Chemical Engineering & Processing: Process Intensification 148 (2020) 107833

Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Design of dividing wall columns involving sustainable indexes for a class of quaternary mixtures

Eduardo Sánchez-Ramírez[a,*], César Ramírez-Márquez[a], Juan José Quiroz-Ramírez[b], Anyeli Yahaira Angelina-Martínez[c], Vicente Vicente Cortazar[c], Juan Gabriel Segovia-Hernández[a]

[a] *Universidad de Guanajuato, Campus Guanajuato, Departamento de Ingeniería Química, Noria Alta s/n, Guanajuato, Gto., 36050, Mexico*

[b] *CONACyT-CIATEC A.C Centro de Innovación Aplicada en Tecnologías Competitivas, Omega 201, Col. Industrial Delta, 37545 León, Gto, Mexico*

[c] *Departamento de Ingenieria Ambiental, Universidad del Mar, Campus Puerto Angel, Ciudad Universitaria, Puerto Ángel, Distrito de San Pedro Pochutla, Oax., 70902, Mexico*

ARTICLE INFO

Keywords:
Sustainable process
Control properties
Inherent safety
Fully thermally coupled distillation
Quaternary dividing wall column
Vapor/liquid split

ABSTRACT

Current policies lead the design of chemical processes towards a sustainability environment. In the downstream process research, the Dividing Wall Columns are well-known for their capabilities of saving energy. Those policies demand continuous improvement. Many authors highlight metrics to define a sustainable process, the energetic saving, greenhouse gas emissions, safety and the controllability of the process; thus avoiding waste materials with negative impacts on the environment and the safety of the environment. The Quaternary Dividing Wall Column is currently a not so well explored option since its architecture and dynamic properties are not completely studied as of yet. In this study, a set of Quaternary Dividing Wall Columns was designed and tested in many performance indexes: energy requirement, environmental impact, Inherent Safety, and dynamic properties. The interesting approach of this proposal is that many of the conventional thermal couplings are substituted for Liquid Splits whose implementation improves the performance indexes already mentioned. In this work several quaternary DWC with a liquid split are presented in order to know the implication of implementing a liquid split. As a result, the schemes with Liquid Splits showed better performance indexes and could be prospected as good alternatives in a framework of sustainable processes.

1. Introduction

Current international policies are more rigorous. Therefore, the new chemical design alternatives must consider at a design stage all new regulations, not only privilege economic and environmental issues. Downstream processes are not an exception. Some authors have proposed to evaluate the new alternatives in an environment of green metrics. For example, Jiménez- González et al. [1] have proposed that processes should incorporate green metrics towards the broader goal of environmental sustainability. Among those green metrics, these authors also make emphasis on the obviously economical aspect, however, the important aspects should not be forgotten, such as energy consumption, greenhouse gas emissions, controllability and Inherent Safety of the process. On one hand, energy consumption is completely related to greenhouse gas emissions and the consumption of non-renewable energy sources. As long as the energy requirements of the process decrease, the CO_2 emissions will decrease as well. On the other hand, process control by means of real-time analysis may prevent waste by identifying process excursions as they occur. From a green perspective, the processes that are not stable from the control point of view, will obviously produce a greater amount of waste, consume a greater amount of raw material, a greater amount of energy per quantity of a finished product and eventually reduce the performance and effective process time. In some cases, by not keeping the process under control it will generate faults in the product specifications; consequently, the materials returned to reprocess will increase, as well as the waste generated. Lastly, poor control of these processes can generate errors in the operation of the process, possibly incurring in risky conditions of safety to the environment of the plant and to the active personnel. In other words, a process that is not well-controlled will have a direct impact on the Inherent Safety of that same process.

Regarding downstream processes, distillation is the most used process. Although distillation possesses many advantages and industrial maturity, it is well known for its drawbacks. In a green process framework, an alternative to increasing the distillation performance, it is called Process Intensification (PI). Basically, an intensified process must

* Corresponding author.
E-mail address: eduardo.sanchez@ugto.mx (E. Sánchez-Ramírez).

https://doi.org/10.1016/j.cep.2020.107833
Received 17 July 2019; Received in revised form 21 January 2020; Accepted 22 January 2020
Available online 22 January 2020
0255-2701/

Nomenclature

DWC	Dividing Wall Column
PI	Process Intensification
NHV	Net Heating Value
α	molar ratio CO2/CO
QRA	Quantitative Risk Analysis
HAZOP	Hazard and Operability
BLEVE	Boiling Liquid Expanding Vapor Explosion
UVCE	Unconfined Vapor Cloud Explosion
P_O	Overpressure
Er	Thermal Radiation
LC50	Lethal Concentration
PI	Proportional Integral
K	Gain
IAE	Integral of the absolute error
t_i	Integral Time
L	Reflux Flow Rate
S	Side stream Flow
V	Vapor Boil Up Rate

achieve improvements through (1) the integrations of operations, (2) the integration of functions, and (3) the integration of phenomena [2]. An alternative to improve the performance in Distillation Columns based on PI concepts is the Dividing Wall Column (DWC). The use of DWC has reported a reduction in investment costs by 25 %, operating costs by 35 %, and space requirements by 40 %, as compared to the Conventional Column System [3]. Yildirim et al. [4] reported more than 116 industrial applications for ternary mixtures. Regarding DWC for more than three components, there are many works approaching the synthesis and design of such alternatives. For example, Rong [5] formulated a procedure for a systematic synthesis of DWC columns for such simple conventional schemes. A four-step procedure was formulated which systematically generates all the possible DWC for four components. Similarly, Halvorsen and Skogestad [6] reported the exact analytical solution of minimum energy in a generalized Petlyuk arrangement for separation of N-component feed. Their solution is very simple to visualize in the V_{min} diagram, simply as the highest peak. For quaternary aromatic mixtures, Dejanovic et al. [7] showed a comparison of a properly dimensioned single-partition wall column for obtaining four products with a three-partition wall column. Their simulation studies indicated a strikingly large energy-saving potential compared to the conventional configuration, resulting in a 40.1 % and 48.2 % lower TAC for single- and multiple partition wall DWC, respectively. On the other hand, Ramapriya et al. [8] have presented a very interesting synthesis easy-to-use step-wise procedure to synthesize an initial-dividing wall column (i-DWC) from any given n-component basic distillation column sequence or its thermally coupled derivative.

However, the several applications of DWC for the separation of mixtures with more than three components are still limited. Probably, a reason for the slow acceptance of dividing wall columns is the fear of expected control problems. Recently a notable application of four DWC was published by Preißinger et al. [9]; they reported a simplified four-product DWCs which can be designed with fewer than three partitioning walls resulting in a DWC pilot plant. In their work, Preißinger et al. [9] claim to operate the DWC without energy penalties, however, they did not show dynamic responses after disturbances or setpoint changes. Additionally, also they mentioned that in DWC it is possible to adjust the liquid split by using specially design liquid distributors, but it is still quite difficult to manipulate the gas split.

Yildirim et al. [4] clearly shows that DWCs are not difficult to control if an appropriate control structure is selected. Also, Wolff and Skogestad [10] reported a study of the dynamic properties of Dividing Wall Column for ternary mixtures, and they find that the DWCs possess no control problems. Additionally, Gomez-Castro et al. [11] have shown the dynamic properties of partially coupled quaternary DWC, highlighting the good dynamic behavior of those designs. Nevertheless, again Quaternary DWCs are not well explored and beyond the Control Properties and energy requirements a question remains, does a DWC possess other performance indexes in a framework of a sustainable process?

On the other hand, even the Control Properties of the DWC have reported relative good dynamic behavior, there is yet a concerning issue regarding the Vapor Split. For example, Lukac et al. [12] presented results of a simulation study that could bring some relief in this respect, indicating that a temperature-based control structure, in conjunction with tight control of temperature profiles in prefractionation section, as well as in the product draw regions of the column, is capable of restoring the operation to health from typical disturbances in feed quality and quantity. However, an important assumption they made was fixing the vapor split, or more correctly leaving the vapor splits to be naturally determined by the wall position and the flow resistance of the internals for the most difficult split (Toluene/Heavy HC).

A physical alternative was already introduced by Harvianto et al. [13] in a ternary DWC. In their study in Benit M, they have developed an enhanced active vapor distributor to overcome the existing problems of DWC associated with the vapor split control. In their distributor, the window opening area of the vapor flow path is hydraulically adjusted by changing the liquid level of a modified chimney tray. The adjustment of the liquid level can be done by operating the control valve in each section of DWC. The results showed that the vapor distributor was able to actively adjust the desired vapor split ratio during operation along with the liquid split ratio variations.

In general terms, the problem associated with the Vapor Split is that the Vapor Split ratio is practically pre-determined in the dimensioning stage and it is self-adjusting in such a way that it cannot be used as a manipulated variable. Clearly, the Liquid Split ratio can be manipulated by external devices, or it can even be fixed in the design stage. Thus, the Vapor Split at the bottom of the vertical partition could dynamically change depending on the disturbances and the mechanical resistances in each parallel zone of the Dividing Wall Column. In this manner, operational complications could increase with the number of components to purify the number of Vapor Splits into the corresponding Dividing Wall Columns. Thus, implementations of Dividing Wall Columns must be carefully carried out to avoid operations far from optimal, and hence reduce all those claimed benefits.

Other alternatives to relieve many of these aspects, Ramapriya et al. [14] initially proposed Dividing Wall Column (DWC) designs equivalent to the Fully Thermally Coupled (FTC) configurations. In this study, Ramapriya et al. [14] presented the first proposals of ternary DWC with Liquid Splits that could improve the dynamic performance of DWC for an industrial application. They claim that distillation configurations with liquid transfers between Distillation Columns are easier to operate and control than configurations with vapor transfers between Distillation Columns. Moreover, they proved that any liquid-vapor traffic in the thermally coupled arrangement can be identically duplicated in the liquid-only transfer arrangement. Thus, both arrangements are only topologically different, but thermodynamically equivalent. Additionally, the first signals of the application of Liquid Splits for DWC with more than three components were introduced. As a product of their research work, Ramapriya et al. [8] for a given n-component distillation, they presented a systematic step-wise methodology to synthesize distinct DWCs corresponding to each column sequence in the entire search space of the basic distillation sequences and their thermally coupled derivatives.

The interesting approach of this proposal is that many conventional thermally couplings (Liquid and Vapor Split) can be substituted for a conventional Liquid Split whose implementation may hypothetically improve the dynamic performance of those DWC alternatives.

