers, and as the most common functional group in pharmaceutical development. The Suzuki−Miyaura synthesis is the most used reaction route for the coupling of amides. A range of environmentally friendly solvents was evaluated in the Suzuki–Miyaura reaction by Lei et al. (2021) due to the fundamental impact of solvents on the environment and the synthesis of active pharmaceutical ingredients. This study identified anisole as one of the most preferred solvents in terms of health, safety and environmental impact in the Suzuki–Miyaura reaction. As can be seen, today anisole is widely used in various industries with sustainable applications and hence the interest and relevance for the study of its synthesis and purification.

Anisole is usually synthesized by a liquid phase process in an alkaline

environment, such as the reaction between sodium phenolate and dimethyl sulfate (Lewis et al., 1930). Due to the toxic nature of reactants, this preparation method has been restricted in recent years (Asha, 2014). Consequently, alternative processes have been sought to produce anisole that is less harmful to human health and the environment. Therefore, the study of new processes for green and sustainable production and separation is necessary.

More efficient and cleaner anisole production routes have been studied in recent years. In this sense, Phenol alkylation with methanol in vapor phase yielding anisole is an economical and green reaction studied by Kirichenko et al. (2008). The formation of cresols in low concentrations as byproducts indicates the occurrence of ortho-alkylation of phenol. Water is also a byproduct formed by the dehydration of phenol, carrying the presence of azeotropes in the mixture. The reaction model by Kirichenko et al. (2008) is the basis for the industrial manufacturing of anisole. However, the purification of anisole from the multicomponent mixture is an important stage in the final design, which strongly determines the safety, economy, environmental impact, and operability of the process. The main problems of the anisole separation route are the high consumption of energy, the safety risk presented by the processes (because of the extreme operating conditions). Also, the handling of substances such as toluene, methanol, etc., implies an environmental hazard. These compounds are toxic and corrosive; then represent safety and environmental problems (Millipore-Sigma, 2021; Merk, 2021). Therefore, it is important to analyze the appropriate separation operations for the anisole purification from de alkylation mixture. The anisole separation process fits perfectly into the search for new sustainable and green processes and this case study is closed with the objectives of the United Nations in terms of economic and sustainable development (Department of Economic and Social Affairs, 2021): the construction of resilient infrastructure, the promotion of inclusive and sustainable industrialization, and the encouragement of innovation.

Several studies have been reported on separation processes used for the recovery of anisole from diferent binary mixtures. The most commonly employed method for anisole recovery is distillation. (Bernot et al., 1990; Noble and Terry, 2004). For example, Wang et al. (2016) and Vani et al. (2021) isolated anisole by distillation. Distillation is a well-known separation process wherein the mixtures can be separated by diferences in the boiling points or volatility of the individual components. It deals with the separation of binary and multi-component mixtures. The removal of hazardous waste and organic solvents from liquid mixtures helps to protect the environment from the contaminants. Distillation plays a crucial role in the separation of multi-component liquid mixture. The process is usually inexpensive if the boiling points are wide apart, but if the relative volatility is close to 1.0, it becomes more expensive (Westerberg, 1985). It is important to note that despite the fact that distillation is one of the oldest separation processes, its ability to purify a large number of mixtures efficiently, have managed to position it among the seven chemical separations to change the world (Sholl and Lively, 2016). As far as the authors are aware, no study is available in the literature on the purification of anisole from a multicomponent mixture with the presence of an azoetrope through the use of intensified distillation columns designed under the concept of sustainability and inherent safety. It provides a wide scope for complex mixture purification concepts in sustainable and inherently safe intensified systems. This point is of the highest industrial relevance today, since the search for separation processes with low energy consumption, low operating cost, low environmental impact, with good dynamic performance and inherently safe are the requirements in industrial public policies (Sholl and Lively, 2016) and all of this is in accordance with the objectives of the United Nations in terms of economic and sustainable development. Intensified distillation configurations can largely meet these goals (Avraamidou et al., 2020).

To achieve all of the above, one of the concepts that has helped chemical processes in recent decades can be used: Process Intensification (PI). There are many definitions of what PI is, but one of the most representative was provided by Ramshaw (1995), who defined PI as a strategy to drastically reduce the size of a chemical plant in order to achieve a given production target. These reductions can come from downsizing individual pieces of equipment and from reducing the number of unit operations or apparatus involved. Both distillation and thermal separation are responsible for approximately 50% of energy consumption in the industry (Sholl and Lively, 2016). So even small improvements in distillation processes can bring significant benefits. Today there are a variety of alternatives available to improve the energy efficiency of distillation processes. To this end, the use of heat pumps for vapor recompression, multi-effect distillation, or cyclic distillation help to mitigate energy consumption (Skiborowski, 2018). However, common heat integration and thermal coupling, are the most basic examples of PI intensification, as they allow the integration of mass and energy in multi-component separation problems (Kiss et al., 2012). The application of intensification principles (such as, interconnection streams instead of auxiliary equipment or Dividing Wall Column) to the design of the anisole separation process will result in operations that make better use of material and energy resources (Segovia-Hernández et al., 2020; Sánchez-Ramírez et al., 2021). Consequently, intensification of the anisole separation process will result in a more energy-efficient, safe, and clean operation (Stankiewicz and Moulijn, 2002). In other words, the appropriate metrics will be met to obtain green and sustainable processes in the separation of anisole. The complexity of these objectives and factors necessitate the use of an integrated approach which addresses the interactions among the different unit operations and technologies within the process. It is also important to reconcile the often-competing objectives dictated by economics, the environment, and inehret safety through the generation of systematized methodologies (El-Halwagi, 2017). Therefore, it is important to highlight that the contribution of this paper is to generate a systematized methodology to find optimal designs of chemical processes where the interactions between the different indicators are balanced to obtain optimal configurations, taking the purification of anisole as a case study.

In this paper, three intensified and one conventional design for the separation of anisole are considered. The designs are intended to visualize whether such intensified proposals will support and improve sustainability and green chemistry indicators, which are primarily represented by safety, economic, and process control (through IR, TAC, and CN, respectively). Therefore, the processes were designed and optimized under the green chemistry and sustainability metrics described by Jiménez-González & Constable (2011). That is, they were optimized under economic, control, and inherent safety indices at the design stage this represents an important improvement in selecting the optimal separation process route. Once each of the processes had been optimized, their environmental impact was evaluated as a post-hoc analysis to corroborate the concordance of sustainability and the concept of green chemistry.

This research aimed to determine the challenges of sustainable sourcing implementation in the anisole industry. The transition from conventional configurations to a new sustainable model poses obstacles and challenges (Barbosa-Póvoa et al., 2018). This study fills the research gap in the design and optimization of sustainable processes and contributes towards theoretical knowledge in the field of sustainable sourcing by providing a detailed study concerning the identification and ranking of “green indexes”.

2. Metrics for assessing sustainability

A popular understanding of sustainability in the context of engineering decisions is conveyed by the “triple bottom line” (Stephanopoulos and Reklaitis, 2011). This highlights the importance of economic, environmental, and social aspects of sustainability. Selecting the most important metrics based only on greenhouse gases or water use is a popular approach, but it may result in loss of important information and shifting of impacts to other resource or emission flows. To reduce the

chance of burden shifting in space along the supply and demand networks and between different types of flows green indexes should be incorporated into the process design if processes with sustainability and green chemistry characteristics are desired (Jimenez-Gonzalez and Constable, 2011). According to Jiménez-González and Constable (2011), the indexes that contribute most to the concepts of sustainability and green chemistry are inherent safety, economy, and process operability (control). By seeking to modify the topology of each of the sequences shown, the aim is to find the right combination that results in the best processes in terms of inherent safety, all framed within the concepts of sustainability and green chemistry. Optimization indexes are described below.

2.1. Safety index (IR)

Process safety analysis has had different approaches over time. Particularly in industrial equipment, several methodologies have been generated to quantify safety and health hazards. Hassim & Hurme (2010) looked at methods are needed to evaluate occupational health hazards as early as possible when the process is still under development. Markowski & Kotynia (2011) used fuzzy logic to apply an integrated bow tie to a layer of protection analysis (LOPA) in a distillation system, considering all potential outcomes rather than just the worst case. A consequence analysis was utilized by Jung et al. (2010) for a distillation plant layout optimization where distillation was the riskiest equipment. All these works are significant contributions to the field of risk management. Despite this, no clear information on how design variables affect plant safety or how that knowledge may be utilized to make a design safer is provided.

In process industries, inherent safety is the most effective method of risk reduction. Kletz (1998) developed the notion in the 1980s, with the goal of avoiding danger rather than depending on control or protective mechanisms. At the early stages of design, inherent safety is more effective and easier to implement. Risk quantification is accomplished by a quantitative risk analysis (QRA) analyzing the effect of the individual risk (IR). The identification of the influence of design variables allows for a more effective ranking of criteria related to inherent safety throughout the design stage.

To assess the safety, the individual risk (IR) was utilized as an indicator. The risk of damage or disease to a person in the proximity of a danger is known as the IR. The main goal of this index is to estimate the chance of being affected by a certain occurrence that occurs on a regular basis (AIChE, 2000). The IR is unaffected by the amount of persons that have been exposed. The following is the mathematical expression for determining individual risk:

$$IR = \sum f_i P_{x,y} \quad [1]$$

where f_i is the likelihood of harm or disease caused by event I and $P_{x,y}$ is the probability of injury or disease induced by incident i. An irreversible damage (disease) is utilized in this study, for which additional data is collected. Quantitative Risk Analysis (QRA), a process for identifying events and accidents as well as their repercussions, may be used to calculate IR. The first step of the QRA is to identify potential occurrences. There are two sorts of events in distillation columns: continuous and sudden discharges. It is important to mention that the safety index used in this case (individual risk) is the multiplication of the frequency with which an accident occurs by its probability of death. Note that the frequency is not a probability, but a number that indicates how frequently a certain accident occurs in a chemical plant. It is important to note that both the frequency and the probability of death are independent of the number of people exposed to the accident. The definition of individual risk was taken from the Center for Chemical Process Safety (CCPS). Shariff and Zaini (2013), comment that for practical releases, it is acceptable to assume that almost any accident occurs due to leakage from the process plant piping results in a near continuous release from the entire process inventory or release over a short period of time. The continuous release from a source that is dispersed into the atmosphere by wind is in this study to evaluate the consequences of the release of toxic gases.

This research seeks to provide a more accurate understanding of risk sources by using a quantitative risk analysis in its entirety (QRA). A QRA recognizes typical scenarios and calculates the risk associated with them. In this approach, a QRA discovers various outcomes, including the most common and the scenario with the most serious implications. Risk management is the process of identifying, assessing, and prioritizing risks. A hazard and operability study (HAZOP), which is produced via the contributions of experienced personnel to analyze likely equipment and operation failures, is a well-accepted risk detection tool in industry. Venkatasubramanian et al. (2003) presented a number of defect detection algorithms and examined their advantages and disadvantages.

