Synthesis and optimization of dividing-wall distillation columns for the separation of a quaternary mixture

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Abstract

Notwithstanding its low thermodynamic efficiency, distillation is among the most used separation processes in industry. As a consequence of the high energy consumption and the related environmental impact the research of more efficient alternatives remains one of the main interests in process engineering. Dividing-wall configurations are a well-known alternative to reduce the energy requirement of ternary distillation. Nevertheless, the design of dividing-wall columns for the separation of quaternary mixtures represents a challenge due to the number of possible configurations. In this work, a synthesis and design procedure is proposed for a double dividing-wall structure to separate quaternary mixtures. The performance of the intensified scheme is analyzed in terms of energy requirements, total annual cost, and CO_2 emissions. Due to the complexity of the system, after initial synthesis the structure is optimized through a meta-heuristic approach. The

direct synthesis procedure leads to a dividing-wall system with higher energy requirements than the conventional sequences. However, after the rigorous optimization, savings in reboiler duty of 14.3% are obtained, with a reduction in TAC of 6.3%.

Keywords: process intensification; dividing wall column; metaheuristic optimization. (we should introduce key words are not already in the title, process optimization, metaheuristic…)

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1. Introduction

As reported by Keller (1987), as a result of its technological matureness, distillation scores the highest commercial application compared to other techniques like adsorption, crystallization, or membranes. It is also recognized as an energy-intensive process; however, its extensive use is due to its simplicity, and effectiveness (Kiss and Smith, 2020). It has been estimated that distillation is used for 90-95 % of liquid phase separations, accounting 2.5 % USA´s total energy consumption (Mathew et al., 2022). Thus, the development of strategies to reduce the energy requirements in distillation is mandatory. Among these strategies, the process intensification (PI) has been distinguished as a powerful tool in the distillation area for achieving energy and economic savings. The PI is a process system engineering branch conceptualized as a set of novel principles applied in process and equipment design, with the objective of enhancing mass, heat and momentum transfer, additionally reducing the equipment size, its environmental impact and improving its profitability and efficiency ensuring operability, feasibility, controllability and safety (Demirel et al., 2019; Kiss and Smith, 2020). The PI involves at least seven defined activities: 1) combination of multiple task or multiple unit operations into a single equipment, 2) conducting process integration strategies, 3) use new multifunctional materials or waste materials for revalorization, 4) reducing size (miniaturization) of process equipment, 5) switching mode of operation to raise the process, 6) application of improved driving forces, and 7) developing advanced operating strategies (Babi et al., 2016). When applied to distillation, Kong et al. (2022) defined two possible strategies. The former, called external intensification, implies using additional auxiliary equipment without alter the distillation scheme; for instance, by heat integration using the energy recovered from the condenser to supply the reboiler energy requirement (Yang et al., 2019; Yang et al., 2019a; Kong et al., 2022), or the implementation of

thermodynamic cycles to improve the system efficiency (Yu et al., 2018; Kong et al., 2022). The second strategy, named internal or advanced intensification, involves altering the distillation configuration through changes to the system's topology. This kind of intensification includes reactive distillation (RD) (Kiss et al., 2019; Chang Shu et al., 2022), thermally coupled distillation (TCD) (Lee et al., 2012; Rong and Errico, 2012), extractive distillation (ED) (Neubauer et al., 2022; Lupachev and Polkovnichenko, 2024), reactive-extractive distillation (RED) (Wang et al., 2024a, 2024b; Li et al., 2025) and divided wall columns (DWC) (Segovia-Hernández et al., 2021; Kong et al., 2024; Waibel et al., 2024). Gómez-Castro and Segovia-Hernández (2019) pointed out that among the PI strategies for distillation, those of internal intensification by integrating various unit operation into a single unit stand out, promoting the synergistic effects to overcome the limitations of the isolated operations; this allows developing structures with reduced size and enhanced thermodynamic efficiency. However, the majority of these technologies have been developed by *ad hoc* considerations and/or heuristics rules, emphasizing the need of reliable synthesis methodologies and well-stablished design algorithms (Errico et al., 2014; Demirel et al., 2019). For specific ternary mixtures, the Petlyuk scheme has been validated as the most energy-efficient scheme reaching up to 30 % and 40 % of energy and capital cost reduction respectively, taking as a basis the conventional distillation schemes (Kiss and Rewagad, 2011). It is worth mentioning that the success of these arrangements is due to the reduction or elimination of the remixing effect of the intermediate component, which diminishes significantly the energy requirements by increasing the thermodynamic efficiency (Dejanović et al., 2010). On the other hand, these schemes are not included into commercial simulators, thus, the design of DWC implies adapting the included modules of distillation columns through the concept of thermal coupling and thermodynamic equivalent configurations (Errico et al, 2015;