Additionally, the implications of substituting a conventional Thermal Coupling by a single Liquid Split are unknown; such as dynamic behavior, energy requirements, and other characteristics linked to greenhouse gas emissions and Inherent Safety. All of them are metrics associated with a sustainable process. Apart from adding shareholder value, why else might designer wants to consider using principles of sustainable development as it considers what is green chemistry?. There are several reasons. First, there are risks to the business from unsustainable business practices. These include risks from greenhouse gas emissions taxes (energy, transportation), pollutants and toxic releases (energy, VOCs, various chemical compounds), the shipment of highly hazardous materials (reagents, intermediates, raw materials, solvents. All of them associated with the inherent safety and concerning process control), etc. Second, there is a desire for a competitive advantage. Companies that reduce cost by decreasing mass intensity (the total amount of mass required to produce a unit of product or service, usually on a wt/wt basis) or energy intensity (the total amount of energy required to produce a unit of product or service) will be more profitable [15].

Under this scenario, the need for studies which validate both the design and the performance indexes of those Quaternary DWC with liquid splits in a framework of a sustainable process in order to encourage the industrial acceptance and applications are necessary.

As mentioned, the main interest of this work is to figure out the implication of includes a liquid split in the topology of a quaternary dividing wall column. So, starting from a fully thermally coupled quaternary DWC, and with a relatively simple synthesis work, the liquid split can be introduced in such a way that a conventional thermal coupling is substituted by a liquid split one at the time. As a result of such simple synthesis work, five schemes are obtained, the schemes are presented in Fig. 1(a)–f)).

These schemes are topologically in concordance with those presented by Ramapriya et al. [16]; moreover, the scheme 1e) has been previously proposed as an easy-to-operate scheme. In other words, it is presumable that scheme 1e) may show better dynamic properties than schemes in Fig. 1a)–d).

Since the main interest of this work is to know the implications of including a liquid split in the topology of a quaternary DWC, we believe necessary to evaluate the schemes obtained from the synthesis work previously mentioned. Additionally, it would be also interesting to compare those designs with schemes with no liquid split. For such purpose, we compare with a non-fully thermally coupled design with no liquid splits but that has previously shown relatively good dynamic behavior [11], (Fig. 1f)

With all these considerations, this paper has analyzed both preliminary design and the performance of those new DWCs with two Dividing Walls. The performance indexes considered here are energy requirements, greenhouse gas emissions, dynamic behavior, and Inherent Safety in order to approach this issue in a sustainable framework according to the methodology presented by Jimenez-Gonzalez et al. [1].

As a concern to the DWC column (See Fig. 1), some works have reported difficulty in operating these columns [14,17]. The main reason for this difficulty is that in both zones of the column (prefractionator and main column) the pressure drop in both parallel zones is commonly constrained to be equal. As a consequence of this constraint and of the mechanical resistance in both zones, there is a natural uncontrolled split of vapor ascending from one zone to the other. This uncontrolled split causes the vapor flow in both zones to be complexly manipulated during the process operation. Although reports to keep the Vapor Split under control during the operation are available, there is no report for application during online operation that we are aware of.

In the same way, a related issue associated with poor dynamic properties is Inherent Safety. As mentioned before, if a process is not under control, it may generate waste materials or operate under risky conditions; thus, the approach of those alternatives must be properly evaluated to guarantee many aspects previously mentioned.

2. Methodology

In the next section, a brief methodology will be described. First, the design and evaluation of all separation schemes will be considered. Furthermore, the calculation and development of all performances index will be finally described.

2.1. Design and performance evaluation of quaternary DWC

For design purposes, the schemes were designed by means of Aspen Plus considering the Chao-Seader method to model all the thermodynamic interactions. The Chao-Seader correlation was used for the prediction of thermodynamic properties. This model is usually recommended for petrochemical plants operating at low or medium pressure [18,19]. For a rigorous simulation of the DWC columns, the RadFrac model of AspenPlus™ was used. Although it also exists the

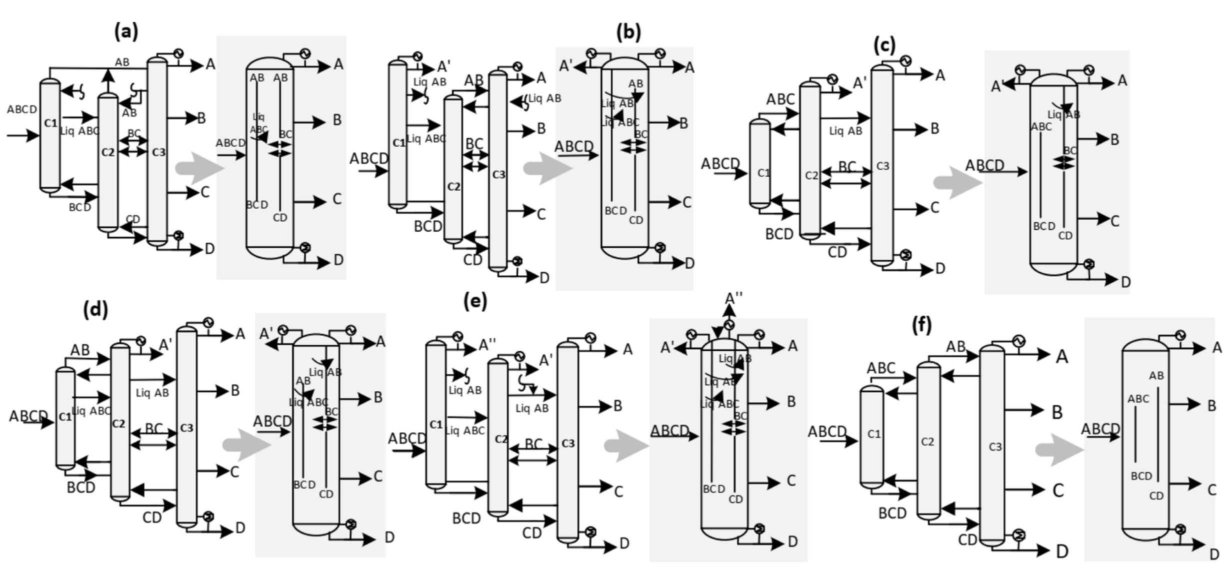

Fig. 1. Quaternary Dividing Wall Column with two walls, used as a case study.

MultiFrac model library that is suitable for solving complex cascade of several columns taken as a single block of columns, as is the case of the DWC columns. Different columns can be interconnected by using connecting streams. MultiFrac model uses these connecting streams as internal variable streams and no extra specification (or extra degree of freedom) is required for the model solution. Despite the above, the DWC column was simulated using rigorous RADFRAC units, this was simulated using a coupled rigorous RadFrac distillation units, the thermodynamic equivalent of DWC. The methodology of the use of rigorous Radfrac units for the assembly of the Petlyuk column is proven by authors such as Kiss et al. [20,21]. The designs were simulated considering a feed stream of light naphtha fraction with standard volatilities among components in the feed stream (see Table 1); the feed stream contains as intermediate components two isomers (2-methyl butane and pentane). The isomers with the closest volatilities make the separation more complex. Additionally, for comparison purposes, a Quaternary Dividing Wall Column was also designed considering only conventional thermal couplings.

Fig. 1 shows the way those Quaternary schemes are designed in Aspen Plus, and their equivalent as Quaternary DWCs. All purities set at 0.99, 0.98, 0.98 and 0.99 % mol for component A–D, respectively, and recovery of at least 98 % in all cases of study.

For modeling and design purposes, the thermodynamically equivalent design of the DWC columns is the Petlyuk columns. For example, to develop a ternary Diving Wall column a set of three conventional columns must be developed as shown in Fig. 2. Note that the initial step is to find a corresponding conventional scheme which will be subject to thermal couplings and column section movement. In the specific case of Quaternaries DWC, a similar procedure is implemented (See Fig. 3). Once the conventional scheme has been obtained with the short-cut methods of Underwood, Fenske, and Gilliland equations. It was possible to obtain the main parameters of conventional Distillation Columns without thermal couplings. Note that the initial design parameter of the short-cut method was adjusted to obtain certain purities and recoveries for the initial conventional distillation scheme without thermal couplings.

Observe that, with the Fenske equation, the minimum number of stages for each column is obtained. Further, the Gilliland equation is then used to estimate the actual number of stages. Thus, once all equations are solved, a preliminary design is obtained (reflux ratio, number of stages, feed location, and so on) for a certain feed, operative pressure and light/heavy key.

Furthermore, taking as an initial point, the model obtained from the commonly named short-cut method (Underwood, Fenske, and Gilliland), the complete set of MESH equations (mass and energy balance, thermodynamic model, restrictions on the sum of compositions) are solved by means of the RADFRAC module in aspen plus.

In Fig. 3, the scheme 3a might be considered as the reference scheme for generating the alternative structures; seven Distillation Columns are utilized for this reference case. The entire mixture is introduced in the first column. In the fourth column, the lightest one is obtained as distillate. And in the seventh column, the heavy components are recovered. It is easy to recognize that the configuration of Fig. 3, from this point on, is possible to generate the subspace of modified thermally coupled sequences by substitution of the heat exchanger/s associated with non-product streams with a liquid-vapor interconnection. For example, Fig. 3b was obtained from the reference scheme by substituting the condenser in the first column with a directional liquid connection. Yet, Fig. 3b is obtained from the reference scheme by substituting the reboilers of both the second and the third column with the thermal coupling. If both the condenser and the reboiler are substituted at the same time, the configuration reported in Fig. 3c is obtained. Note, from the thermally coupled configurations it is possible to generate the corresponding thermodynamic equivalent configurations by moving a column section that provides the common reflux ratio or the vapor boil up between two consecutive columns.

Once the thermal couplings are introduced, many degrees of freedom associated with them resulted. Moreover, in case there is a need for movable column sections, the generation of all of the thermodynamically equivalents schemes are associated with the same thermal coupling before movement and, in consequence, with the same degrees of freedom [22,23].

Many combinations of liquid/vapor in the interconnection flow may accomplish the purity and recovery targets, however, just a few flows may accomplish the same target but with the minimum energy consumption, the real motivation of thermal couplings.