A risk matrix is the primary approach for qualitative evaluation (Ni et al., 2010), but a QRA is a more extensive method that needs the identification of failures, failure rates data, and a consequence analysis. Qualitative approaches are easier to use and are a good place to start, but quantitative methods provide more detailed data and a better risk prioritization. A quantitative study has the drawback of being unsure about failure rates and environmental factors. Within chemical plants, certain studies have demonstrated the usefulness of utilizing plant-specific failure rates predictions rather than generic numbers (Meel et al., 2008)

A QRA is considered in this study. Fig. 1 depicts a visual illustration of risk quantification using a QRA, which requires both frequency and effects to be quantified. Fault trees, which identify the probable failures that produce a material release, and event trees, which identify the outcomes caused by the material released, can be utilized to do the probability quantification. A bowtie analysis is created by combining both analyses into one. As a result, based on historical plant-specific data and expert assessment, the likelihood of all eventualities may be calculated using a bowtie analysis (top part of Fig. 1). After the bow tie analysis has identified the outcomes, a consequence analysis is used to quantify the implications. Dispersion models, characterisation of the causative variable (thermal radiation flux, created overpressure, quantity and duration of the release), and impacts quantification using a probit model are all part of an outcome consequence analysis.

Hazard and operability studies were used to determine these events (HAZOP). The method works effectively in detecting risks and is widely used in the chemical industry. Through a series of questions like as:

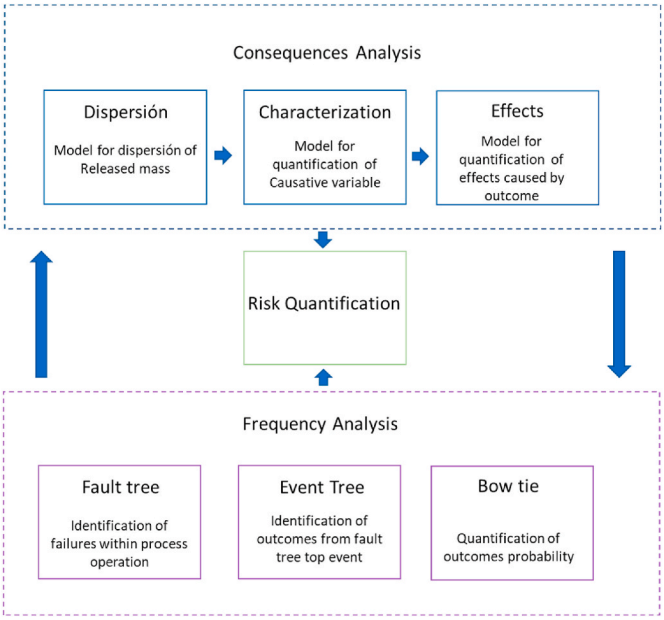

Fig. 1. Graphic representation of a Quantitative Risk Analysis.

how?, where?, when?, etc., the approach consists of carefully analyzing the reasons and effects that might cause deviations in the operating conditions of process that can result in an accident. AIChE, (2000) and Crowl and Louvar (2001) give more information on this approach.

A frequency analysis, which offers the probability component of risk for each of the possibilities, is used to identify potential results of an aberrant procedure. On the one hand, a fault tree is a visualization tool that depicts the causes (failures) of a major event (in this case release of hazardous material). An event tree, on the other hand, is a visualization tool that aids in the identification of outcomes as a result of an initial event. To do frequency analysis, bow tie graphs merge fault and event trees (Modarres et al., 2016). Failure rates and event probabilities are used to compute outcome frequencies.

Here, the most typical failures with high implications are considered: (1) process equipment rupture, (2) liquid pipe rupture, and (3) vapor pipe rupture. Depending on the extent of the rupture, such failures might result in two sorts of discharges (total or partial). A partial rupture is defined as a rupture of less than 20% of the total diameter, while a total rupture is defined as a rupture of 20% or more of the whole diameter. An immediate release generated by a whole rupture and a sustained release induced by a partial rupture are the two sorts of releases that might occur. Once the material has been discharged, the results may be predicted based on the likelihood of igniting and atmospheric conditions. Examples of bow tie graphs are shown in Fig. 2.

Fig. 2 depicts the consequences of a boiling liquid expanding vapor explosion (BLEVE), an unconfined vapor cloud explosion (UVCE), and a flash fire due to instantaneous release (FFI). Following the result route, the probabilities of these are determined. The total of the failure rate of catastrophic rupture of dangerous equipment, and catastrophic leaking from pipelines, determines the frequency of immediate release. The total of the failure rate ruptures of at least 20% of medium and large diameter pipes, and times the pipeline length of medium and large size, and Within the mathematical model, the likelihood of an instantaneous ignition, the probability of a delayed ignition, and the probability of atmospheric circumstances promoting UVCE, are all considered factors.

The event tree diagrams generated with all probability of instantaneous and continuous occurrences, as well as their relative frequencies, are depicted in Fig. 3. Boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), flash fire, and toxic release are immediate occurrences, whereas jet fire, flash fire, and toxic release are continuous release situations. Supplementary Material provide the entire set of equations for calculating the IR, as well as further information about these equations. Once the events have been discovered, the probability $P_{x,y}$ may be determined using a consequence assessment, which involves evaluating physical factors such as heat radiation, overpressure, and leak concentration caused by occurrences, as well as their associated damages. The physical properties for each substance used for the consequence assessment were taken from the National Institute for Occupational Safety and Health (NIOSH), those properties include LC50, liquid and vapor densities, heat combustion, molecular weight, upper and lower flammability limits, etc. The dispersion is calculated using the atmospheric stability type F, which corresponds to a wind speed of 1.5 m/s. This is the worst-case situation because the low wind speed prevents flammable and poisonous components from dispersing quickly, lengthening exposure time and increasing the risk of coming into touch with an ignite source. A vulnerability model, also known as the probit model is used to calculate the harm caused by physical factors in each occurrence. The mortality of individuals was evaluated in this study due to fires, explosions, and hazardous discharges, and all estimates were done at a realistic distance of 50 m. Eq. (2) and Eq. (3) are the probit models for fatalities caused by thermal radiation (t_eE_r) and overpressure caused by explosions (p°):

$$Y = -14.9 + 2.56\, ln\left(\frac{t_e E_r^{\frac{4}{3}}}{10^4}\right) \quad [2]$$

$$Y = -77.1 + 6.91\, ln(p^\circ) \quad [3]$$

Because there are no published toxicity probit models for the components studied in this study, the damage to hazardous releases was calculated using the LC50; additional details on this calculation may be found in the Supplementary Material. Finally, the probability $P_{x,y}$ is determined by plugging Eq. (4) probit findings into the following equation:

$$P_{x,y} = 0.5\left[1 + erf\left(\frac{Y-5}{\sqrt{2}}\right)\right] \quad [4]$$

The physical properties for each substance used for the consequence assessment were taken from the National Institute for Occupational Safety and Health (NIOSH).

2.2. Economic index (TAC)

Estimating total costs is crucial for evaluating product and processing alternatives. The Total Annual Cost (TAC) is an index used to compare the economic viability of the proposed schemes. In general terms, it is calculated as the sum of the annualized cost of capital of each separate unit, plus the cost of operation.

The equations and data used to estimate capital costs by the Guthrie method are reported by Turton et al. (2008).

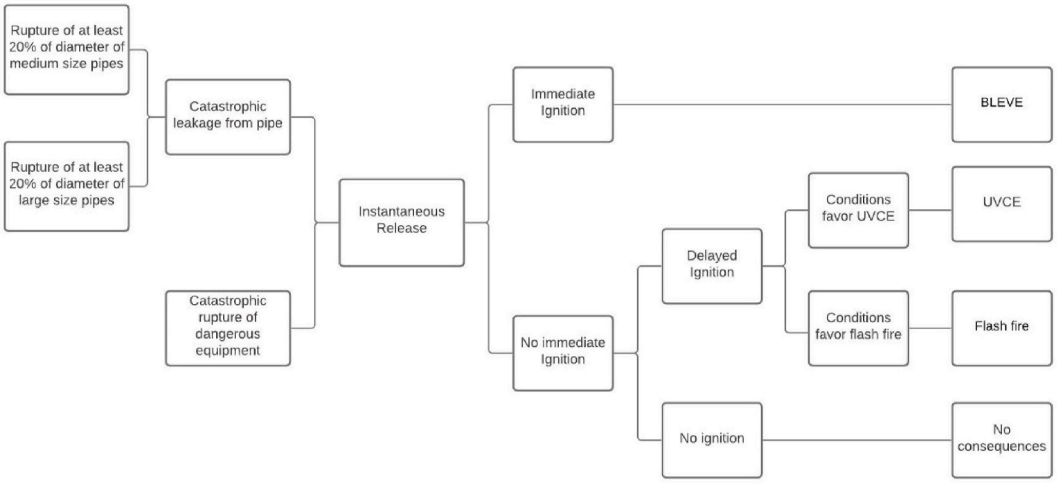

Fig. 2. Instantaneous Release Bow tie.

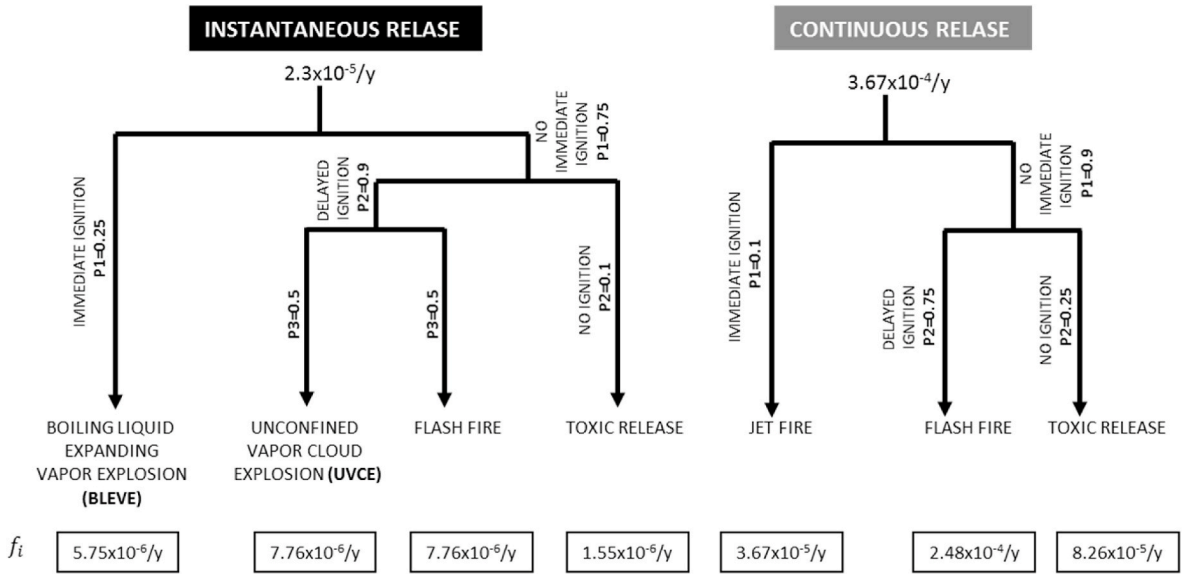

Fig. 3. Possible accidents and frequencies can happen in a process (Kumar, 1996).