Buitimea-Cerón et al., 2021). Moreover, to initialize the design of a DWC, it is necessary to provide a certain number of parameters such as, feed stage, number of stages for each column section, the side draw flowrate, vapor and liquid split ratios, reflux ratio,; (Kiss and Rewagad, 2011; Buitimea-Cerón et al., 2021). DWC design methodologies for DWC can be grouped in three categories (Buitimea-Cerón et al., 2021): 1) methodologies that consider the structural design (topology), 2) methodologies that take into account only the operational variables of the column, for instance, internal flows, and 3) methodologies that include both design objectives, for instance, feasible column structure and its hydraulics. A detailed comparison of the methodologies to design DWC using ternary mixtures is presented in the work of Buitimea-Cerón et al., (2021). Given the high number of degrees of freedom associated to the design of DWC's, it is commonly necessary to implement monoobjective or multiobjective optimization techniques (e.g. Gómez-Castro et al., 2011; Vázquez-Castillo et al., 2015)

Several works about the DWC have been reported in the literature, as those employing Petlyuk-like configurations (Segovia-Hernández et al., 2005; Kiss and Suszwalak, 2012), reactive-DWC (Santaella et al., 2015; Yang et al., 2019), extractive-DWC (Torres-Ortega et al., 2013; Cordeiro et al., 2017), azeotropic-DWC (Yu et al., 2015; Wang et al., 2018), others focused on the implementation of strategies as the use of heat pumps to improve the energy performance of DWC (Yang et al., 2019; Yuan et al., 2017), cryogenic-DWC (Torres-Ortega et al., 2013), batch-DWC (Lopez-Saucedo et al., 2016), control and optimization strategies for DWC (Zavala-Guzmán et al., 2016; Cabrera-Ruiz et al., 2017), along with experimental designs of DWC (Hernández et al., 2009; López-Ramírez et al., 2016). However, most of these works are based on ternary mixtures. Few studies reported the use of four, five or multi-components mixtures. Specifically, the quaternary DWC is not a well-explored scheme, due to its complex topology and controllability (Sánchez-

Ramírez et al., 2020). In relation to DWC synthesis methodologies for four-component mixtures, few works have been presented. Ramapriya et al., (2014) developed a four-step methodology to generate a set of DWCs with n-2 dividing walls, for a mixture of n-components, taking as basis thermally coupled designs; in some DWCs the vapor flow in every section is controlled during the operation. Then, Errico et al., (2015) presented a set of new alternative distillation schemes to the four-component Petlyuk configuration, using a mixture of a hydrocarbon and alcohols. According with their results, for all evaluated configurations, at least one presented better or the same performance of the Petlyuk arrangement. Other interesting work was presented by Madenoor Ramapriya et al., (2018), in which a systematic method was reported to synthesize an initial DWC using any given n-components basic distillation sequence or its thermally coupled derivative. According to the authors, the procedure is dependent on the nature of the basic distillation sequence; however, the methodology was validated using ternary mixtures. Then, Rawlings et al. (2019) presented the modelling, optimization and conceptual design of a DWC using a mixture of 4 compounds, referred as Kaibel column. The work was conducted by three optimization formulation, considering a rigorous tray-by-tray model; next, it was reformulated to include a mixed-integer nonlinear programming and a general disjunctive programming formulation to construct the conceptual design problem for this scheme. Finally, Sánchez-Ramírez et al., (2020) proposed a set of quaternary DWCs, designed and tested using some performance indicators, such as energy requirement, environmental impact, inherent safety and dynamic properties. According to the authors, in some generated designs many of the conventional thermal couplings were substituted by liquid splits, improving the design performance. Although these methodologies are significant, the contribution of other novel proposals is relevant to increase the technology maturity and the applicability of double or multiple walls configurations. For