Waltermann [24,25], mentions that the minimum energy demand, which directly relates to the minimum vapor and liquid flow rate, principally depends on the distribution of the intermediate boiling product in the prefractionator that needs to be resolute as design degrees of freedom. Nevertheless, by a study of the Underwood equations, indicate that there is usually not a single optimal distribution of the intermediate boiling product in the prefractionator, but a range of distributions that result in the same minimum energy demand for the thermally coupled configuration. This range is restricted by the preferred split, at which the prefractionator as a simple column would operate at minimum energy demand, and a balanced distribution, at which the vapor and liquid flow rate in the subsequent columns are equal. In this sense, for this work, a parametric procedure is performed to find the minimum energy demand for a fixed column structure with a finite number of stages. The idea is to cover a wide range of liquid and vapor with a relatively simple method; to fix a liquid or vapor value of interconnection flow and to vary the other flow until a local minimum energy demand for such point is found. Then, the next value of liquid or vapor is fixed and varied again, the corresponding interconnection flow until a local minimum energy demand is found again. Note, this loop must be repeated in each thermal coupling/ Liquid Split until each thermal coupling reaches the correct value in order to find the values of the minimum energy demand for a fixed column structure. A graphic explanation for such methodology is shown in Fig. 4. This type of methodology, where the physical topology of complex schemes is fixed has been used to obtain preliminary designs for complex schemes successfully to separate ternary and Quaternary mixtures. With this methodology, many authors have obtained designs with minimum energy requirements compared to their conventional pairs varying both the liquid and vapor flow in the thermal coupling [5,22,26–29].

Once the initial design was obtained, the second task is to figure out if there is an implication for using a liquid split instead of a conventional thermally coupling. For such a task, before the evaluation of the dynamic properties, greenhouse gas emissions, and the Inherent Safety, we evaluated all schemes.

2.2. Sustainable indexes

The importance of considering sustainability issues early in the design of intensified processes can help to differentiate between processes that can be operated with ease and those that are difficult to handle. According to Jiménez-González et al. [1], the incorporation of

Table 1
Feed Characterization.

Temperature [K]			298
Vapor fraction			0
Flow rate [kmol h-1]			100
	Mix II		
	Component	Mole Fraction	Purity at the out stream
A	BUTANE	0.1	0.99
B	2-METHYLBUTANE	0.4	0.98
C	PENTANE	0.4	0.98
D	HEXANE	0.1	0.99

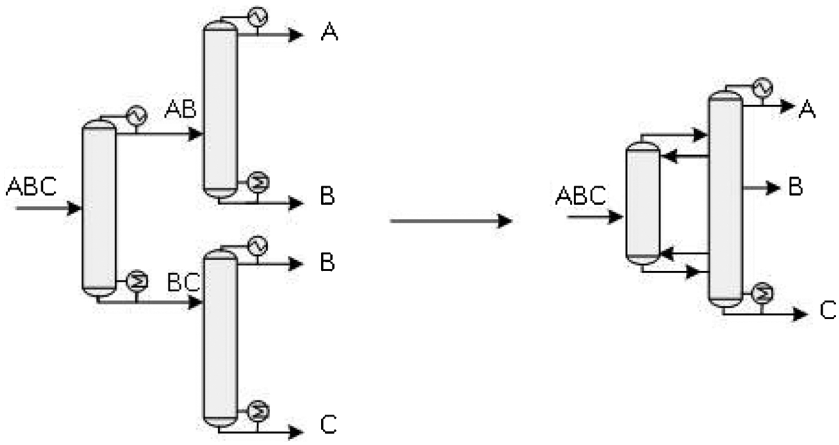

Fig. 2. Design of DWC by means of preliminary conventional Distillation Columns.

"green metrics" when designing an intensified process towards the broader goal of environmental sustainability should be considered. Among those green metrics, the aspects of environmental, safety and process control must be highlighted. Green Chemistry Principle #11 (monitoring a chemical process as it is occurring can help prevent the release of hazardous and polluting substances due to accidents or unexpected reactions. With real-time monitoring, warning signs can be spotted, and the process can be stopped or managed before such an event occurs) expresses a desire to have a real-time process analysis and monitoring in place [1]. The aim of this principle is simple enough—to prevent waste and safety issues by identifying process excursions as they occur. By doing so, there may be sufficient time to modify process parameters such that the excursion may be reversed and that no subsequent impact on safety and/or on the final product quality may occur. Real-time analyses and process controls are necessary to carry out this action. In the same sense, the magnification of processes, associated with the reduction of the number of equipment and change in the topology of the system, can also modify Control Properties and dynamic performances compared to non-intensified systems [2].

2.2.1. Greenhouse-gas emissions

Greenhouse gas emissions were calculated using the methodology previously proposed by Gadalla et al. [30]. By supplying the necessary heat duty of each scheme, an excess of air is used to ensure complete combustion, so that CO emissions are avoided. CO2 emissions are related to the amount of burnt fuel in the reboiler according to:

$$[CO_2]_{emiss} = \left(\frac{Q_{Fuel}}{NHV}\right)\left(\frac{C\%}{100}\right)\propto \tag{1}$$

Where α is equal to 3.67 and represents the molar ratio and CO2 and CO, while NHV (kJ/kg) represents the Net Heating Value of a fuel (methane = 49675 kJ/kg) with a carbon content of C%.

In order to quantify the Inherent Safety of a process, it is possible to evaluate individual security (IR) of the same. IR is defined as the risk a person may be exposed to, considering their physical position in the process plant. Within the calculation of the risk, the damage caused, whether it be injury or death, its frequency and the probability of affectation is considered. The calculation of IR does not depend on the number of people exposed to risk.

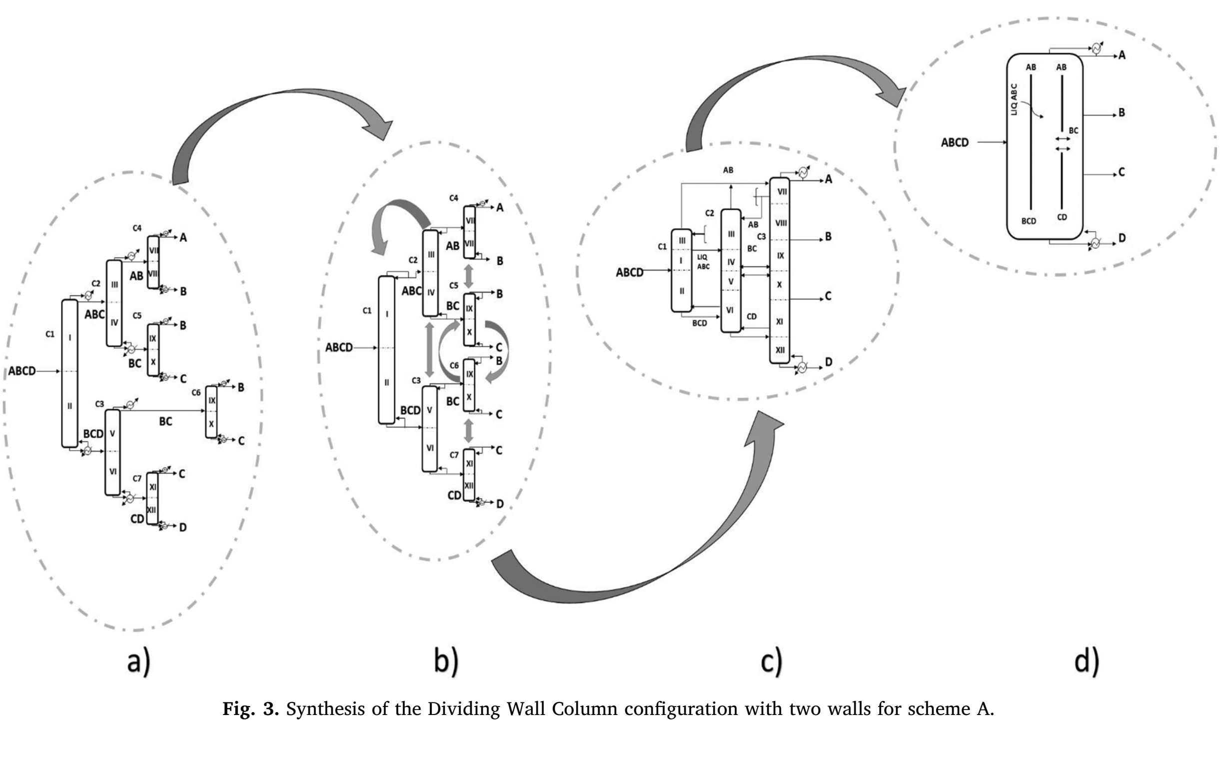

Fig. 3. Synthesis of the Dividing Wall Column configuration with two walls for scheme A.

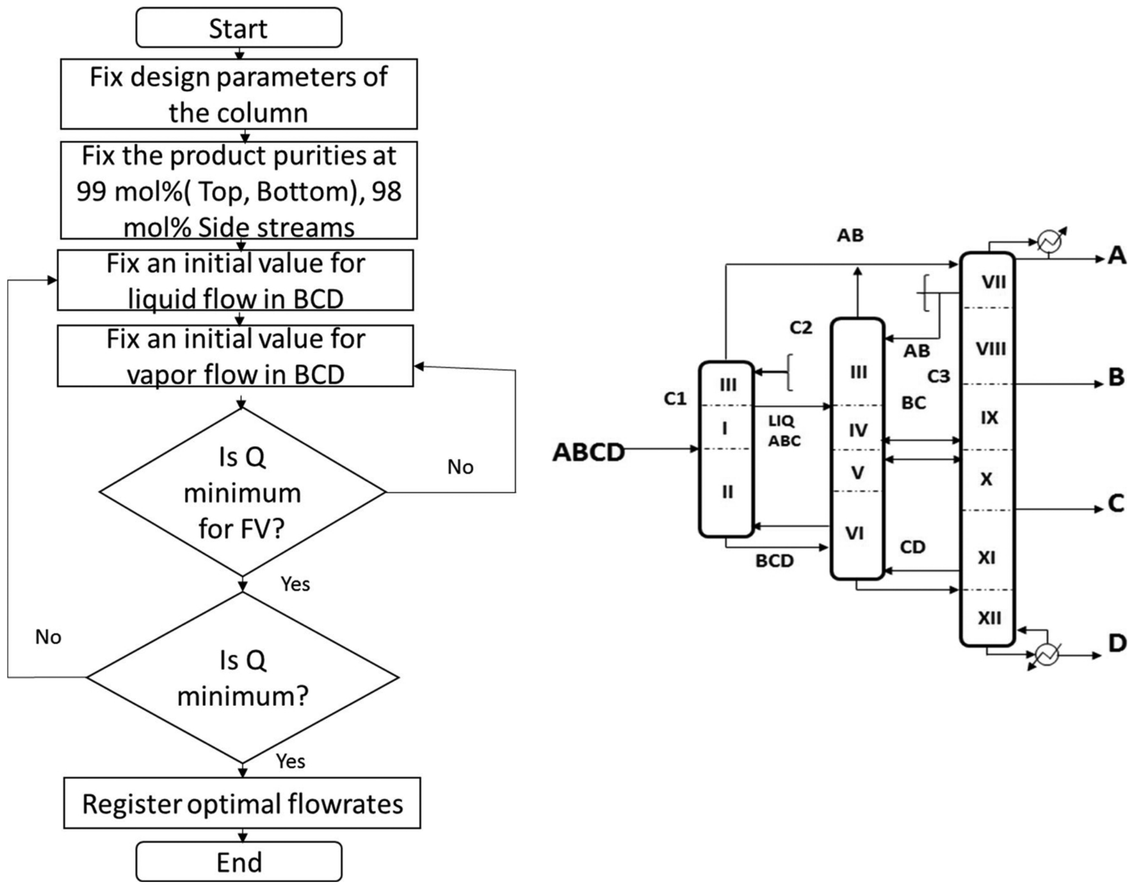

Fig. 4. A representative strategy for obtaining minimum energy requirements of a single thermal coupling.