$$TAC = \frac{\sum_{i=1}^{n} C_{TM,i}}{r} + \sum_{j=1}^{n} C_{ut,j} \quad [5]$$

The total module cost is calculated from equation (6).

$$C_{TM} = 1.18 \sum_{i=1}^{n} C^{0}_{BM,i} \quad [6]$$

Where the term C^{0}_{BM} represents the cost of the bare module, which reflects the direct and indirect costs for each unit. This term is calculated by equation (7).

$$C^{0}_{BM} = C_p F^{0}_{BM} \quad [7]$$

And in most cases F^{0}_{BM} is calculated by equation (8).

$$F^{0}_{BM} = (B_1 + B_2 F_M F_P) \quad [8]$$

Where $C_{TM,i}$ represents the cost of capital of the plant, r the number of years of return on investment, n is the total number of individual units, $C_{ut,j}$ is the cost of services, $C^{0}_{BM,i}$ represents the cost of the bare module, C_p is the purchase cost of the equipment under base conditions (carbon steel as construction material and ambient operating conditions), F^{0}_{BM} is the cost factor of the bare module which contains all the adjustment factors, F_M is the material factor, F_P is the pressure factor, finally B_1 and B_2 are factors that depend on the type of equipment.

The recovery period is estimated to be 5 years in the economic research. The facility is expected to operate for 8500 h each year. High-pressure (HP) steam (42 bar, 254 °C, $9.88 GJ1), medium-pressure (MP) steam (11 bar, 184 °C, $8.22 GJ1), low-pressure (LP) steam (6 bar, 160 °C, $7.78 GJ1), and cooling water ($0.72 GJ1). This economic assessment has been successfully applied in several studies where relatively similar separation equipment was considered (Alcocer-García et al., 2019; Bravo-García et al., 2021).

2.3. Operability index (CN)

Most of the chemical plants are designed to operate in a steady-state, each unit of the process must operate under constant conditions for a long period until the plant undergoes a maintenance phase. The alteration of any of these conditions will cause the final product not to meet the desired specifications, so that, to maintain the ideal conditions in the event of irregularities in the plant, it is valuable to manipulate the operating variables to return the system to its stationary state.

One of the basic and most important tools of modern numerical analysis is the Singular value decomposition (SVD). There are numerous important applications of the SVD when quantitative and qualitative information is desired about linear maps. One important use of the SVD is in the study of the theoretical control properties in a chemical process. The application of the SVD technique provides a measure of the controllability properties of a given dynamic system. More than a quantitative measure, SVD should provide a suitable basis for the comparison of the theoretical control properties among distillation sequences under consideration (Moore, 1986)(. To prepare the information needed for such test, each of the product streams of each of distillation systems was disturbed with a step change in product composition and the corresponding responses were obtained. A transfer function matrix relating the product compositions to the intended manipulated variables was then constructed for each case. The transfer function matrix can be subjected to SVD:

$$K = U \sum V^T \quad [9]$$

where U is the matrix of left singular vectors, V is the matrix of right singular vectors and sigma is a diagonal matrix whose entries are the singular values of the matrix K [more details about mathematic fundaments in Klema & Laub (1980)]. In the case where the SVD is used for the study of the theoretical control properties, two parameters are of interest: the minimum singular value (σ_{min}) the maximum singular value (σ_{max}), and its ratio known as condition number (γ):

$$\gamma = \frac{\sigma_{max}}{\sigma_{min}} \quad [10]$$

The condition number reflects the sensitivity of the system to uncertainties in process parameters and modeling errors. This parameter provide a qualitative assessment of the theoretical control properties of the alternate designs. The systems with lower condition numbers are expected to show the best dynamic performance under feedback control (Häggblom and Waller, 1992; Klema and Laub, 1980; Luyben, 1994). A nice feature of the SVD test is that it is independent of the type of controller to be implemented; the basic idea is that the controllability properties of the system are instead limited or imposed by its inner dynamic structure. This information should be sufficient at this point for the intended comparative analysis on the controllability properties of several distillation systems. Vázquez-Castillo et al. (2015) and Cabrera-Ruiz et al. (2017) have recently demonstrated the use of the condition

number as an index of dynamic performance and even as an objective function in a process of simultaneous optimization design-control.

2.4. Environmental impact assessment

As a subsequent evaluation of the optimization process, the environmental impact of the proposals of this work was evaluated. The evaluation of this indicator was carried out at various optimal points of the Pareto front. Eco indicator 99 (EI99) was used to assess the environmental impact after the optimization was carried out. The EI99 is a methodology centered on the Life Cycle Assessment (LCA), where the hierarchical weighting in the relative evaluation of the damage is reasoned. The EI99 makes possible the environmental load evaluation related to: an activity, a process, that identifies and quantifies the material and the energy used.

The method is based on the evaluation of three major damage categories: human health, ecosystem quality, and resources depletion. The steam required to supply the heat duty, the energy used to pump the cooling water, and the steel used to build the apparatus are the factors that have the most impact on EI99 in distillation columns. According to Eq. (11), the eco-indicator 99 may be expressed mathematically as follows:

$$EI99 = \sum_i \omega \cdot c_i \cdot as + \sum_i \omega \cdot c_i \cdot asl + \sum_i \omega \cdot c_i \cdot ae \quad [11]$$

where ω is a weighting factor for damage, c_i is the value of impact for category i, as is the amount of steam utilized by the process, asl is the amount of steel used to build the equipment, *ae* is the electricity required by the process. For example, the amount of steam used to provide energy to plant is multiplied by the damage impact of each category, and subsequently the summation of all the products is performed to obtain the eco-indicator due to steam, the procedure is the same for steel and electricity. For the weighting factor ω_d, we have followed the method of eco-indicator 99, 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 % species m^2yr), and damage to resources (expressed as the surplus energy needed for future extractions of minerals and fossil fuels, "MJ surplus"). 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, extractions and land-uses (Goedkoop and Spriensma, 2021). The values presented in Table S1 represent the damage caused in category *k* per unit of chemical *b*.

Finally, the total EI99 is obtained by the summation of eco-indicator due to steam, electricity and steel. For compute the EI99, a hierarchical perspective is considered for the evaluation of environmental impact in order to have a balance between short- and long-term effects (Goedkoop and Spriensma, 2021). Table S1 of Supplementary Material shows the impact categories and values used in this study. These values were taken from the work reported by Goedkoop and Spriensma (2021) these values are associated and corresponding with the use of steel for building the equipment and with the use of energy utilized during the plant operation, two factor that are independent of the type of process. This type of environmental impact assessment has been successfully carried out in several studies where relatively similar separation equipment was considered (Sánchez-Ramírez et al., 2015; Contreras-Zarazúa et al., 2018; Ibarra-Gonzalez et al., 2021).

The scale of the values considered in Table S1 of Supplementary Material is chosen such that the value of 1 point is representative for a 1000th of the yearly environmental load of one average European inhabitant.

3. Case study

The multicomponent mixture considered in this study consists of methanol, water, anisole, phenol, and cresols. It is assumed that the reactions took place with an excess of methanol. The outlet stream composition from a reactor is calculated based on a conversion of 50% for phenol and selectivity of 85.75% towards anisole and the reaction mechanism was taken from the study made by Kirichenko et al. (2008). Kirichenko et al. (2008), based on experimental data, proposed the following scheme of chemical transformations for anisole formation (as shown in Fig. 4). The component's flow rates and their compositions are shown in Table 1.

The thermodynamic model selected for the properties calculation of compounds is the NRTL, which has been applied to this type of compound previously (Li et al., 2015), in addition to its ability to detect the azeotropes present, as well as the multiple phases.

4. Methodology

The purification of anisole from the alkylation mixture has not been studied. As a first choice, distillation column sequences are proposed to achieve the purification of each of the components (See Fig. 5). The order of relative volatility of components are following: $\alpha_{methanol} > \alpha_{water} > \alpha_{anisole} > \alpha_{high\ boiling\ mixture}$, where the high boiling mixture is constituted by the last three heaviest components (Lange, 1967). Since this research is limited to anisole purification; the high boiling mixture purification is not analyzed.

Heuristics for the design of distillation sequences are used to obtain a preliminary design (Smith, 2005). Three of these rules are highlighted here: 1) A component composing a large fraction of the feed should be removed first. 2) The direct sequence. 3) Do the most difficult separation last. As a result, a direct distillation sequence composed of two conventional distillation columns and a heterogeneous distillation column is the base configuration for the purification of anisole from de alkylation mixture.

However, advanced distillation technologies offer an opportunity to improve the performance of the separation process. It is appropriate to study and analyze the intensified designs applied to the separation of the multicomponent mixtures, since each configuration presents different advantages, not only in the reduction of energy expenditure, but also the investment cost, and environmental impact, and aiming for a sustainable and green chemistry approach. The description of each of the distillation sequences proposed for anisole purification is detailed in the forthcoming sections. These designs are based on conventional processes as well as the intensified ones.

There is evidence about the formation of azeotropes between water and some products of phenol alkylation mixture (Lange, 1967). Between water and anisole, a low-boiling azeotrope (96.45 °C) is formed at 0.55 and 0.45 w/w% (red node at 96.45 °C of Fig. 6), respectively. Therefore, it is necessary to feed an additional component in the water separation column to break the azeotrope. Toluene is an effective carrier for phase split (Li et al., 2019), which makes it possible to obtain the light component in a decanter as a distillate product (Fig. 5). The formation of a heterogeneous azeotrope between water and toluene at 0.197 and 0.803 w/w%, respectively, can also be identified (red node at 84.39 °C in Fig. 6).