this reason, in this work, a synthesis and design procedure are proposed for a double-dividing wall structure to separate a quaternary mixture. The proposed system aims to ensure reaching the desired recoveries and purities for the products, while reducing the energy requirements in comparison to a conventional distillation sequence. The intensified scheme is analyzed and assessed in terms of energy requirements, total annual cost and CO_2 emissions, optimizing the scheme by a meta-heuristic approach.

2. Case study

A quaternary mixture composed by n-butane (nC4), n-pentane (nC5), n-hexane (nC6) and n-heptane (nC7), with a feed flow rate of 100 kmol/h and compositions of 40, 10, 10 and 40 mol%, respectively was considered as case study. The mixture is fed as saturated liquid. The desired recoveries are set to 99 mol% for each component. This mixture was selected due to its almost ideal behavior, which allows testing the synthesis methodology and assessing the proposed alternatives. Phase equilibrium has been modelled through the Chao-Seader equation, since it allows adequate predictions for hydrocarbon mixtures (Handogo, 2012; Segovia-Hernández et al., 2018; Wang et al., 2020).

3. Methodology

3.1. Synthesis methodology

The synthesis strategy takes as a basis the methodology proposed by Rong and Errico (2012). The procedure is summarized in Fig. 1 and starts with the design of a conventional distillation sequence (CDS). For a quaternary mixture, this sequence requires three columns to obtain the four pure components, the direct sequence in Fig. 1a is used to exemplify the procedure. Taking as basis the design of the CDS, the reboilers are replaced by interconnections to obtain an original thermally coupled configuration

(OTC). Then, a sections rearrangement takes place to obtain a thermodynamically equivalent structure (TES). In this case, such structure consists of a main column with two side rectifiers. As a following step, instead of eliminating the side rectifiers, they are incorporated in the main column. First, the upper rectifier is incorporated, maintaining the lower rectifier as a side column. This originates the quaternary dividing wall column with side rectifier (QDWC-SR). Finally, the lower rectifier is incorporated to the main column, finally obtaining the quaternary double dividing wall column (QDDWC). These last two alternatives, reported in Fig 1.d and 1.e respectively represent a set of intensified configurations where less than 3 columns are used for the separation.

Figure 2 presents the distribution of the sections and the strategy followed to rearrange them. Sections 1 and 2 are the rectifying and stripping sections for the first column in the conventional sequence. Similarly, sections 3 and 4 and sections 5 and 6 are the corresponding sections for the second and third column of that sequence. To determine the number of sections for the subsequent configurations, the sections are rearranged as shown in Figure 3. The OTC configuration is not shown since the sections are the same as the CDS. This correspondence was proved to facilitate the design since the configuration parameters of the sections are transposed from one configuration to another according to the method proposed by Errico et al. (2014).

3.2. Simulation methodology

Simulations of all the configurations described in section 3.1 and reported in Figure 1, have been performed in the software Aspen Plus. First, the simulation of the CDS takes place. The pressure at the top of each column was defined as the minimum above the atmospheric pressure to ensure a condensation temperature of approximately 50 °C,

assuring the use of cooling water. The design of the columns in the sequence has been performed through the Winn-Underwood-Gilliland shortcut method, by using the DSTWU model. The reflux ratio for the shortcut method has been set as 1.33 times the minimum reflux ratio. The pressure drop along the column has been fixed as 0.68 bar, and the pressure of the feed stream is assumed as the average between the pressure at the condenser and the reboiler of the column. Once the number of stages and feed stage have been determined through the shortcut method, the CDS system is rigorously simulated through the tray-by-tray RadFrac model. To ensure that the required purities are obtained, design specifications are used. The purities of the products obtained in the top of each column are fixed by manipulating the reflux ratio. On the other hand, the purity of the product obtained at the bottom of the last column is fixed by manipulating the reboiler duty. The products´purities, evaluated from the mass balance using the specified recoveries, are: 99.75 mol% for nC4 and nC7, and 95.15 mol% for nC5 and nC6 95.15 mol% for nC6.