2.2.2. *Inherent safety*

To model the individual risk, it is necessary to multiply the frequency of an accident (fi) by the probability of affectation in a specific position (P_{xy}) according to Eq. 2

$$IR = \sum f_i P_{x,y} \tag{2}$$

The frequency and probability of involvement can be determined by quantitative analysis (QRA). This methodology allows for the identification of potential accidents and the evaluation of their consequences and damages. Firstly, the QRA analysis identifies possible accidents, which is any release of matter or energy [31]. For Distillation Columns, incidents can be grouped as continuous and/or instantaneous releases. These incidents were previously determined through a risk and operability analysis (HAZOP). Fig. 5 shows a tree of events that includes the possible accidents associated with a Distillation Column as well as their respective frequencies (f_i). Similarly, the frequencies were taken by a previous study of the American Institute of Chemical Engineers [31]. The event tree considers the following possible accidents: Boiling Liquid Expanding Vapor Explosion (BLEVE), Unconfined Vapor Cloud Explosion (UVCE), flash fire, and toxic release. On the other hand, continuous releases, such as jet fire, flash fire, and toxic release.

Once possible accidents have been identified, the causative variables are known as the second step. For example for BLEVE, jet fire and flash fire the causative variable are Thermal Radiation (E_r), for UVCE it is the overpressure (P_o) and for the toxic release is the concentration (C). In this work, a distance of 50 m was considered for all the variables. The calculations of causative variables for each accident have been shown previously by many authors [33,34].

2.2.2.1. *Probability of affectation (Consequences analysis)*.

As a final stage for the calculation of IR, the probability of affectation must be calculated (probability of injury or death). This probability can be obtained with probit models. A probit model relates a person's response to the dose received from a certain incident, such as heat, pressure or radiation. In this work, a probit function was used to model the probability of death due to overpressure and third-degree burns [31,35,36]. The parameters to Eq. 3 are shown in Table 2, *K1* and *K2* are constants, the term $\frac{(t_e E_r^{4/3})}{10^4}$ is in KJ/m^2, and p^o in N/m2. The probability of damage is obtained by replacing probit values in Eq. 4 [36].

$$Y = k_1 + k_2 \ln V \tag{3}$$

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

Finally, the result obtained by Eq. 4 is replaced together with data of LC50, inside the equation Eq. 2 to obtain the individual risk (IR).

2.3. *Dynamic analysis*

In order to evaluate the dynamic behavior of all schemes, all of the schemes were tested under a closed-loop control test in two different scenarios: a setpoint change and a disturbance in the molar flow of the feed stream.

To develop the control strategy, it is necessary to convert the steady-state model to a dynamic one. The model developed in Aspen Plus is exported to Flow-Driven simulation in Aspen Dynamics. Before exporting to Aspen dynamics, the size and the initial specification of each equipment must be identified. For example, in Aspen Plus column dynamics, the reflux drum size has a diameter of 2 ft and the length of 3 ft and the sump is sized with a diameter of 2 ft and height is 3 ft according to sizes reported by Buckley et al. [37]. In column hydraulics, a rigorous

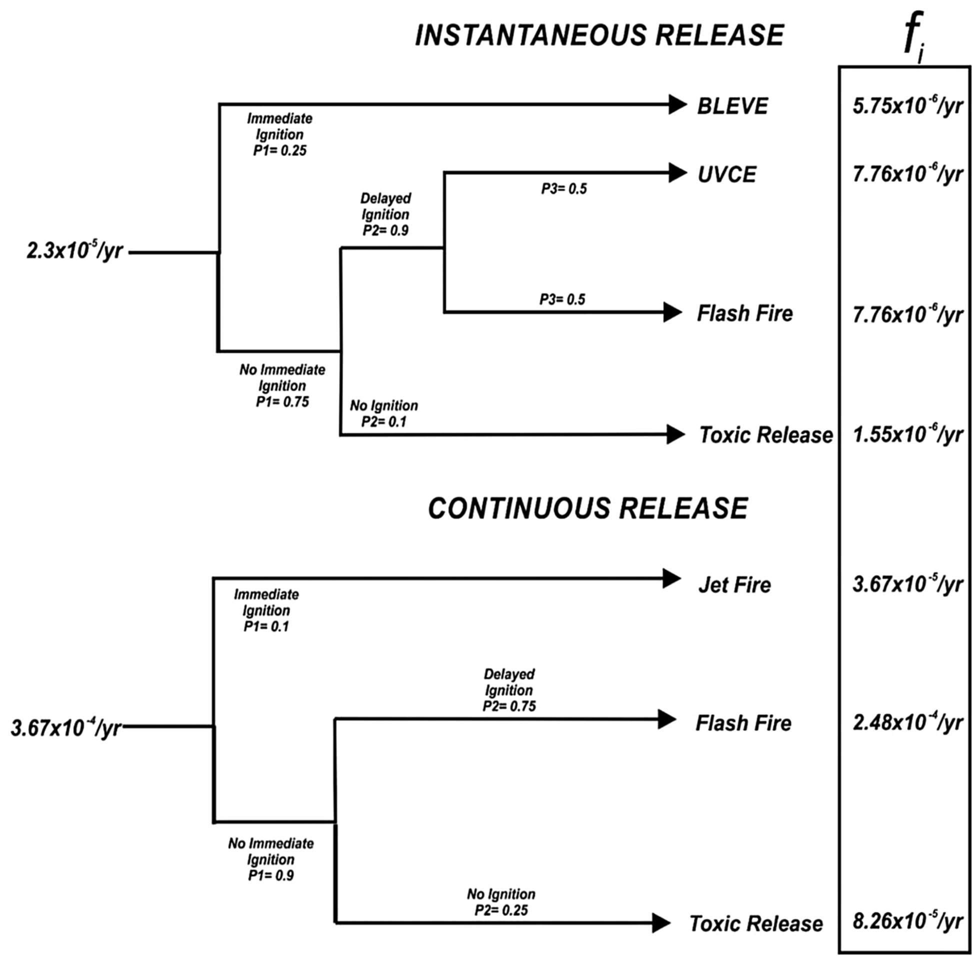

Fig. 5. Events trees diagrams for Distillation Columns [32].

Table 2
Probit Parameters.

	K_1	K_2	V
Thermal Radiation	−14.9	2.56	
Overpressure	−77.1	6.91	p^o

model has been mentioned to complete the geometry of the distillation column.

2.3.1. Closed-Loop analysis

Within Aspen Dynamics simulator the composition control test was performed as follows: (1) a negative step change was induced in the set point for each product composition under single-input and single-output feedback control at each output flow rate and (2) a −0.5 % change in the molar flow of the feed stream for each scheme. For the closed-loop control policy, the analysis considered proportional-integral (PI) controllers. We compared the dynamic performance by using the integral of the absolute error (IAE) criterion [38]. Regarding the manipulated variables of control in the distillate column, bottom and side stream output composition, structures based on energy balance considerations were used. This structure yields the so-called LV control structure. (see for instance Häggblom and Waller [39]). The control loops for the integrated systems were chosen from extensions of the practical considerations observed for conventional Distillation Columns. The control objective was to preserve the output streams at their design purity specifications. This control structure uses the reflux flow rate L, vapor boil up rate V and side stream flow S as the manipulated variables respectively. All control loops arise naturally from the experience of the operation of conventional columns. For the control of the product stream as an overhead product, the reflux flowrate was used, whereas for the control of the product stream is obtained as a bottom product the reboiler heat duty was chosen. When the product stream is obtained as a side stream, its control was simply set through the manipulation of the side-stream flow rate. It should be mentioned that such control loops have been used with satisfactory results in previous studies with complex systems [40–43]. A representative scheme of the control structure used in this work is shown in Fig. 6.

To tune-up each controller, an initial value of proportional gain was set, and a range of integral reset time was tested with a fixed value until a local optimum in the IAE value was obtained. This methodology was repeated with other proportional gain values until a minimum in the IAE value was detected. This procedure was performed considering one control loop at a time until all control loops were considered.