Fig. 6 is a ternary diagram developed using the NRTL model. In this figure, the concentrations (molar) and temperatures at which azeotropes are formed, the individual boiling temperatures, and the equilibrium between phases are easily found. From this figure, the effectiveness of Toluene as an extractant for the separation of water and anisole is remarkable, since it meets the required characteristics. The blue area within the diagram is limited by the equilibrium curve, and it indicates the conditions in which multiple phases are present. Instead, the distribution lines within this region indicate the concentrations that each of the liquid phases present will have. As can be seen, there are regions in

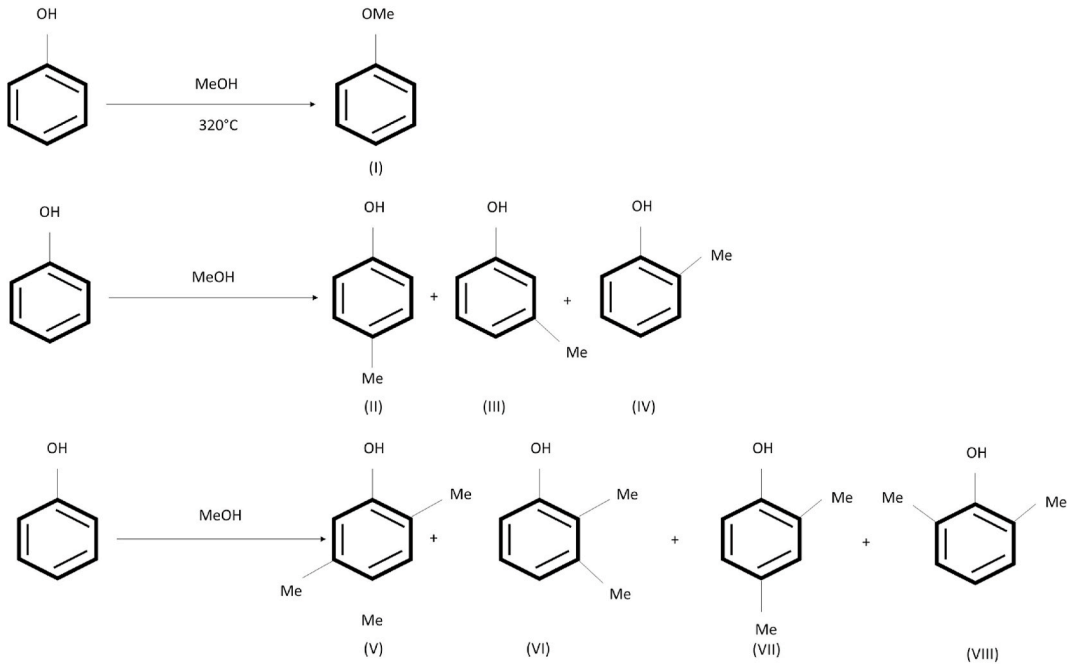

Fig. 4. Scheme of chemical transformations of phenol during alkylation.

Table 1
Component flow rates and their compositions (according to the work of Kirichenko et al., 2008).

Component	Flow Rate (kmol/h)	Mole fraction	Flow Rate (kmol/h)	Mole fraction
Phenol	13.59	0.0369	6.85	0.0186
Methanol	353.82	0.9623	346.74	0.9434
Anisole	–	–	5.78	0.0157
Water	–	–	7.09	0.0192
O-Cresol	–	–	0.41	0.0011
P-Cresol	–	–	0.54	0.0014

which it is possible to obtain an organic phase composed almost entirely of toluene and another phase composed of water, which will be facilitated with the implementation of a decanter.

4.1. Conventional sequence (CS)

Conventional configurations require N-1 number of columns (concerning the number of components). Key products are obtained in the distillate by following the order of their relative volatilities as depicted in Fig. 6. The outlet stream from the alkylation reactor is fed to column C–I, where methanol is obtained in the distillate. It is important to guarantee the maximum possible recovery of methanol to avoid undesired contamination in subsequent columns. Moreover, methanol is the alkylating agent for phenol, so the recovery ratio most makes its recirculation possible to the reactor. Column C-II in Fig. 7 is a column that performs a heterogeneous azeotropic distillation. The use of toluene as entrainer displaces the region in which azeotropes are present, at the same time toluene forms a heterogeneous azeotrope with water. In this way, it is possible to recover the extractant and water as top products in a decanter. Finally, anisole is recovered through column C-III. The bottoms product correspond to the heavy mixture that contains phenol and cresols, which their separation will not be analyzed in this work.

4.2. Thermal Coupled Sequence 1 (TCS1)

Using the CS (a conventional anisole separation process) as a base design, TCS1 is built by the lower coupling between Columns C–I and C-II as shown in Fig. 8. A side stream of vapor from column C-II is fed to the bottoms of column C–I. Therefore, the side stream of vapor from C-II should be located one stage below the feed. The vapor flow in the interconnection will generate the required stripping steam in column C–I.

4.3. Thermal coupled sequence 2 (TCS2)

This sequence is assembled in the same way as TCS2, where coupling

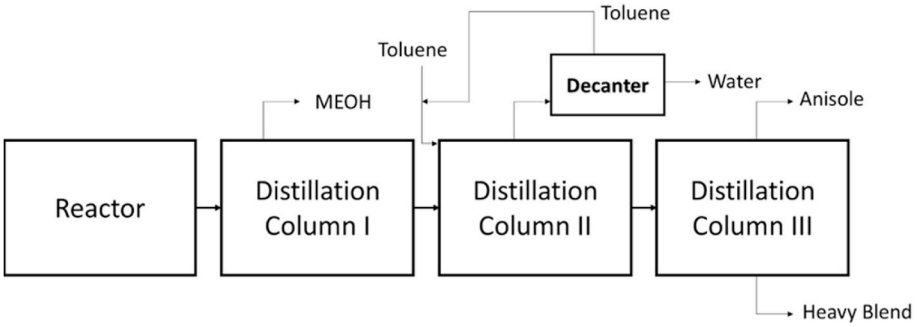

Fig. 5. Flow diagram of the anisole production and separation process.

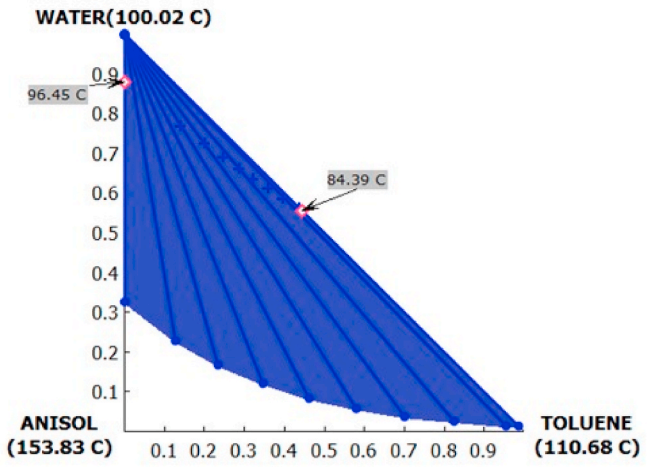

Fig. 6. Ternary phase diagram for anisole separation.

between columns is created from the CS. In this case, column C-II and column C-III have a vapor flow interconnection to generate the stripping steam in column C-II (Fig. 9).

4.4. Distillation sequence with a Divided Wall Column (DWC)

The movement of sections between two columns results in a Petlyuk column scheme. The integration of the prefractionation section and the main column into a single column results in a column with a dividing wall, which is thermodynamically equivalent to the Petlyuk scheme. The condition for this thermodynamic equivalence to be valid is that the number of stages between the liquid and vapor interconnection must be equal to the number of stages of the prefractionation section in the Petlyuk scheme. The bottom product of column C–I is fed to the prefractionator C-II, as well as the extractant. In the prefactionator, the light compounds are distributed towards the upper part and the heavy ones towards the bottom. The medium volatility component is distributed in both streams of the pre-fractionator, therefore the remixing effect is inhibited. Water and toluene are obtained as distillate products from the decanter in main column C-III. Anisole is the component of medium volatility, the amount of this component that is in the upper part of Column C-III condenses and flows to the lower stages, while the amount of anisole in the bottom of the column evaporates and flows towards the higher stages. The maximum concentration of anisole is reached at an intermediate point of column C-III and not Column C-II. The rest of the components leave the column as the bottom product (Fig. 10).

However, there are multiple alternatives to generate a greater number of separation alternatives, many of them are based on the same principles by which these alternatives were generated. That is, a considerable number of alternatives can be generated based on thermal couplings, elimination and movement of sections, etc (Triantafyllou and Smith, 1993; Liu and Qian, 2000). The existence of connection between the alternatives contained in the various subspaces has been thoroughly demonstrated (Errico et al., 2009). It indicates that after the best structure in a subspace of alternatives has been found, only the configurations deriving from that structure should be considered promising. In this sense, although it would be interesting to explore all the probable alternatives for separation, it is highly probable that the results not obtained would have been similar. In the present work we intend to observe the effect of the intensification of streams with high energy content (such as the reboilers in C–I and C-II), as well as the effect of the implementation of a DWC column (between columns II and III), this under the perspective of the sustainability indicators with which anisole separation from the alkylation mixture schemes are evaluated. This work will lead to the study of new intensified schemes for the purification of anisole from the alkylation mixture, such as schemes with internal heat integration, schemes with vapor-recompression, etc.

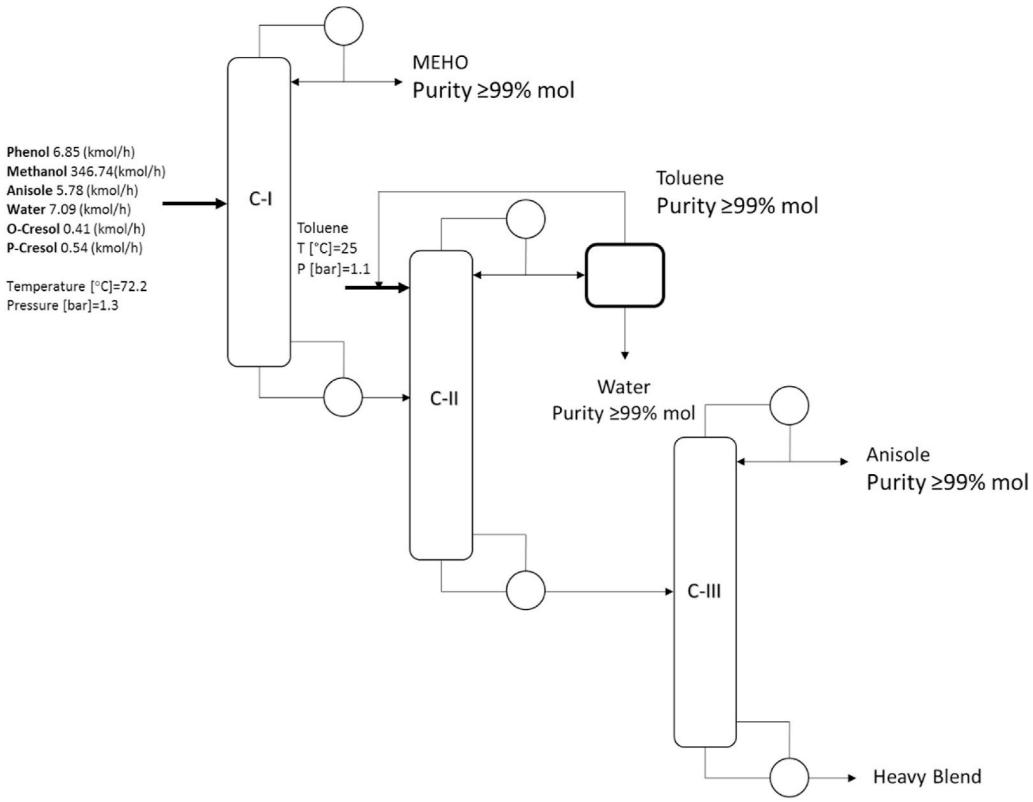

Fig. 7. Diagram of the conventional anisole separation process (CS).