Using the configuration of the CDS, the OTC is obtained by replacing the reboiler of the columns C-1 and C-2 by a liquid and a vapor interconnection. With this modification, a new variable appears for the columns C-2 and C-3; this is, the vapor flow rate of the interconnecting streams FV1 and FV2. To set their values, the vapor boil up of the eliminated reboilers in the columns in the CDS is taken as a first guess. Then, their values are manipulated through recursive simulation to ensure maintaining the required purities while minimizing the heat duty of the reboiler connected to the third column.

The structure of the TES is determined by column section rearrangement, as described in the synthesis methodology. The pressure at the top of the main column (MC) equals the pressure in the condenser of the column C-1 in the CDS, since the obtained product in the referred zone is nC4 for both cases. On the other hand, the pressure at the top of each side

rectifier has been defined to allow the vapor transfer between the MC and the rectifiers. The same principle was followed for the QDWC-SR and QDDWC configurations of Fig. 2.d and 2.e respectively. This allows for the two dividing-wall configurations to have the same pressure at both sides of the wall. In this case, the flowrates of FV1 and FV2 were defined using as first guess the flowrates obtained in the TES, then manipulating these flowrates to ensure maintaining the required purities while avoiding excessive heat duties. To represent the configuration QDWC-SR in the simulation environment, the structure shown in Figure 3.a is used. A splitter is used to represent the split of the vapor ascending from section 4, while the mixer represents the incorporation of the liquid flows descending from sections 2 and 3 to section 4. In this case, the split fraction and the vapor stream FV2 are used to maintain the purities on their required values. A similar structure is used to represent the configuration QDDWC, where two splitters and two mixers are used to represent the distribution of the vapor and liquid streams along the column (Figure 3.b). For this configuration, both split fractions are used to satisfy the purity requirements.

3.3. Optimization

Due to the relative complexity of the QDDWC, a rigorous optimization methodology has been employed to ensure a design with the lowest energy requirements. Because of the highly nonlinear equations that represent the system, the existence of discrete variables, and the high interaction between the variables, it was decided to use a metaheuristic algorithm to perform the optimization, namely a genetic algorithm. To initialize the algorithm, the simulation of the QDDWC previously generated is employed as a basis. However, it is important to mention that the simulation of the design directly obtained through the synthesis methodology was unstable for the optimization strategy. In other

words, any small change in the variables caused non convergence. Thus, a relaxed simulation has been obtained by generating a design with a higher total number of stages, taking as a reference the design from the synthesis procedure. This relaxed simulation has been used to initialize the optimization algorithm. The process diagram shown in Figure 4 represents in detail the complete QDDWC modeled in Aspen Plus.

The optimization problem has as objective functions the minimization of both total stages in the column (Equation 1), and the reboiler duty (Equation 2). Recoveries of 99% for each component are defined as constraints (Equations 3 and 4). Equation 1 shows that the total number of stages in the column is a function of the stages on columns 1, 3, and 5 of the simulation scheme. Equation 2 depends on the number of stages, the distillate rates, the boil-up ratio, the internal mole flowrates, and the feed stages. Thus, the optimization problem is stated as follows:

minimize

$$OF_1: TS = S_{C1} + S_{C3} + S_{C5} \quad (1)$$

$$OF_2: Q = f(D_{C1}, D_{C2}, D_{C4}, B_{C5}, FV_1, FV_2, S_{C1}, S_{C3}, S_{C5}, FS) \quad (2)$$

s.t.

$$0.988 \leq R_i \leq 0.9903 \quad (3)$$

$$R_i = \frac{\dot{n}_{i(o)}}{\dot{n}_{i(f)}} \quad (4)$$

Where OF_1 = objective function 1, OF_2 = objective function 2, TS = total number of stages in the dividing wall column, S_{C1}= stages on column 1, S_{C3}= stages on column 3, S_{C5}= stages on column 5, Q = reboiler duty, D_{C1}= distillate rate in column 1, D_{C2}= distillate rate in column 2, D_{C4}= distillate rate in column 4, B_{C5}= boil-up ratio in column 5, FV_1= vapor molar flow from column 3 to column 2, FV_2= vapor molar flow from column

5 to column 4, FS= feed stage, R= molar recovery, ṅ= molar flow. Subscripts: i= molecular specie (butane, pentane, hexane, heptane), (o)= output stream for specie *i*, and (f)= feed stream for specie *i*.