3. Results

3.1. Design and performance of quaternary DWC

The complete set of designs presented in Fig. 1a)–e) with Liquid Splits, and Fig. 1f) the conventional scheme, were developed in Aspen Plus. As mentioned, before any evaluations, it was necessary to guarantee minimum energy of all designs in order to make a fair comparison among schemes (all designs working with the minimum energy requirements). Halvorsen and Skogestad [6] showed that the properties determining minimum energy in each sub-column can be found from the previous column. This practically means that regardless of the

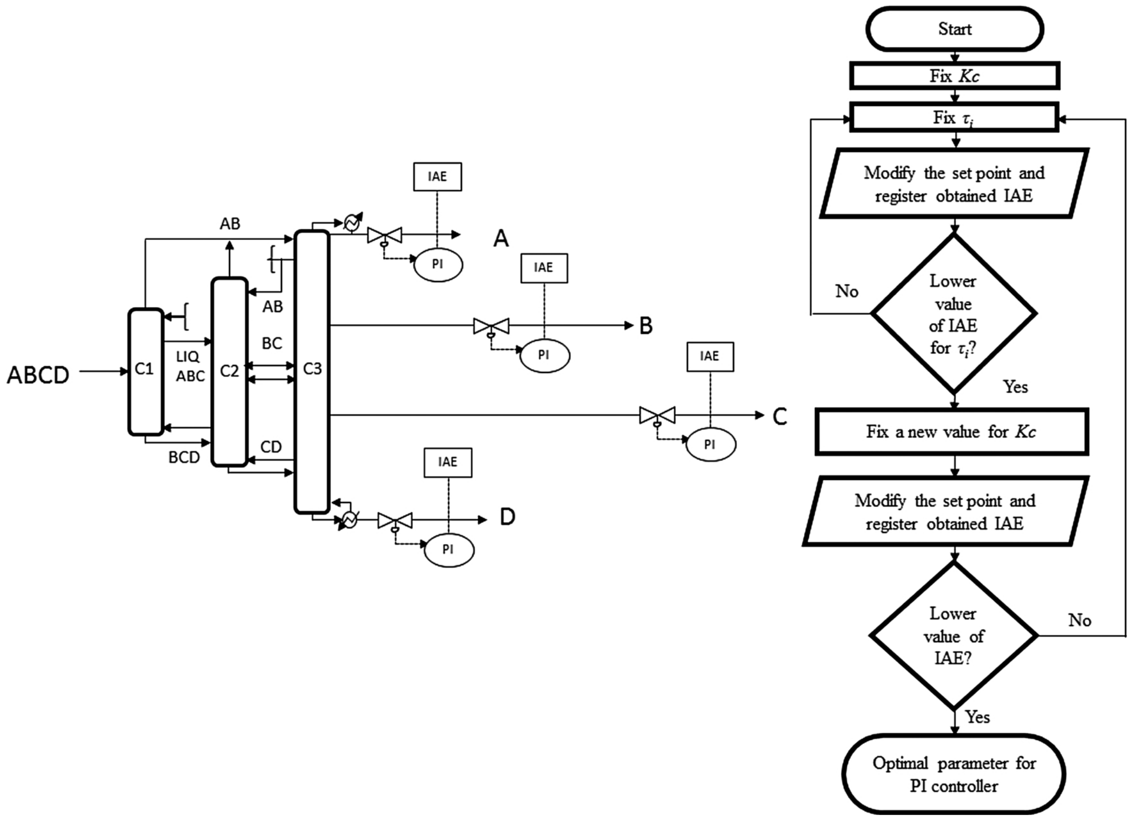

Fig. 6. Tuning methodology for PI controllers with minimization of IAE criteria.

complexity of a situation, the V_{min} diagram containing all necessary information can be constructed based on feed data only. Also, Hernández and Jiménez [44] have proposed a strategy to minimize energy consumption in Petlyuk type columns by finding the optimal values of interconnection flows between the columns. They have shown that energy consumption of arrangement is directly associated with the variation of interconnection flows. This strategy can be considered as a way of posing an optimization problem by minimizing energy consumption (objective function) by varying the value of interconnection flows (degrees of freedom). Using the strategy proposed by Hernández and Jiménez [44], Fig. 7 shows the common behavior obtained in the minimization of the energy requirements process until the scheme reaches its minimum heat duty value. The resulted designs are reported are in Tables 3–8. A point must be highlighted, given that all extended configurations in Fig. 1 represent modifications of the fully thermally coupled DWC there is effectively no need for Vmin diagram. However, it should be pointed out that besides the possibility to analyze the minimum vapor load, the Vmin diagram also enables the identification of the limiting split, which is not possible from the depicted optimization results in Fig. 7, such that there is no direct exchangeability between these diagrams. However, the strategy proposed by Hernández and Jimenez [44] has been widely used to minimize energy consumption as a function of interconnection flows in the design of various thermally coupled distillation column [26,45,46]

In Tables 3–8, note that practically all schemes with Liquid Split and conventional thermally coupling consumed relatively the same amount of energy for the same kind of separation. This behavior allows us to know that all schemes can perform the same purification task with relatively the same efficiency. In other words, all schemes are thermodynamically equivalent.

3.2. Greenhouse gas emissions and inherent safety

In distillation systems, carbon dioxide is generated mainly from furnaces, gas turbines, and boilers. Fuel is burnt when mixed with air, producing CO_2 duty. According to Gadalla et al. [30], carbon dioxide emissions are a direct function of the reboiler duty. In this way, it is not a big surprise that Table 9 shows similar values of CO_2 emissions. Because thermodynamically equivalent designs consume the same reboiler duty, similar values in carbon dioxide emissions are calculated. Nevertheless, although all schemes perform the same separation task with relatively the same energy it does not mean that the thermal couplings are designed with the same amount of liquid and vapor. A

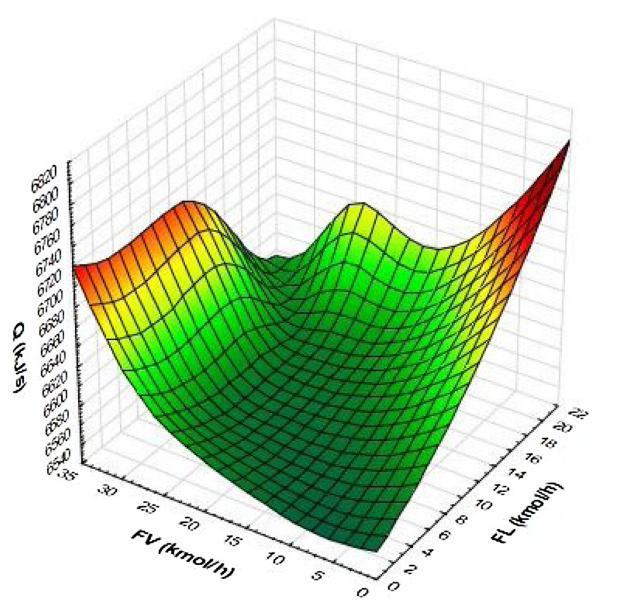

Fig. 7. Heat duty tendency evaluated at different values of liquid and Vapor Splits in a thermal coupling for Fig. 1f).

Table 3
Design parameters for scheme A.

	Pre-Frac II	Pre-Frac I	Main Column
Number of stages	35	42	118
Feed stage	1, 6, 35	1, 7, 16, 32, 42	11, 55, 55, 73
Top Temperature [K]	349.52	351.54	320.45
Bottom Temperature [K]	355.22	365.87	405.06
Top Pressure [kPa]	367.11	471.23	436.65
Bottom Pressure [kPa]	371.32	540.45	574.7
Reflux rate [kmol h^{-1}]	N/A	N/A	1265.12
Reboiler duty [kJ]	N/A	N/A	6562.31
Product stage	1, 6, 35	1, 13, 31, 42	1, 10, 13, 13, 20, 72, 101, 118
ABC liquid flow [Kmol h-1]	12.006	AB vapor/liquid flow [Kmol h-1]	48.9867/13
BCD vapor/liquid flow [Kmol h-1]	44/93.4133	BC vapor/liquid flow [Kmol h-1]	22/73
CD vapor/liquid flow [Kmol h-1]	80/118.225		

Table 4
Design parameters for scheme B.

	Pre-Frac II	Pre-Frac I	Main Column
Number of stages	10	42	118
Feed stage	9, 10	1, 7, 10, 32, 42	4, 5, 11, 72
Top Temperature [K]	314.09	347.2	320.45
Bottom Temperature [K]	348.78	370.33	404.45
Top Pressure [kPa]	367.11	471.23	437.21
Bottom Pressure [kPa]	436.22	540.54	574.35
Reflux rate [kmol h-1]	56.09	N/A	1213.95
Reboiler duty [kJ]	N/A	N/A	6516.92
Product stage	1, 2, 3, 10	1, 13, 42, 31	1, 3, 10, 20, 72, 101, 118
AB liquid flow [Kmol h-1]	1.3	ABC liquid flow [Kmol h-1]	2.89
BCD vapor/liquid flow [Kmol h-1]	27/126.159	BC vapor/liquid flow [Kmol h-1]	31/2
AB vapor/liquid flow [Kmol h-1]	74.9252/55	CD vapor/liquid flow [Kmol h-1]	85/118.225

Table 5
Design parameters for scheme C.

	Pre-Frac II	Pre-Frac I	Main Column
Number of stages	10	42	118
Feed stage	1, 9, 16	3, 12, 22, 30	3, 15, 27
Top Temperature [K]	339.53	323.353	320.46
Bottom Temperature [K]	34.04	364.285	404.938
Top Pressure [kPa]	669.76	640.37	640.37
Bottom Pressure [kPa]	675.84	654.56	655.57
Reflux rate [kmol h^{-1}]	N/A	217.63	77.54
Reboiler duty [kJ]	N/A	N/A	6514.12
Product stage	1, 16	1, 3, 7, 12, 12, 30	1, 7, 15, 23, 27, 41
ABC vapor/liquid flow [Kmol h-1]	31.439/25	BC vapor/liquid flow [Kmol h-1]	31/17
BCD vapor/liquid flow [Kmol h-1]	25/118.561	CD vapor/liquid flow [Kmol h-1]	85/176.318
AB liquid flow [Kmol h-1]	20.021		

representative example of such behavior is Fig. 7. The 3D plane is a representation of all values of liquid/vapor that satisfy the recovery and purity constraints, however, note that not all of them guarantee the minimum energy requirement, and many values of liquid and vapor are in the zone of minimum energy.

Also, Table 9 shows the difference of all schemes regarding Inherent Safety, all schemes designed with a Liquid Split are safer than the scheme designed only with conventional thermal couplings.

Even reboiler heat duty represents a great contribution to the Inherent Safety, there are much more variables included in their calculations. For example, the operative pressure is a design variable that also contributes to the IR value; however, considering that all schemes are previously designed with the same pressure, there is no difference in pressure contribution.

Considering Tables 3–8, the main differences among all schemes is the association with the amount of liquid and vapor in the conventional thermal couplings and the Liquid Split on the new alternatives. Those differences promote the small differences regarding IR. The explanation is relatively simple; an operative condition associated with the Inherent Safety is the amount of material inside the column. With this in mind, both the conventional thermal coupling and Liquid Split are the variables responsible for the transportation of material in the column; therefore, the presence of material in each column section and the combination of all factors contributed directly to the difference of IR values. It is important to highlight that if only the energy consumption is analyzed as a criterion for choosing the best configuration, without considering the rest of the criteria (carbon dioxide and inherent safety) an incomplete view of the configuration is reached and the designer does not would know which process is the most sustainable. Since these additional criteria are necessary and indispensable for the election of a "green process".