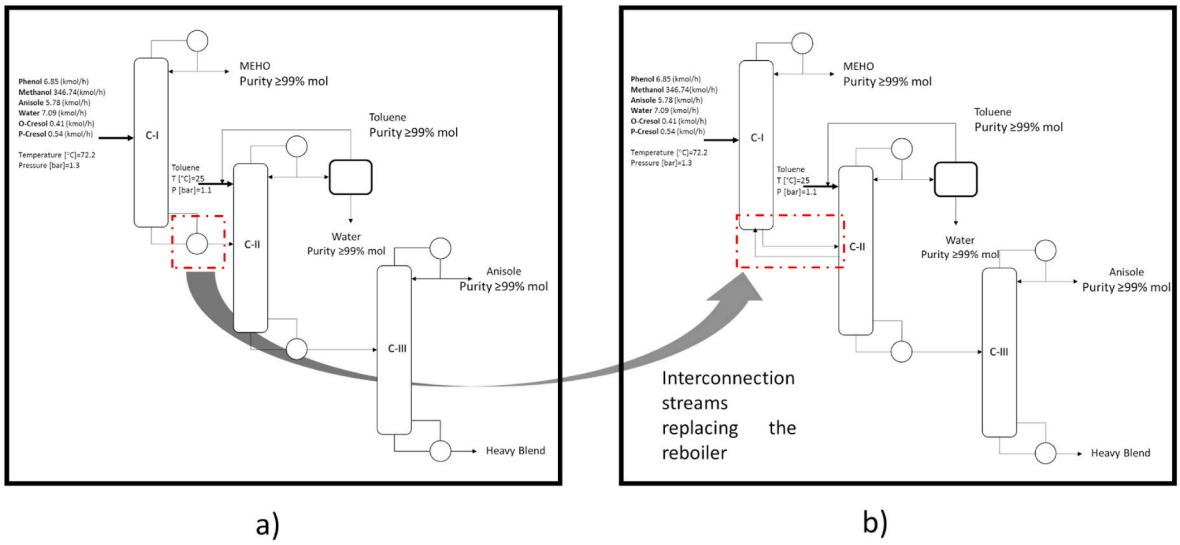

Fig. 8. a) Diagram of the conventional anisole separation process (CS), b) Diagram of the Thermal Coupled Sequence 1 (TCS1).

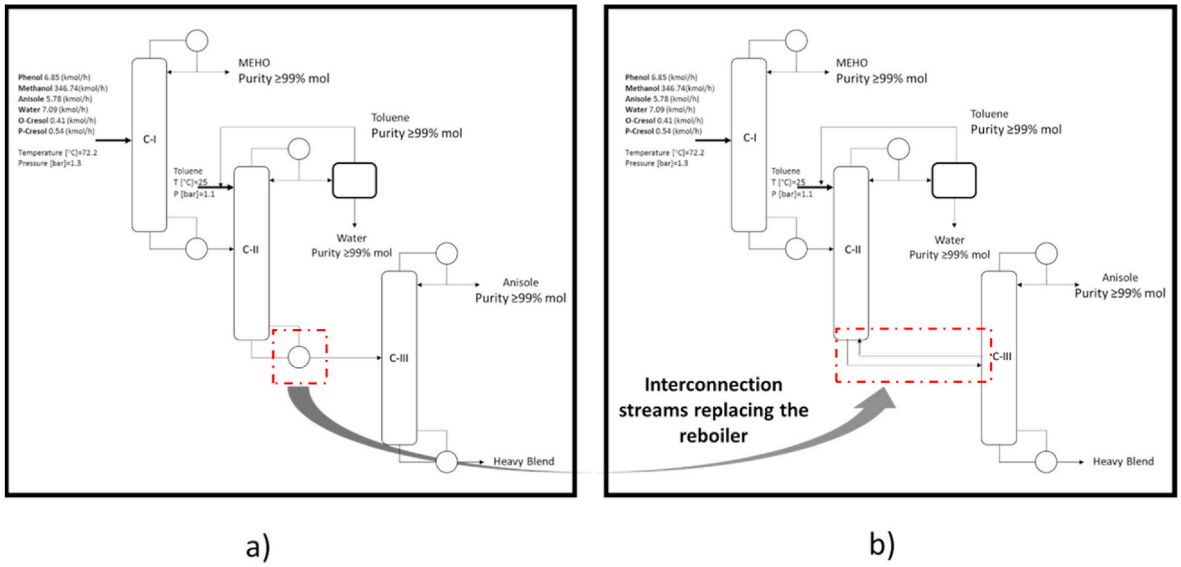

Fig. 9. a) Diagram of the conventional anisole separation process (CS), b) Diagram of the Thermal coupled sequence 2 (TCS2).

4.5. *Optimization procedure*

In engineering, typical objective functions are minimization of total costs, maximization of process yield, or minimization of environmental impact. In this work, the aim is to obtain sustainable processes that are framed by the concept of green chemistry, which is why multi-objective optimization must be achieved. The optimal design of anisole separation processes involves a nonlinear (present in the matter and energy balances, as well as in the equilibrium equations) and multivariate problem, and the objective functions used as optimization criteria are usually non-convex with several local optima, therefore, a stochastic optimization technique based on Differential Evolution (DE) is chosen. Differential Evolution (DE) is a population-based stochastic optimization technique. This method imitates the biological process of evolution through the sequence of mutation, crossing, and selection. It was introduced by Storn and Price, 1997. The method consists of three important control variables: population number (Np), mutation factor (F), and crossover factor (Cr). The value of these values is a subject that still has intense research (Gämperle et al., 2002). Tabu Search (TS) was proposed by Glover and Laguna (1997). It is based on solving a problem intelligently, incorporating adaptive memory and responsive exploration.

Srinivas and Rangaiah (2007) proposed a hybrid differential evolution algorithm with tabu list (DETL), which combines the characteristics of DE and TS to obtain good reliability as in DE, and at the same time a good computational efficiency as in TS. DETL has proven to be effective in the multi-objective optimization of conventional and complex distillation sequences (Contreras-Zarazúa et al., 2017; Alcocer-García et al., 2019).

4.5.1. *Methodology for global optimization*

The different distillation sequences presented in the previous section will be optimized using the DETL method. The optimization is done through a hybrid platform using Microsoft Excel and Aspen plus. The implementation of the DETL algorithm (see Fig. 11) is programmed in a Visual Basic module of Microsoft Excel program. The vector containing the decision variables is sent from Microsoft Excel to Aspen Plus. After the simulation has been carried out, the results are sent to Microsoft

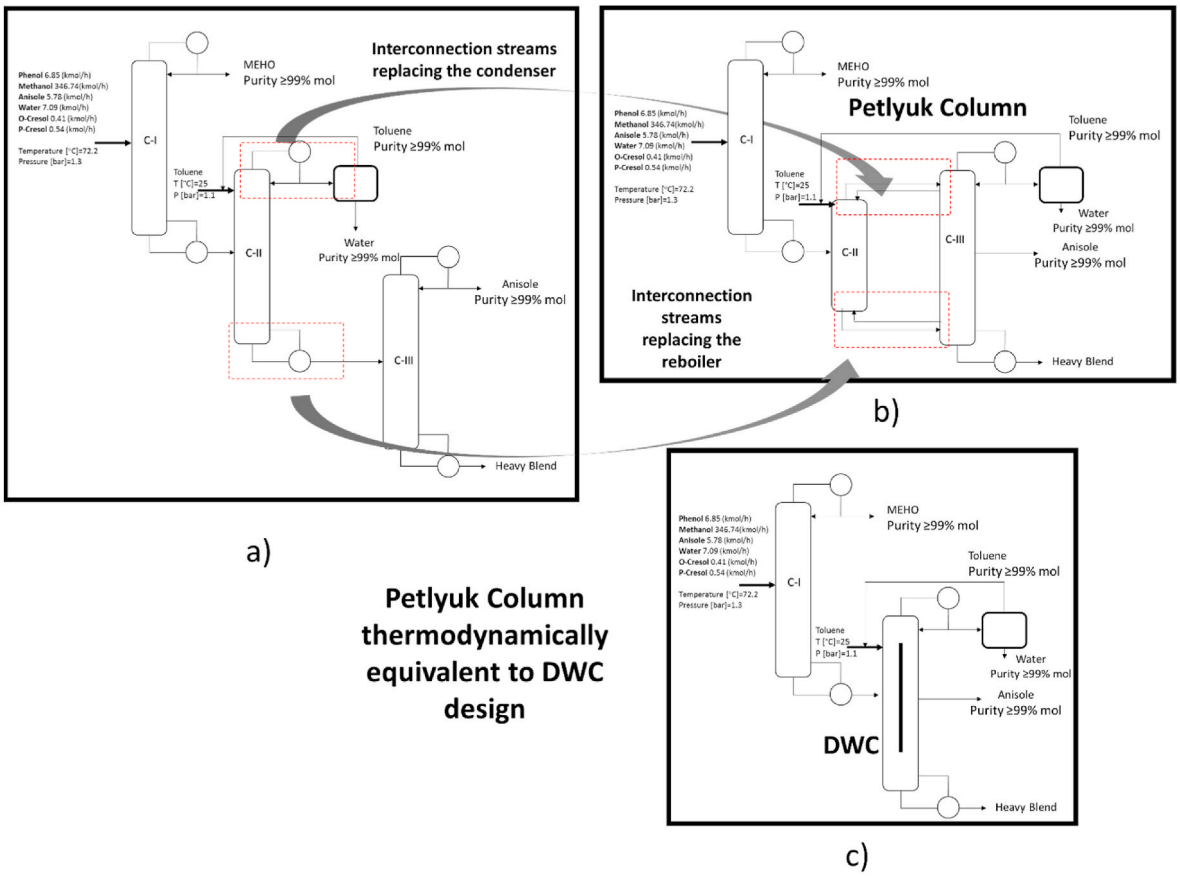

Fig. 10. a) Diagram of the conventional anisole separation process (CS), b) Diagram of the distillation sequence with a Petlyuk Column, c) Diagram of the distillation sequence with a Divided Wall Column (DWC).