It is important to highlight that the recovery constraint must be relaxed to facilitate the algorithm convergence; thus, the lower and upper bounds shown by Equation 3 are used for the recovery of each component, rather than the exact 99 mol% aforementioned. Equation 4 defines the recovery as the ratio between the moles of *i* leaving the system and those that are fed to the system.

Once the model has been defined and the base simulation tested, the objective functions are evaluated simultaneously. A coupling between different Matlab, Visual Basic, and Aspen Plus, has been implemented for such purpose. Matlab starts with the procedure by generating a data set corresponding to manipulated variable values through a genetic algorithm. The values are sent to Visual Basic, which is used as an interface between Matlab and Aspen Plus. Aspen Plus receives the data vector and solves the mass and energy balances with rigorous methods, taking into account thermodynamic calculations. After Aspen Plus has finished the balances, a check for error convergence is carried out; if errors are not found, the software returns the information obtained (response variables, such as reboiler duty and mole flow from output streams for each component) to Visual Basic (Gutiérrez-Antonio and Briones-Ramírez, 2015; Segovia-Hernández and Gómez-Castro, 2017). Then, Visual Basic evaluates the process constraints and calculates the objective functions using an Aspen Plus data set. The results are sent to Matlab for the evaluation of the objective function in the optimization algorithm. The metaheuristic method is iterative, so Matlab generates another data set, and the process is repeated. Figure 5 shows a schematic representation of the optimization procedure (Guzmán-Martínez et al., 2021).

The manipulated variables and their variation range are shown in Table 1. It is important to mention that in the optimization procedure the pressure drop for each stage is defined as 0.017 bar. This allows keeping consistence with the pressure drop employed by the base simulation (0.68 bar as the pressure drop along the column

The genetic algorithm uses 40 generations, a population of 300 individuals, an elite count of 15, a crossover fraction of 0.8, and a mutation rate of 0.01. These parameters are obtained from a tuning process prior to the final optimization runs. A 2-dimensional Pareto front is plotted once the multiobjective optimization is finished. The criteria for selecting an optimal point from the Pareto front is to choose a solution in the middle region between the two extreme points. The project is developed using a computer with an *Intel ® Xeon ® CPU ES-2630 v3 @2.4 GHz 2.4 GHz* Processor and 128.0 GB RAM. The software used for optimization is MATLAB R2021a®, Visual Basic for applications®, and Aspen Plus.

3.4. Economic and environmental assessment

Economic and environmental analyses have been conducted for the CDS and the QDDWC, since the other sequences are only intermediate configurations used to obtain the structure of the double dividing wall system. The economic assessment of the column has been performed using as indicator the total annual cost (TAC), which is given by the annualized capital cost (CC) and the operational costs (OC):

$$TAC = \frac{CC}{n} + OC \quad (5)$$

The capital costs are given by the equipment cost. On the other hand, *n* is the payback period, which has been assumed as 5 years, which is in the range on typical values of *n*, according to Turton et al (2012). Moreover, such period is in the range used by recent studies, *e.g.* Leybert and Khalikova (2022) and Hamidu et al. (2022).

Equipment costs are estimated through the Guthrie's method, according to the description provided by Turton et al. (2012). The diameter and height of the columns is important information required to compute the equipment costs. The diameter of the conventional columns could be retrieved in Aspen Plus. However, this tool cannot be used to determine the diameter of the QDDWC. Instead, the expression reported by Gómez-Castro et al. (2011) has been used to compute the diameter of the trays of both systems:

$$D = \sqrt{\frac{4G}{\pi \rho_V V_{act}}} \tag{6}$$

Where D is the diameter of the tray, G is the flowrate of the vapor across the tray, ρ_V is the density of the vapor and V_{act} is the operating vapor velocity. Diameter is computed for all the trays of the column, and the value used for the calculation of the costs is the largest one. Height of the column is computed through the correlation reported by Heaven (1969), which is still used for such calculations (e.g. Cui et al., 2018).

$$H_C = 0.61 \cdot \left(\frac{N}{\eta}\right) + 4.27 \tag{7}$$

Where H_c is the height of the column (m), N is the number of theoretical stages, and η is the stage efficiency. Once the equipment costs have been estimated, they are updated with the Chemical Engineering Plant Cost Index of March 2023, which is 799.1.