3.3. Closed-loop analysis

The results of the individual closed-loop test are shown in Figs. 8 and 9. Note, all figures regarding the step change in the setpoint.

When the control loop is applied to adjust the dynamic response of butane, obtained at the top, all schemes showed a good dynamic behavior since the new purity is reached near 0.1 h. Even scheme B took a long time in comparison with the other schemes to reach the new setpoint; this time is not really considerable. In the same way, the second stream to purify butane in scheme E named as E', showed many oscillations, however, that stream reached the new set point in a relatively low time. Regarding the conventional scheme, only scheme B showed a worse dynamic behavior, on the other hand, all new schemes overcame the conventional scheme. For the numerical purpose, Table 10 shows the IAE values for such comparison. Note that A, A' and A'' refer to the multiple streams where component A is obtained (See Fig. 1).

Moreover, when 2-methyl butane is obtained in a side stream, the schemes E and D showed the lowest IAE values and settling times despite all loops oscillating quite considerably before they reach the new setpoint, the conventional scheme is the worst of all schemes. Regarding the pentane loop, both A and B showed the lowest IAE values and both are of the same magnitude order. Diversely, the conventional scheme exhibited a worse scenario.

Finally, when the purity of hexane is controlled at the bottom of the column, all loops reach the new purity in little time; however, both B and C showed the lowest IAE values.

Regarding the second closed-loop analysis, Fig. 9 shows the dynamic response of these control tests. For butane, in general terms, scheme B shows the smallest settling time. Moreover, Table 11 confirms the *IAE* values for this component in all schemes. Furthermore, when the purity of 2-methyl butane is controlled, scheme E shows the lowest settling time as well in comparison with other schemes. When pentane purity is controlled, scheme E showed better IAE values in comparison with other schemes. Finally, regarding the purity of hexane, both schemes B and E reached the set point in little time, and its IAE values were the lowest.

Finally, Fig. 10 shows both the composition and the temperature profile of scheme A and E from Fig. 1. The composition and temperature profiles in the schemes shown are practically the same. Specifically, the temperature profiles of each scheme have the same behavior; this is because the schemes respect the same design specifications as is the number of stages, as well as the A and E schemes are very similar to each other. The composition profiles of schemes A and E are also

Table 6
Design parameters for scheme D.

	Pre-Frac II	Pre-Frac I	Main Column
Number of stages	10	42	118
Feed stage	1, 6, 10	4, 7, 11, 32, 42, 42	4, 11, 73
Top Temperature [K]	334.898	323.357	320.459
Bottom Temperature [K]	347.898	361.031	405.689
Top Pressure [kPa]	669.76	640.37	640.37
Bottom Pressure [kPa]	675.84	655.57	654.56
Reflux rate [kmol h^{-1}]	N/A	241.9	69.65
Reboiler duty [kJ]	N/A	N/A	6504.98
Product stage	1, 4, 10	1, 9, 12, 13, 31, 42	1, 10, 20, 72, 101,118
AB vapor/liquid flow [Kmol h-1]	14.4551/10	AB liquid flow [Kmol h-1]	3.001
ABC liquid flow [Kmol h-1]	3.002	BC vapor/liquid flow [Kmol h-1]	31/5
BCD vapor/liquid flow [Kmol h-1]	10/102.545	CD vapor/liquid flow [Kmol h-1]	95/216.533

Table 7
Design parameters for scheme E.

	Pre-Frac II	Pre-Frac I	Main Column
Number of stages	10	42	118
Feed stage	6, 10	4, 7, 42, 32	4, 4, 11, 73
Top Temperature [K]	273.639	310.274	320.46
Bottom Temperature [K]	308.561	351.11	404.894
Top Pressure [kPa]	669.76	640.37	640.37
Bottom Pressure [kPa]	678.88	654.56	654.56
Reflux rate [kmol h^{-1}]	46.48	133.86	70.99
Reboiler duty [kJ]	N/A	N/A	6548.27
Product stage	1, 2, 7, 10	1, 9, 13, 42, 31	1, 10,20, 72, 101, 118
AB liquid flow [Kmol h-1]	1.02	AB liquid flow [Kmol h-1]	5.03
ABC liquid flow [Kmol h-1]	5.01	BC vapor/liquid flow [Kmol h-1]	10/4
BCD vapor/liquid flow [Kmol h-1]	100/ 192.171	CD vapor/liquid flow [Kmol h-1]	168/264.83

Table 8
Design parameters for conventional scheme F.

	Pre-Frac II	Pre-Frac I	Main Column
Number of stages	10	42	118
Feed stage	6, 10	1, 11, 32, 42	11, 73
Top Temperature [K]	360.215	353.918	320.46
Bottom Temperature [K]	361.604	365.263	404.65
Top Pressure [kPa]	669.76	640.37	640.37
Bottom Pressure [kPa]	678.88	654.56	654.56
Reflux rate [kmol h^{-1}]	6.81724	29.9451	2322.79
Reboiler duty [kJ]	N/A	N/A	6510.39
Product stage	1, 10	1, 12, 31, 42	1, 12, 20, 72, 97, 118
AB vapor/liquid flow [Kmol h-1]	95.8624/7	CD vapor/liquid flow [Kmol h-1]	118.989/45
ABC vapor/liquid flow [Kmol h-1]	127.958/ 139.095	BC vapor/liquid flow [Kmol h-1]	155/180.969

Table 9
CO_2 emissions and Inherent Safety.

Scheme	Reboiler Heat Duty (kJ/s)	CO2 emissions (ton/h)	IR (Probability/y)
A	6562.31	32.775	2.7431E-04
B	6516.92	32.548	2.7351E-04
C	6514.12	32.534	2.7502E-04
D	6504.98	32.488	2.6747E-04
E	6548.27	32.705	2.6029E-04
Conventional or F	6510.39	32.515	2.7605E-04

similar, but with a small variation in the intermediate components around stage 72. This variation is caused by the amount of vapor and liquid [kmol/h] entered into the schemes distillation in the interconnection flow BC. In scheme E they are 7 times more vapor than in scheme A, and 2.5 more liquid than in scheme A; therefore, there is a small alteration in the profiles due to the high feeding in the interconnection flow BC, which is normalized in the distillation column. As a preliminary conclusion regarding the first control test, it is clear that these kinds of Quaternary schemes are able to control the purity of our interest compounds. Some loops showed a better dynamic behavior, in other words, it was easier to control the purity of those components obtained as a bottom product. In addition, all top products were relatively easy to control, but not as easy as bottoms product were. Variously, the purity of the products obtained in a side stream was relatively more difficult to control after the step change.

Regarding the dynamic behavior of the new and the conventional schemes, for setpoint changes, all new thermally coupling schemes, as well as conventional schemes, show the ability to absorb the disturbances made at set point. In a different way, for feed disturbances, the conventional scheme only showed better results than the new schemes when the two most volatile components were analyzed.

In general terms, scheme E was the best conditioned to handle both disturbances. Note in Fig. 1, the main physical difference lays in the fact that scheme E is designed with more substitution of Liquid Splits than the rest of new schemes; in the same way, the vapor associated in each LV thermally coupling in scheme E is the highest in comparison with all the conventional thermally couplings of all schemes. Additionally, scheme E perform the purification of the lightest component in three different streams at the top of the column.

Finally, according to all reported results, it was possible to observe the trend and implication of designing this kind of complex schemes with a Liquid Split instead of the traditional thermal coupling. It was clear that the design with a bigger number of Liquid Splits is thermodynamic equivalent to those with fewer Liquid Splits and even with that of only conventional thermal couplings, as a result, there is no more energy demand for such topology. Otherwise, Liquid Split shows its advantages in dynamic behavior and the Inherent Safety. Initially, scheme E showed the lowest value regarding IR; this behavior is totally consistent with the dynamic results. A well-controlled process will produce less waste material or reprocessed material, and produce a good quality product; in the same way, the operative condition of the process would be under certain conditions which evidently avoids risky conditions with fatal consequences. Hence, there is a direct correlation of using Liquid Splits, improving both the dynamic behavior and the Inherent Safety, but without more energy demand and consequently no environmental penalties.

In summary, our studies generally indicate that mass and energy (associated with energy consumption, carbon dioxide emissions, inherent safety, and dynamic performance) appear to be good leading indicators of overall environmental impact. In the short term, rigorous management of those criteria results in the greatest improvements to making processes 'greener.' A point to highlight in this case study is that the consideration of any of these criteria of sustainability effectively no results in a different conclusion if only an exclusive analysis of energy consumption is performed, but a priori this conclusion is not necessarily obvious. In general, the evaluation of arrangements using a sustainability metrics framework clearly differentiates between several configurations doing the same operation.

4. Conclusions

In this work, several Quaternary DWC were tested with several performance indexes in a framework of a sustainable process. The novelty of those DWC lays in the substitution of any conventional thermally coupling by a single liquid stream. After the design and minimization of energy requirements, all schemes, new and conventional,

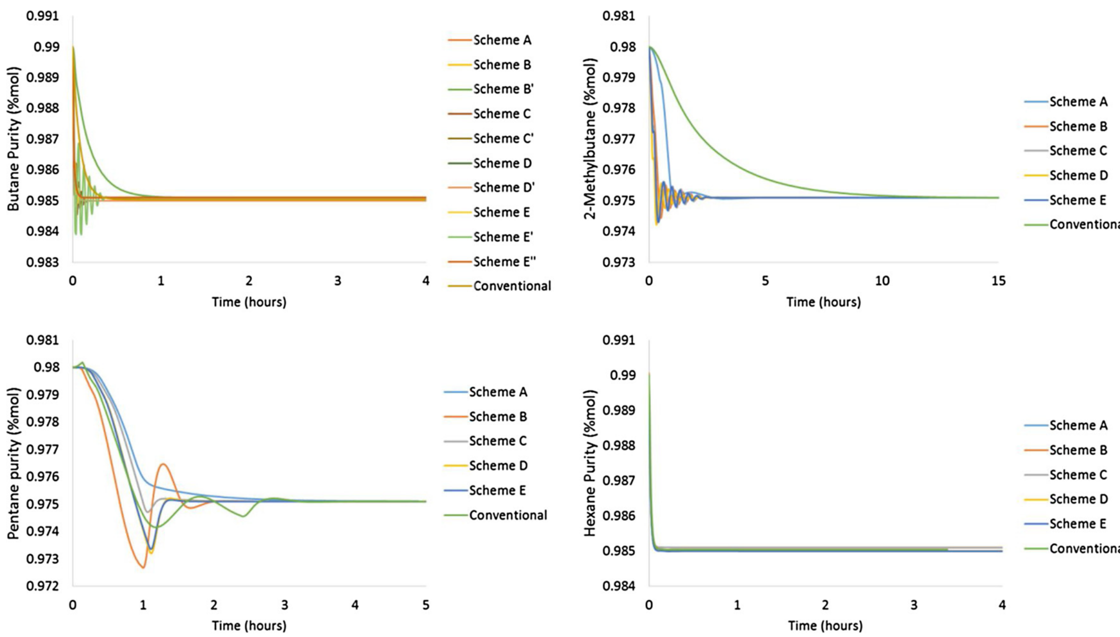

Fig. 8. Dynamic responses changing the purity set point.