Excel, so this software finally evaluates the objective function and proposes new decision variables (Segovia-Hernández and Gómez-Castro, 2017).

Since DETL is a population-based procedure, it is necessary to set the method parameters for the algorithm adjustment. The values of the parameters used were compiled from previously reported works in which the DETL algorithm is integrated with a process simulator for the optimization of distillation sequences, Np: 120, 600 generations, Cr: 0.8, F: 0.6, TR: 0.0025, Tl: 60 (Contreras-Zarazúa et al., 2017; Sánchez-Ramírez 2019). As mentioned above, the problem with multicomponent mixing is the formation of heterogeneous azeotropes between ethers and water, which complicates the purification of compounds.

4.5.2. *Multi-objective function*

The independent variables in the model provide values to the objective function, while optimization techniques are based on finding the values of the independent variables that offer the point at which the objective function or functions reach their maximum or minimum value, depending on the problem. Discrete variables are those that can only

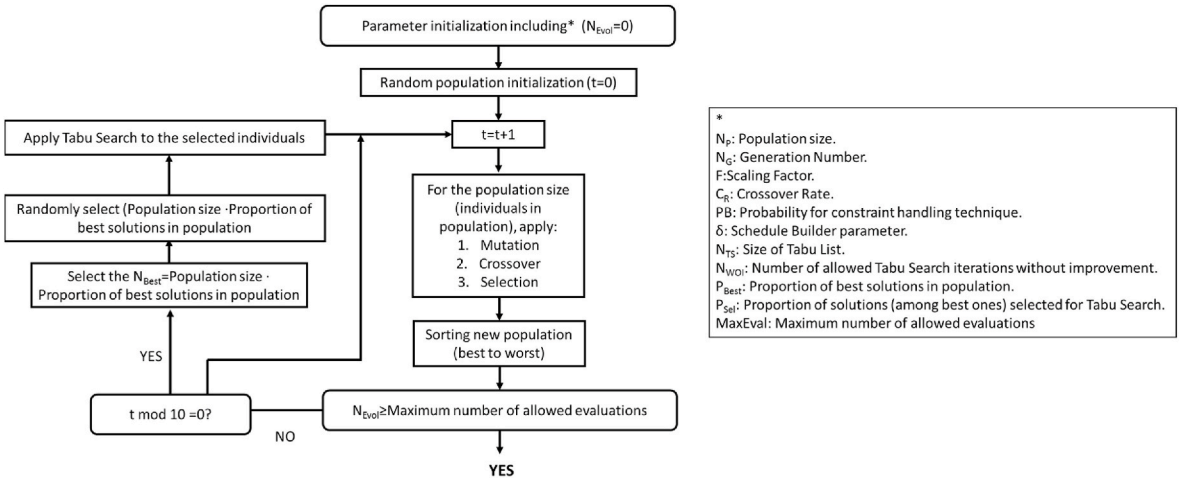

Fig. 11. Flowchart of the DETL algorithm (Ponsich and Coello 2013).

take integer values; continuous variables can take both integer and fractional values. The input data to the optimization algorithm are the specific design variables of each of the schemes. To get the algorithm starts, it is necessary to specify the type of variables and their limits. Table S2 of Supplementary Material shows the variables established for the case studies of this work. When working on theoretical studies, it is possible to get results that are not feasible at the experimental level. A clear example is the size of distillation equipment, a column with a very small diameter is not recommended for its industrial application, since it makes maintenance procedures difficult. Therefore, it is important to delimit the values that the decision variables can take, to obtain feasible designs. The ranges of some of the variables are considered based on design heuristics (Douglas, 1988). Other variables can be limited by a preliminary analysis of the behavior of the columns, for example, the thermal loads of the reboilers and the interconnection flows.

The optimization of the conventional and intensified schemes for the purification of anisole will be restricted to the flow and concentration data shown in Table 2, this is due to the demand for anisole and the purities required in the market for each product (Global Market Insights, Inc. (2018). The indexes described above are used as the objective function, subject to:

$$Min(TAC, IR, CN) = f\left(N_T, N_{Feeding}, Distillateflow, QR, Diameter, Solventflowrate, N_{Solvent}\right) \quad [12]$$

Subject to:

$$y_i \geq x_i w_i \geq u_i$$

In each of the iterations is calculated the three indexes for each secuence. The unit's indexes depends of their size and operating cost.

The weights used for the three different objective functions were equally distributed. That is, one third of the weight is for the IR, another third for the CN, and finally another third for the TAC. The reason for following such weighting is exhibited by Jimenez-Gonzalez and Lund (2021), they show that there is no unified metric available to measure the sustainability of a process. And that it is better to incorporate metrics such as IR, CN and TAC with the same weight value if a representation of the overall sustainability of the process is to be developed.

4.5.3. Normalization procedure

In general, under a multi-objective optimization scheme, it can be difficult to identify which sequence is the best in the whole concept of sustainability and green chemistry. For this reason, this work aims to provide a broader view of the selection of the best design employing a normalization procedure. The normalization of the objective functions (TAC, IR, and CN) makes it possible to identify the sequence best suited to the concepts of sustainability. Koski (1985) suggests the normalization of the objective functions as follows:

$$f_i(x) = \frac{F_i(x) - min\ F_i(x)}{max\ F_i(x) - min\ F_i(x)} i = objectivefunctions, X \in NP \quad [13]$$

If points are treated as vectors in a plane or space that start from the origin, it is possible to determine the length of each of these vectors to detect the one closest to the minimization of both axes. Applying the Pythagorean Theorem, the Euclidean distance can be calculated in a general way as:

$$Distance = \sqrt{\sum_{i=1}^{i=NF} f_i^2}, NF = Numberofobjectivefunctions \quad [14]$$

Using this method of global selection criteria, the multiobjective optimization problem becomes the optimization of a scalar for the selection of the best solution. The benefit of using normalization is that it shows us how far away is the optimum of an objective function of a sequence, concerning the optimum of the same objective function of another sequence. That is, how far we are from the ideals of a sustainable process.

5. Results

The results section will present the main results obtained, as well as various trends that were observed in the optimization process. In this circumstance, the optimization algorithm was used to design distillation sequences to minimize three of them. Due to the dispute between the objective functions, the final generation of the evolutionary method offers vectors with design variables that can be inclined to a greater minimization of a particular objective but decreasing the quality of the rest of the objectives. The optimal solution will correspond to the set of variables that contemplates the minimization of the objective functions simultaneously.

In this section, the value of the objective functions of each distillation sequence is represented in Fig. 12. The points in space are the population that makes up the best individuals evaluated after 600 generations. The optimal point is highlighted and was determined by carrying out the normalization procedure and the application of the Pythagorean double theorem.

The distribution of the points in Fig. 12 can be interpreted as a surface in space, in which they attempt to get closer to the minimum value that leads to a distance from it. Tables 3–4 and Tables S3 and S4 (Supplementary Material) contains the values of the variables of three of these points in space (P_{TAC}, P_{IR}, and P_{CN}), which are those that individually minimize the Total Annual Cost (TAC), the condition number (CN), and the Individual Risk index (IR), respectively. The last column of these Tables contains the variables of the optimal design (OP) that produces the best values of the objective functions (contains the best decision variables). From these databases, some criteria considered by the algorithm for the selection of vectors can be observed.

In the analysis of the CS configuration, it is noticed that the P_{TAC} leads to distillation columns with a greater number of stages (C–I 32, C-II 35, and C-III 57 stages); however, this is reflected in lower reboiler duties (C–I 1′452,162.46, C-II 91,905.33, and C-III 58,726.74 cal/s) and, therefore, lower use of auxiliary services. Remember that there is an inverse relationship between the number of stages and the reboiler duty. On the other hand, the P_{CN} contains the lowest values for the number of stages (C–I 28, C-II 32, and C-III 55 stages) and the highest reboiler duty (C–I 1′473,316.93, C-II 94,946.18, and C-III 63,324.41 cal/s). It is also possible to appreciate that the point with the lowest condition number uses a higher flow of toluene (26.02 kmol/h) in Column C-II to keep the concentrations in the decanter more sensitive to the controller. Now, as expected, this design results in the highest IR (6.889E-05 1/y), since the

Table 2
Flow and concentration data of Process Routes for separation of anisole.

Component	Concentration (x_i)	Flow rate (u_i) kmol/h
Methanol	0.99	346
Toluene	0.986	Toluene flow rate
Water	0.99	6.5
Anisole	0.99	5.5

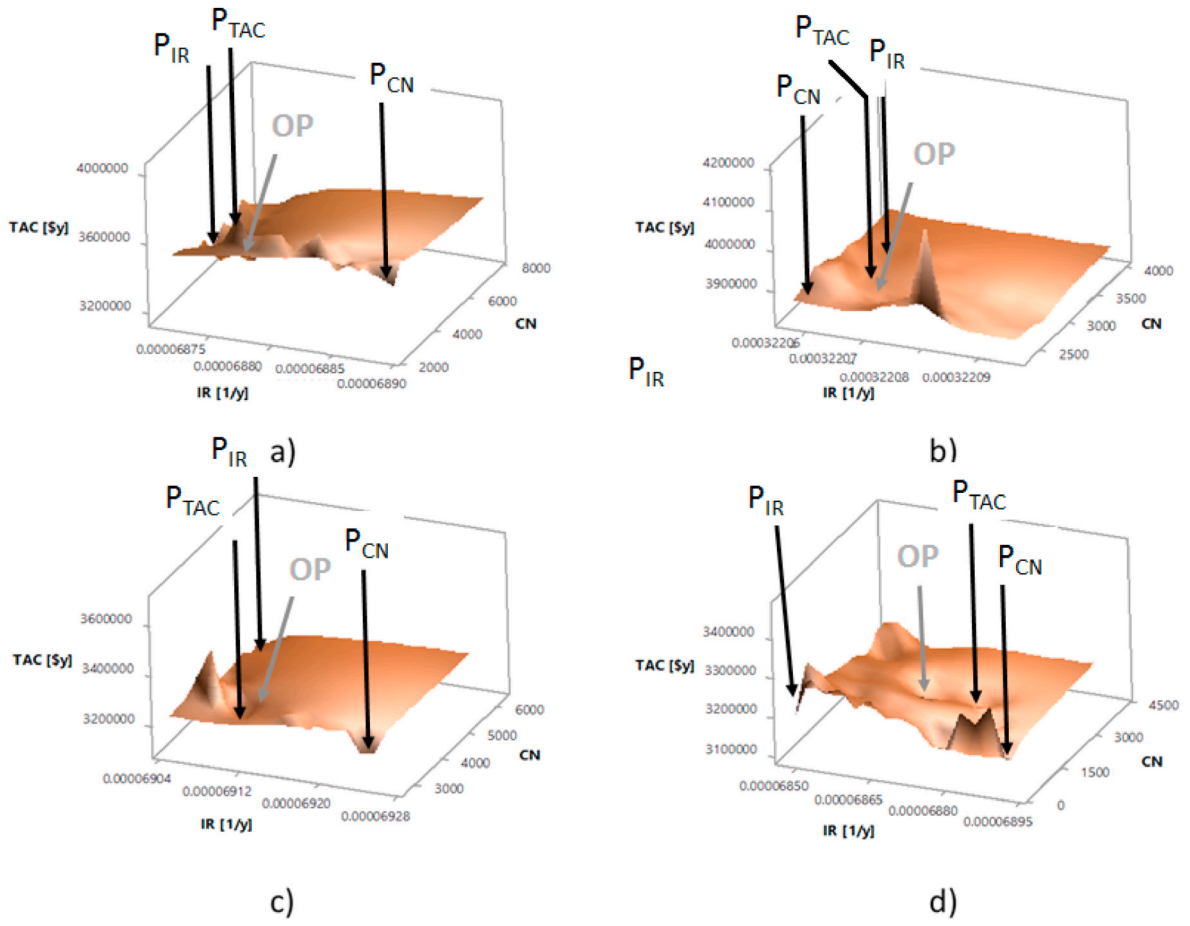

Fig. 12. Response surface of the economic, safety and control indexes of the: a) CS, b) TCS1, c) TCS2, and d) DWC sequences.