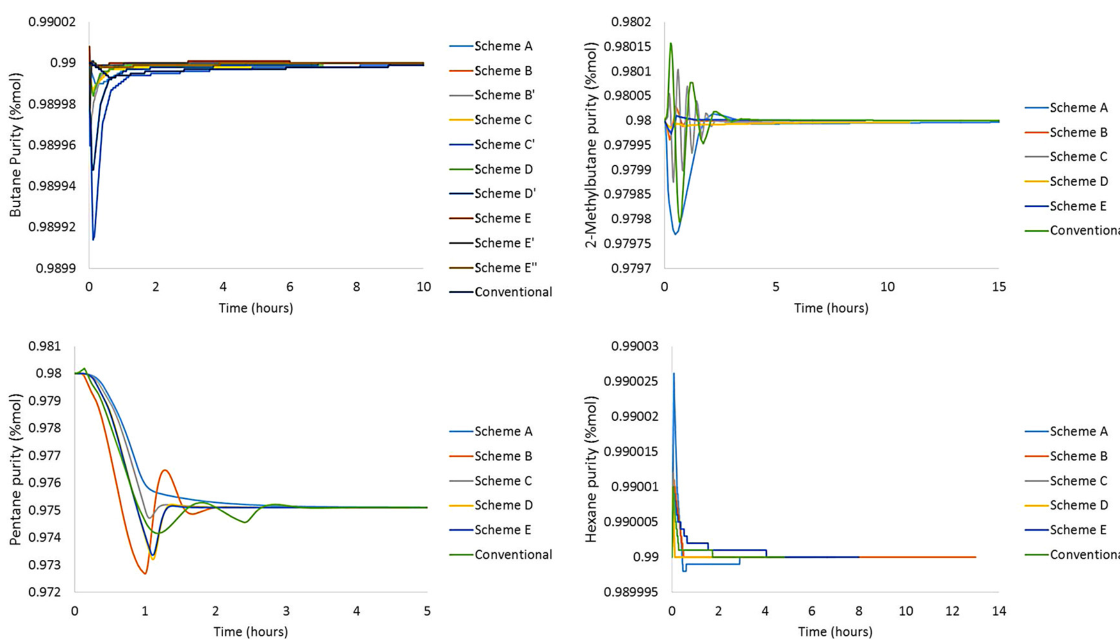

Fig. 9. Dynamic responses changing the molar flow rate of the feed stream.

Table 10
IAE values for set point change.

	Component A			Component B			Component C			Component D			Component A'			Component A"		
	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]
Scheme A	250	1	7.90E-05	250	40	3.43E-03	250	50	4.10E-03	250	1	8.05E-05	–	–	–	–	–	–
Scheme B	250	1	7.90E-05	250	1	1.40E-03	250	10	3.22E-03	250	1	8.00E-05	–	–	–	250	10	8.29E-04
Scheme C	250	1	8.06E-05	250	1	1.28E-03	250	40	3.36E-03	240	1	7.96E-05	250	1	1.01E-04	–	–	–
Scheme D	250	1	8.09E-05	250	1	8.96E-04	250	30	3.34E-03	250	1	8.11E-05	250	1	8.03E-05	–	–	–
Scheme E	250	1	7.90E-05	250	1	1.19E-03	250	30	3.27E-03	250	1	8.12E-05	250	1	2.44E-04	250	1	8.40E-05
Conventional	250	5	4.11E-04	250	150	1.23E-02	250	10	3.39E-03	250	1	1.16E-04						

Table 11
IAE values for disturbance in molar flow in the feed stream.

	Component A			Component B			Component C			Component D			Component A'			Component A"		
	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]	K [% mol/ % mol]	Ti [min]	IAE [-]
Scheme A	240	20	3.09E-06	250	40	2.61E-04	250	50	8.00E-04	250	10	4.30E-06	–	–	–	–	–	
Scheme B	250	20	1.42E-06	250	1	1.66E-05	250	10	1.05E-04	250	10	1.60E-06	250	10	7.508E-06	–	–	
Scheme C	250	10	5.21E-06	250	1	8.38E-05	250	40	6.16E-04	240	1	2.45E-06	250	10	3.48E-05	–	–	
Scheme D	250	10	6.19E-06	250	1	8.42E-06	250	30	4.29E-04	250	1	1.15E-06	250	10	2.43E-05	–	–	
Scheme E	250	10	9.79E-07	250	1	1.31E-05	250	30	1.81E-04	210	40	4.44E-06	250	1	1.48E-06	250	10	8.30E-07
Conventional	250	5	1.41E-06	250	5	1.54E-04	250	10	1.27E-03	250	5	1.04E-05	–	–	–			

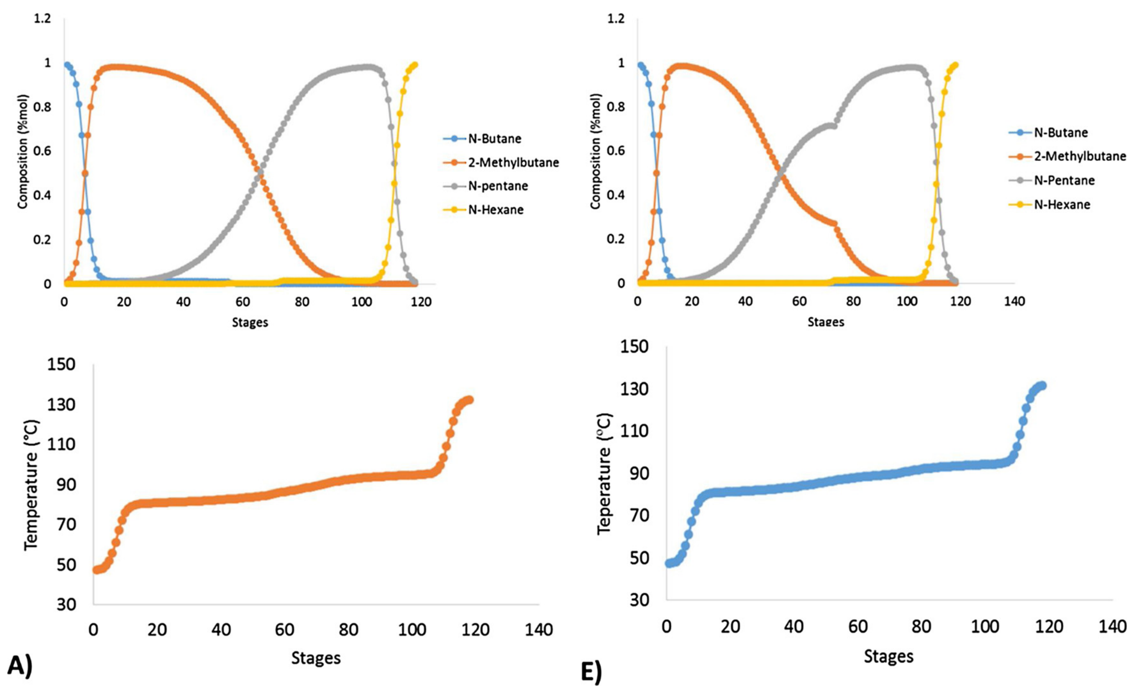

Fig. 10. Temperature and composition profile of schemes A and E.

resulted as thermodynamic equivalents.

As dynamic results, scheme E resulted as the most promissory designs since its *IAE* were relatively better than the other schemes; additionally, its performance indexes were superior to the other schemes. The improvement in dynamic behavior lays in the fact that scheme E was designed with more Liquid Splits than the other schemes.

Additionally, a remarkable difference among schemes is that butane is obtained in several streams. However, in the schemes that include a conventional thermal coupling (steam/liquid), it was observed that the greater the amount of steam in the thermal coupling, the dynamic performance improves. For the liquid split, an opposite behavior was observed. In general terms, the substitution of conventional thermally coupled by a single liquid stream also improves the Control Properties; additionally, a correlation of the Inherent Safety with the dynamic behavior was found; as long as dynamic behavior improves, the Inherent Safety improves as well. Therefore, in a framework of sustainable processes, scheme E accomplishes with all those metrics and relations that Jimenez-González et al. [1] claims as a sustainable process: a low energy demand process, a well-controlled process, with low CO_2 emissions are inherently safe.

Additionally, and to summarize, this kind of study approach of Quaternary DWC and the validation of relatively good dynamic behavior promotes its acceptance and furthers its future application in industry, as well as the application of Liquid Split for current green policy could also be also supported.

Author statement

All the authors of this paper collaborated in an equitable manner in all areas for the development of this work (Writing, Investigation, Methodology, etc).

Declaration of Competing Interest

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

Acknowledgments

Financial support provided by the Universidad de Guanajuato and CONACyT (México) is gratefully acknowledged.