high toluene flows make this column increase the probability of an incident occurring and the magnitude of its effects. Regarding the best value of the IR (6.8716E-05 1/y), the preference for a lower flow of extractant to minimize the indicator is notable. About the size of the columns, the values are in an intermediate point of those of the other points. Medina-Herrera et al. (2014) conclude that larger equipment results in lower IR, however, when considering the TAC as an objective function, the optimization method should find a point at which the values of the variables find equilibrium between objective functions. Finally, a conventional distillation sequence that includes the three objective functions, the OP shows the best compromise relationship between the three objective functions and contains the best decision variables that, although not the most economical (3′250,219.40 $/y), the safest (6.874E-05 1/y) or with the best condition number (3748.12) of all, their design specifications are focused on minimizing objectives in such a way that their commitment is affected the least. Although it can be observed that the P_{TAC}, P_{CN}, and P_{IR} solutions are near to the optimal solution (OP), the advantage of this OP lies in the balance of the indexes. That is, values such as CN and IR are highly lower than in the other solutions that did not minimize these objectives. This is directly related to the diameter, reboiler duty, and reflux ratio of each column.

For the design TCS1, the TAC (3′836,882.07 $/y) is higher than that of the conventional sequence (P_{TAC}). Although the columns are similar in size, the total reboiler duty is higher in this configuration (C–I 1′452,162.46, C-II 91,905.33, and C-III 58,726.74 cal/s). Of the total flow that is fed to the C–I Column, more than 90% is obtained as a distillate product, leaving a stream with less flow (for the feeding) as a bottom product. As there is no reboiler in C–I Column, the reboiler for the C-II Column must supply the stripping steam of both types of equipment. This extra reboiler duty in the C-II column implies an excessive increase in the vapor flow of heavy compounds in the column, concerning those required in the conventional sequence, which is reflected in high-energy requirements. The condition number (2900.77) in this sequence remains in ranges like the conventional sequence, on the other hand, the IR (3.22066E-04 1/y) is highly affected. As the reboiler duty of the C-II Column increases, the reflux also increases, which causes the requirement of a greater quantity of extractant for the purification of the water. Something similar happens in the cases of P_{CN} and P_{IR}. The results of the TCS1 sequencing OP dictate that the TAC is 3′866,473.64 [$/y], the IR is 3.22062E-04 [1/y], and the CN is 2582.75. Table S3 of Supplementary Material shows the main design parameters of scheme TCS1.

Unlike the TCS1, the P_{TAC} design in TCS2 is associated with columns with a lower reboiler duty (1′566,963.4 cal/s); its value is below that of the conventional sequence (1′602,794.53 cal/s). The weak improvement in this indicator is because the highest percentage of the total annual cost is addressed in the C–I Column since this column has a higher energy requirement (92.67%). Therefore, the thermal coupling of this sequence focused on energy savings between the last two columns does not have a high impact. As in the previous sequences, the CN is attended by high toluene flows and a high amount of reboiler duty that assist in the conservation of the concentrations of the products when a disturbance is applied. At the same time, the IR rises. Its value is similar to those obtained in the conventional sequence. The P_{IR} is the design with the lowest risk index (6.9045E-05 1/y) and its value is higher than that of the conventional sequence (6.8716E-05 1/y). This can be understood by the increase in the vapors inside the C-II column since by creating the interconnection with the C-II columns, the internal flows are affected to supply the necessary depletion steam in the column that lost the reboiler. Table S4 of Supplementary Material shows the main

Table 3
The feasible and optimal solution of the conventional anisole separation process (CS).

Variable	P_{TAC}	P_{CN}	P_{IR}	OP
Number of stages C–I	32	28	30	28
Number of stages C-II	35	32	31	33
Number of stages C-III	57	55	41	56
Feed stage C–I	14	13	15	14
Feed stage C-II	26	22	25	23
Feed stage C-III	26	21	21	19
Toluene feed stage	4	3	4	4
Distillate flow rate C–I (kmol/h)	347.06	347.06	347.02	347.06
Distillate flow rate C-II (kmol/h)	17.72	26.03	16.74	18.84
Distillate flow rate C-III (kmol/h)	5.77	5.78	5.66	5.78
Toluene flow rate (kmol/h)	11.07	19.83	10.09	12.19
Reboiler duty C–I (cal/s)	1452162.46	1473316.93	1460825.04	1473873.80
Reboiler duty C-II (cal/s)	91905.33	94946.18	93710.26	91962.05
Reboiler duty C-III (cal/s)	58726.74	63324.41	61120.20	63732.15
Diameter C–I (meters)	0.60	2.67	1.37	0.51
Diameter C-II (meters)	0.73	3.56	2.50	1.82
Diameter C-III (meters)	0.52	3.02	1.63	0.88
TAC ($/y)	3174295.16	3502372.97	3271595.18	3250219.40
CN	4121.32	2573.86	7638.39	3748.12
IR (1/y)	6.874E-05	6.889E-05	6.8716E-05	6.874E-05
Component TAC	0	0.3928	0.1165	0.0909
Component CN	0.2915	0	0.9542	0.2212
Component IR	0.1962	1	0	0.2015
Magnitude of a vector	0.35147	1.0743	0.9613	0.3127

design parameters of scheme TCS1.

The synthesis and principles of operation of the DWC configuration were described in previous sections. Column C–I maintained its structure, so its design variables follow the same as the conventional sequence (Table 3). On the other hand, the blending of columns C-II and C-III brought with it an increase in the number of degrees of freedom. The P_{TAC} (3′096,914 $/y) results show that this distillation sequence has the potential to improve the economic index concerning the conventional sequence (3′836,882.07 $/y), as well as the Condition Number shown by the P_{CN} (308.88) and the risk index by the P_{IR} (6.84829E-05 1/y). Specifically, through the optimal design, the improvement of the indicators offered by the DWC is appreciable. In other words, the DWC represents the most features of sustainability and green chemistry. The reduction in energy demand by the columns that had section movement and the number of stages by the rectifying (or enriching) section, is reflected in a reduction in the TAC. The presence of toluene for the separation of water from anisole maintains the risk index with values similar to that of the conventional sequence. Therefore, its best attributes are in the reduction of the TAC and the improvement of the CN. Fig. 13 shows the optimal DWC sequence. The DWC sequence composition profiles are shown in Figs. 14 and 15. It can be seen that from the CI, the largest amount of MeOH is separated. In the DWC feed there is a large amount of water, anisole, and phenol, and small amounts of the cresols. From the composition profile of the DWC column it is important to note that water and toluene are separated by the column dome, which are subsequently separated in the decanter. From the sidestream (stage 24) of the DWC, it is observed that the purity of 99% mol of the anisole, which is the component of interest, is reached. And by the bottom of the DWC both phenol and cresols are obtained.

Table 4
The feasible and optimal solution of the Dividing Wall Column (DWC).

Variable	P_{TAC}	P_{CN}	P_{IR}	PO
Number of stages C–I	24	24	23	25
Number of stages C-II	21	23	25	25
Number of stages C-III	62	58	64	56
Feed stage C–I	12	12	11	12
Feed stage C-II	16	17	15	17
Toluene feed stage	3	4	3	3
Vapor feed stage	16	22	21	12
Liquid feed stage	37	45	46	37
Side product stage	23	32	32	24
Distillate flow rate C–I (kmol/h)	347.05	347.12	347.09	347.12
Distillate flow rate C-III (kmol/h)	19.59	20.84	20.69	20.78
Lateral product flow (kmol/h)	5.68	5.66	5.66	5.83
Vapor interconexion flow (kmol/h)	31.63	31.24	30.08	30.33
Liquid interconexion flow (kmol/h)	0.48	0.54	0.51	0.50
Toluene flow rate (kmol/h)	12.94	14.19	14.04	13.85
Reboiler duty C–I (cal/s)	1450114.81	1518924.78	1461387.37	1450378.94
Reboiler duty C-III (cal/s)	112224.21	118383.12	113742.12	110654.33
Diameter C–I (meters)	1.37	1.45	1.70	0.51
Diameter C-II (meters)	0.81	2.34	1.66	2.39
Diameter C-III (meters)	0.58	1.60	1.46	1.46
TAC ($/y)	3096914.00	3298150.46	3171204.51	3136495.89
CN	29367.02	308.88	356.65	3527.72
IR (1/y)	6.89245E-05	6.88406E-05	6.84829E-05	6.8514E-05
Component TAC	0	0.53	0.19	0.10
Component CN	0.14	0	0	0.01
Component IR	0.96	0.78	0	0.06
Magnitude of a vector	0.97	0.95	0.19	0.12

The values obtained for each indicator ($P_{TAC,}$ $P_{CN,}$ and P_{IR}) show that the topology of each of the processes varies according to the indicated metric. When performing the multi-objective optimization (PO), the results show a quantitative analysis of the safety, economics, and control of each of the processes. This quantitative analysis has revealed that the intensification of a process certainly contributes to the concept of sustainability and that inherent safety is an indicator that is directly related to it. When evaluating the economic and control conflicts with the safety of each of the processes shown, it can be observed that the more intensified the process is, the more sustainable it is, as expressed by Jiménez-González and Constable (2011).

Measuring the sustainability of processes for anisole separation must continue the evolution toward widespread use of life cycle analysis to ensure a more holistic approach. This can be challenging in the early stages of development given the partial data, but this hurdle can be circumvented through the development and use of process synthesis, design, intensification and optimization tools, alone or in combination with metrics such as TAC, IR, CN and Eco99 attributes.