References

[1] C. Jiménez-González, D.J.C. Constable, C.S. Ponder, Evaluating the "greenness" of chemical processes and products in the pharmaceutical industry – a green metrics primer, Chem. Soc. Rev. 41 (2012) 1485–1498, https://doi.org/10.1039/c1cs15215g.
[2] J.M. Ponce-Ortega, M.M. Al-Thubaiti, M.M. El-Halwagi, Process intensification: new understanding and systematic approach, Chem. Eng. Process. Process Intensif. 53 (2012) 63–75, https://doi.org/10.1016/j.cep.2011.12.010.
[3] M.A. Schultz, D.G. Stewart, J.M. Harris, S.P. Rosenblum, M.S. Shakur, D. O'Brien, Reduce Costs with Dividing Wall Columns, CEP Mag. (2002).
[4] Ö. Yildirim, A.A. Kiss, E.Y. Kenig, Dividing wall columns in chemical process industry: a review on current activities, Sep. Purif. Technol. 80 (2011) 403–417, https://doi.org/10.1016/j.seppur.2011.05.009.
[5] B. Rong, Synthesis of dividing-wall columns (DWC) for multicomponent distillations — a systematic approach, Chem. Eng. Res. Des. 89 (2011) 1281–1294, https://doi.org/10.1016/j.cherd.2011.03.014.
[6] I.J. Halvorsen, S. Skogestad, Minimum energy consumption in multicomponent distillation. 3. More than three products and generalized petlyuk arrangements, Ind. Eng. Chem. Res. 42 (2003) 616–629, https://doi.org/10.1021/ie0108651.
[7] I. Dejanovic, L. Matijasevic, I.J. Halvorsen, S. Skogestad, H. Jansen, B. Kaibel, Z. Olujic, Designing four-product dividing wall columns for separation of a multicomponent aromatics mixture, Chem. Eng. Res. Des. 9 (2011) 1155–1167, https://doi.org/10.1016/j.cherd.2011.01.016.
[8] G.M. Ramapriya, M. Tawarmalani, R. Agrawal, A systematic method to synthesize all dividing wall columns for n -component separation — part I, AIChe 64 (2018) 649–659, https://doi.org/10.1002/aic.15964.
[9] U. Preißinger, L. Ränger, T. Grützner, Design considerations of a simplified multiple dividing wall column pilot plant, Chemengineering 3 (2019) 1–17, https://doi.org/10.3390/chemengineering3020034.
[10] E.A. Wolff, S. Skogestad, Operation of integrated three-product (petlyuk) distillation columns, Ind. Eng. Chem. Res. (1995) 2094–2103, https://doi.org/10.1021/ie00045a018.
[11] F.I. Gómez-Castro, J.G. Segovia–Hernández, S. Hernández, C. Gutiérrez-Antonio, A. Briones-Ramírez, Dividing wall distillation columns: optimization and control properties, Chem. Eng. Technol. (2008) 1246–1260, https://doi.org/10.1002/ceat.200800116.
[12] G. Lukac, I.J. Halvorsen, Z. Olujic, I. Dejanovic, On controllability of a fully thermally coupled four-product dividing wall column, Chem. Eng. Res. Des. 7 (2019) 367–377, https://doi.org/10.1016/j.cherd.2019.04.041.
[13] G.R. Harvianto, K. Kim, K. Kang, M. Lee, Optimal operation of dividing wall column using enhanced active vapor distributor, Chem. Eng. Res. Des. 69 (2018) 512–519, https://doi.org/10.1016/j.cherd.2019.02.038.
[14] G.M. Ramapriya, M. Tawarmalani, R. Agrawal, Thermal coupling links to liquid-only transfer streams: a path for new dividing wall columns, AIChE J. 60 (2014) 2949–2961, https://doi.org/10.1002/aic.
[15] A.D. Curzons, D.J.C. Constable, D.N. Mortimer, V.L. Cunningham, So you think your process is green, how do you know? - Using principles of sustainability to determine what is green – a corporate perspective, Green Chem. 3 (2001) 1–6, https://doi.org/10.1039/b007871i.
[16] G.M. Ramapriya, M. Tawarmalani, R. Agrawal, Thermal coupling links to liquid-only transfer streams: an enumeration method for new FTC dividing wall columns, AIChE J. 62 (2016) 1200–1211, https://doi.org/10.1002/aic.
[17] F. Lestak, C. Collins, Advanced distillation saves energy & capital, Chem. Eng. 104 (1997) 72–76.
[18] A. Technology, Aspen Plus User Guide, (2000), https://doi.org/10.1007/BF00447266.
[19] M. Errico, G. Tola, M. Mascia, Energy saving in a crude distillation unit by a preflash implementation, Appl. Therm. Eng. 29 (2009) 1642–1647, https://doi.org/10.1016/j.applthermaleng.2008.07.011.
[20] R.M. Ignat, A.A. Kiss, Optimal design, dynamics and control of a reactive DWC for biodiesel production, Chem. Eng. Res. Des. 91 (2013) 1760–1767, https://doi.org/10.1016/j.cherd.2013.02.009.
[21] A.A. Kiss, Novel applications of dividing-wall column technology to biofuel production processes, J. Chem. Technol. Biotechnol. 88 (2013) 1387–1404, https://doi.org/10.1002/jctb.4108.
[22] B. Rong, A. Kraslawski, I. Turunen, Synthesis and optimal design of thermodynamically equivalent thermally coupled distillation systems, Ind. Eng. Chem. Res. 43 (2004) 5904–5915, https://doi.org/10.1021/ie0341193.
[23] S. Hernández, A. Jiménez, Design of optimal thermally-coupled distillation systems using a dynamic model, Chem. Eng. Res. Des. 74 (1996) 357–362 https://doi.org/01.12.1996.
[24] T. Waltermann, M. Skiborowski, Conceptual design of highly integrated processes – optimization of dividing wall columns, ChemieIngenieurTechnik 89 (2017) 562–581, https://doi.org/10.1002/cite.201600128.
[25] T. Waltermann, S. Sibbing, M. Skiborowski, Optimization-based design of dividing wall columns with extended and multiple dividing walls for three- and four-product separations, Chem. Eng. Process. - Process Intensif. 146 (2019) 107688, https://doi.org/10.1016/j.cep.2019.107688.
[26] C.J. Calzon-Mcconville, M.B. Rosales-zamora, J.G. Segovia-Hernández, S. Hernández, Design and optimization of thermally coupled distillation schemes for the separation of multicomponent mixtures, Ind. Eng. Chem. Res. 45 (2006) 724–732, https://doi.org/10.1021/ie050961s.
[27] S. Wang, C. Yu, H. Huang, Plant-wide design and control of DMC synthesis process via reactive distillation and thermally coupled extractive distillation, Comput. Chem. Eng. 34 (2010) 361–373, https://doi.org/10.1016/j.compchemeng.2009.05.002.
[28] Y. Luo, X. Yuan, Simultaneous optimization of complex distillation systems with a new PTC model, Ind. Eng. Chem. Res. 56 (2017) 6266–6274, https://doi.org/10.1021/acs.iecr.7b00380.
[29] M. Errico, B. Rong, G. Tola, M. Spano, Optimal synthesis of distillation systems for bioethanol separation. Part 2. Extractive distillation with complex columns, Ind. Eng. Chem. Res. 52 (2013) 1620–1626, https://doi.org/10.1021/ie301829n.
[30] M.A. Gadalla, Z. Olujic, P.J. Jansens, M. Jobson, R. Smith, Reducing CO2 emissions and energy consumption of heat-integrated distillation systems, Environ. Sci. Technol. 39 (2005) 6860–6870, https://doi.org/10.1021/es049795q.
[31] A. Kumar, Guidelines for evaluating the characteristics of vapor cloud explosions, flash fires, and bleves, AIChE J. 15 (1996).
[32] R.A. Freeman, CCPS guidelines for chemical process quantitative risk analysis, Plant/Operations Prog. 9 (1990) 231–235, https://doi.org/10.1002/prsb.720090409.
[33] M. Kumar, K. Gayen, Developments in biobutanol production: new insights, Appl. Energy 88 (2011) 1999–2012, https://doi.org/10.1016/j.apenergy.2010.12.055.
[34] N. Medina-Herrera, A. Jiménez-Gutiérrez, M.S. Mannan, Development of inherently safer distillation systems, J. Loss Prev. Process Ind. 29 (2014) 225–239, https://doi.org/10.1016/j.jlp.2014.03.004.
[35] D.A. Crowl, J.F. Louvar, Chemical Process Safety: Fundamentals with Applications, Pearson Education, 2001.
[36] P.U. De Haag, B.J.M. Ale, Guidelines for Quantitative Risk Assessment: Purple Book, Sdu Uitgevers, The Hague, The Netherlands, 2005.
[37] P.S. Buckley, W.L. Luyben, J.P. Shunta, Design of Distillation Column Control Systems, First, Butterworth-Heinemann, North Carolina, United States of America, 1985.
[38] M. Gabor, P. Mizsey, A methodology to determine controllability indices in the frequency domain, Ind. Eng. Chem. Res. 47 (2008) 4807–4816, https://doi.org/10.1021/ie070952e.
[39] W.K. Häggblom, Control Structures, Consistency, and Transformations, First, Springer, NY, 1992, https://doi.org/10.1007/978-1-4757-0277-4_10.
[40] S. Skogestad, M. Morari, Understanding the dynamic behavior of distillation columns, Ind. Eng. Chem. Res. 27 (1988) 1848–1862, https://doi.org/10.1021/ie00082a018.
[41] A. Jiménez, S. Hernández, F.A. Montoy, M. Zavala-García, Analysis of control properties of conventional and nonconventional distillation sequences, Ind. Eng. Chem. Res. 40 (2001) 3757–3761, https://doi.org/10.1021/ie000047t.
[42] J.G. Segovia-Hernández, S. Hernández, A. Jiménez, Control behaviour of thermally coupled distillation sequences, Chem. Eng. Res. Des. 80 (2002) 783–789, https://doi.org/10.1205/026387602320776858.
[43] J.G. Segovia-Hernández, A. Bonilla-Petriciolet, L.I. Salcedo-Estrada, Dynamic analysis of thermally coupled distillation sequences with undirectional flows for the separation of ternary mixtures, Korean J. Chem. Eng. 23 (2006) 689–698, https://doi.org/10.1007/BF02705913.
[44] S. Hernández, A. Jiménez, Design of energy-efficient Petlyuk systems, Comput. Chem. Eng. 23 (1999) 1005–1010, https://doi.org/10.1016/S0098-1354(99)00257-4.
[45] R. Gutiérrez-Guerra, J.G. Segovia-Hernández, S. Hernández, Reducing energy consumption and CO2 emissions in extractive distillation, Chem. Eng. Res. Des. 87 (2009) 145–152, https://doi.org/10.1016/j.cherd.2008.07.004.
[46] J.R. Alcántara-Ávila, J. Cabrera-Ruiz, J.G. Segovia-Hernández, S. Hernández, B.G. Rong, Controllability analysis of thermodynamically equivalent thermally coupled arrangements for quaternary distillations, Chem. Eng. Res. Des. 86 (2008) 23–37, https://doi.org/10.1016/j.cherd.2007.10.006.