5.1. Results of the normalization procedure

A clearer way to identify the best sequence in terms of sustainability

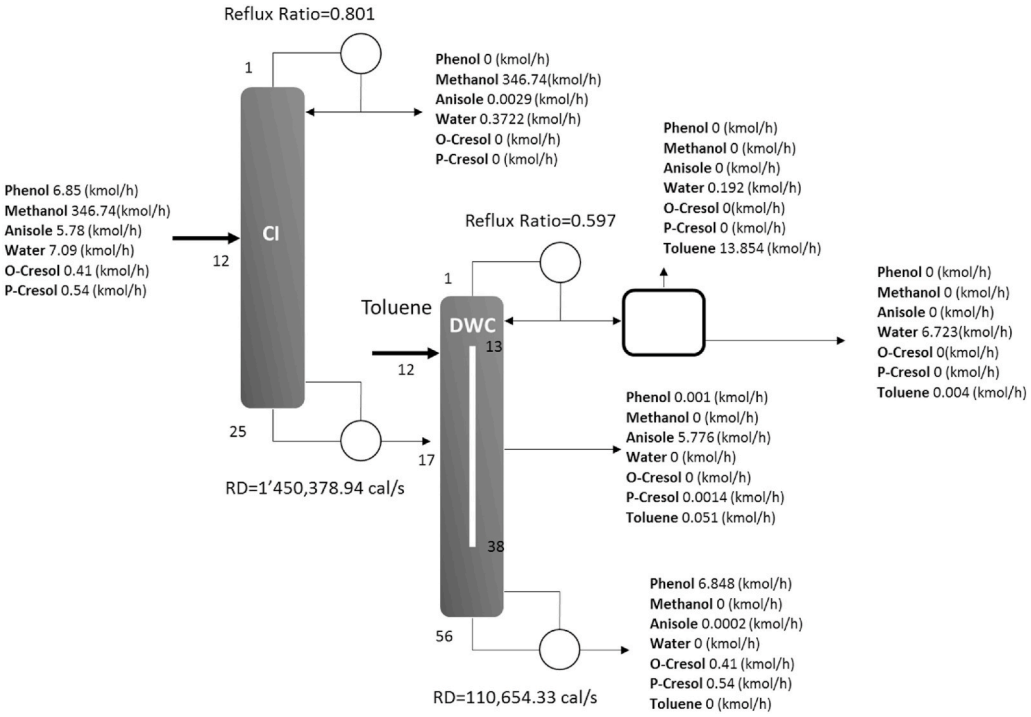

Fig. 13. Optimal DWC sequence design for anisole separation.

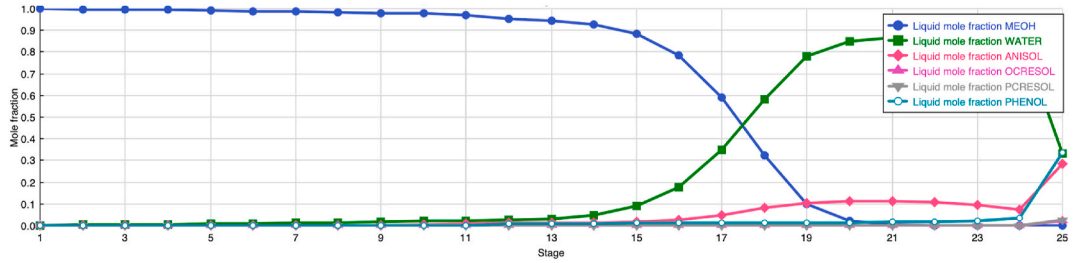

Fig. 14. CI: Composition profiles.

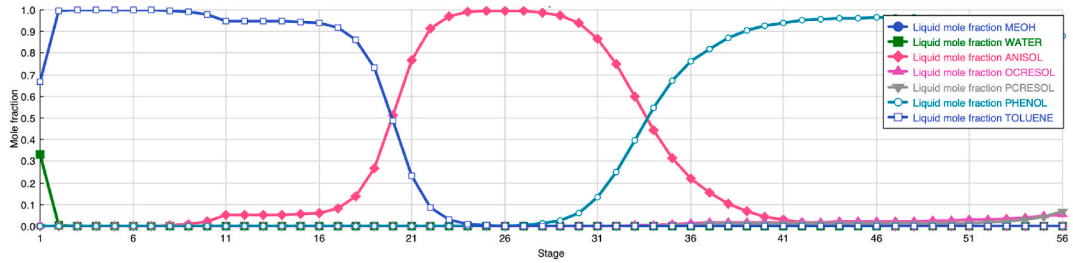

Fig. 15. DWC: Composition profiles.

Table 5
Objective functions from Optimal Designs.

Sequence	TAC $/year	CN	IR 1/year	Eco-indicator [MP/y]
CS	3250219.4	3748.12125	6.87E-05	1.489
TCS1	3866473.64	2582.74612	3.2206E-04	1.548
TCS2	3169914.52	3462.48733	6.9081E-05	1.444
DWC	3171204.52	356.650461	6.8483E-05	1.439

Table 6
Normalized objective functions from Optimal Designs.

Sequence	Index TAC	Index CN	Index IR	Magnitude of a vector
CS	0.11528797	1	0.0010453	1.00662426
TCS1	1	0.65638061	1	1.55911369
TCS2	0	0.91577875	0.00235752	0.91578178
DWC	0.00185196	0	0	0.00185196

is to perform a normalization of the objective functions (as shown in section 4.5.3). Table 5 contains the values of the objective functions corresponding to the optimal designs, in addition to the results of the evaluation of the environmental indicator. Table 6 contains the normalized values and magnitudes of the resulting vectors in ascending order.

As can be seen in Table 5, the DWC configuration is the best in the minimization of the objective function. Despite not being the one that provides the lowest TAC, it has the potential to improve CN and IR compared to the rest of the sequences. It's a rather low Technological Readiness Level and plenty of room for its further development. Therefore, we can expect the TAC decreases in the years to come as the cost of manufacturing and operating DWC Will decrease as it develops further. The reduction of the total reboiler duty and the size of the equipment are the two variables that most improve this sequence. In second place is the TCS2 sequence, with a slight improvement in the TAC but an increase in the value of the remaining indicators, compared to the DWC sequence. It is worth mentioning that although these first two configurations focus on the enhancement and enhancement of the C-II and C-III columns, they are positioned above the sequences focused on the C–I Column.

It is important to mention that the percentages of improvement in the indicators of the best sequence (DWC) with respect to the CS might seem small, with 2.43% savings in economic terms, 0.31% in inherent safety, improved controllability performance and a 3.35% reduction in environmental impact. However, the first aspect to emphasize is that it is not the individual improvement of each index, but the sequence that balances the indexes. Now, the improvement in economic terms represents US$79,014.88 annually, and as mentioned by Skiborowski (2018), small economic improvements in industrial processes can bring economic benefits to the product market. Hansson (2010), and Khan and Amyotte (2003) mention, that any IR improvement eliminates a hazard rather than managing it through various additional equipment and procedures. The index that benefits the most is the CN, which evidently being lower, provides greater stability and quality of the process in a dynamic state (Segovia-Hernández et al., 2007). For the eco-indicator, an improvement of 0.05 [MP/y] represents mainly a decrease in electricity consumption and in the construction material used in the process, although it is not a significant decrease in this item, it does have a lower environmental impact. However, the most important aspect of the work is the overall improvement of all indexes, which represents a sustainable process with a green engineering character, as expressed by Jiménez-González and Constable (2011).

Finally, the TCS1 sequence is the furthest from the point where the three objective functions are minimized. Despite being the configuration with the second best value of the CN, its deficiencies in improving the economic and safety index place it below all the proposed sequences. Specifically, to achieve the design of a process that meets the aspects of a fully sustainable and green chemistry process, it is essential to consider all the indexes simultaneously, an optimal design is based on the most favorable conditions for the minimization of the indicators as objective functions. Also noting that the reason we consider steady-state and transient indexes is the conflicting trade-offs between design objectives. All this becomes more evident with the results shown in the environmental impact assessment.

It is important to emphasize that despite the fact that the sustainability indicators show improvements in the intensified systems, compared to the base design, in no more than 4% this improvement is relevant. El-Halwagi and Foo (2021), establish that even small improvements in sustainability indicators are relevant due to current environmental public policies and the needs of current industry according to international environmental legislation. Therefore, although the improvements may seem minimal, in the indicators analyzed in this work, they are relevant for a possible implementation of the process according to the current legislation on sustainability.

To give an overview of the results, the number of different green metrics described (TAC, CN, IR, and Eco99) demonstrates that there is no unified metric available and widely accepted to measure the sustainability of a process. In the case of process design and optimization for anisole separation, the green metric of safety fits the context. However, it is ideal to incorporate life cycle analysis impacts if a representation of the overall sustainability of the process is to be developed. Therefore, the DWC sequence is the one with the best sustainability projection and the lowest environmental impact with a value of 1.43 [MP/a], thus demonstrating that the sustainable criteria are met, conditions specified by Jiménez-González and Constable (2011) to have a green process.

6. Conclusions

With the growing awareness of the importance of conserving natural resources and mitigating the negative impact on the environment, sustainable design of industrial processes is emerging as an effective framework for supporting sustainability initiatives. To obtain anisole purification processes that comply with the principles of inherent safety in a framework of sustainability and green chemistry, the design and optimization of intensified distillation sequences using appropriate metrics (IR, TAC, and CN) were carried out through a systematized methodology using a stochastic optimization model. When minimizing the three objective functions, the intensified sequence DWC is the one that achieves the best results of the indicators, with 2.43% savings in economic terms, 0.31% in inherent safety, improved controllability performance, and a 3.35% reduction in environmental impact, concerning the conventional sequence. The intensified sequences TCS1 and TCS2 also improve both IR and CN (percentages higher than 100% in the case of IR), and although they do not reduce TAC by the same magnitude as the DWC sequence, they are presented with close TAC values (only 0.04% difference). The evaluation of the environmental impact through eco-indicator 99 shows that the intensified sequences improve this index, about 4% of the total. By not considering the environmental impact as an objective function in the optimization, this index does not give them an advantage over the other sequences when applying the selection criterion of an optimal configuration. Intensified processes significantly reduce the inherent safety, which could set the trend in terms of sustainability and the green chemistry of a process. Therefore, if a sustainable process is desired for the purification of anisole from the alkylation mixture that provides low investment and operating costs, inherent controllability, and improves process safety, the intensified sequences are the most suitable. In general terms, when a process is intensified, it will inherently reduce the size of the process, which represents better economy, reduction of accident zones, potentially easier to operate, and also represents a lower environmental impact; in other words, all of this signifies green and sustainable processes. In summary, the proposed methodology to generate designs based on a framework of sustainability indicators can be generalized to evaluate more parameters and applied to the design of any chemical process.

Author statement

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Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlp.2022.104899.

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