Utilities costs include the costs associated to the steam used in the reboilers, and the cooling water for the condensers. These costs are computed by multiplying the unitary cost for each utility by the flowrate required to satisfy the needs of the process. Table 2 shows the unitary utilities' costs employed in this work. To estimate the utilities costs in a yearly basis, 8600 operating hours per year have been assumed (Cabrera-Ruiz et al., 2011; Udugama et al., 2024).

Commentato [f1]: Here, I use this references since some reviewers on previous papers asked us to justify the use of 8600 operating hours per year.

Carbon dioxide emissions due to the generation of steam are computed by using the methodology proposed by Gadalla et al. (2006). According to this method, CO_2 emissions can be computed as follows:

$$[CO_2]_{em} = 3.67\left(\frac{Q_{fuel}}{NHV}\right)\left(\frac{C\%}{100}\right) \quad (8)$$

$[CO_2]_{em}$ are the carbon dioxide emissions (kg/s), Q_{fuel} is the duty of fuel burnt to generate the steam (kW), NHV is the net heating value of the fuel (kJ/kg), and $C\%$ is the carbon content of the fuel. Natural gas is used as fuel in this work, thus NHV = 51,600 kJ/kg and $C\%$ = 75.4. Q_{fuel} is estimated from the heating requirements of the process, as shown in Equation 4.

$$Q_{fuel} = \frac{Q_{proc}}{\lambda_{proc}}\left(h_{proc} - 419\right)\frac{T_{FTB} - T_0}{T_{FTB} - T_{stack}} \quad (9)$$

λ_{proc} and h_{proc} are the latent heat and enthalpy of the steam delivered to the process. T_{FTB} is the flame temperature of the boiler flue gases, which is assumed as 1,800 ºC. T_{stack} is the stack temperature, assumed as 160 ºC, and T_0 is the ambient temperature, assumed as 25 ºC. The values for these temperatures have been taken from the work of Gadalla et al. (2006).

4. Results

4.1. Synthesis and simulation

Table 3 shows the designs of the CDS, the OTC configuration and the TES. It is observed that the reflux ratio and the distillate rate are slightly different for both configurations. This is because the values for FV1 and FV2 have been assumed, thus the distillate rate and the reflux ratio are adjusted to maintain the purity specifications. The design obtained for the TES shows how the sections have been rearranged to obtain the structure of the main column. (if the comparison is between the CDS and the 2 alternatives why do you report also the intermediate OTC and TES configurations?)

Commentato [f2]: It is only to show how the stages are distributed, mantaining the total number of stages

The configurations and main operating variables for the systems with dividing walls are presented in Table 4. For a better understanding of the distribution of stages, the information is presented in terms of the sections that conform the QDWC-SR and the QDDWC. Sections 1 and 2 are presented together since they are represented by a single column in the simulation, where section 1 is the rectifying zone of that column, while section 2 is its stripping zone. The hydrocarbons stream is fed in the stage 11 of the column. The feed stage indicated in the column representing the sections 4-6 represents the location of the stage where the interconnecting flow coming from the rectifier REC-1enters. In the case of the QDDWC, only the location of the entering stage for the external hydrocarbon stream is reported, since all the other feed streams shown in the simulation are internal streams for the dividing-wall system. The total number of stages for the QDDWC is given by the number of stages in sections 1, 2, 4 and 6. On the other hand, sections 3 and 5 represent the stages with dividing walls. However, in the design directly obtained by the synthesis methodology, sections 2 and 3, and sections 4 and 6, have a different number of stages, which may lead to a mismatch for the physical implementation of the column. This will be corrected in the optimization procedure.

It is important to recall that the systems that have potential to be implemented are the CDS and the QDDWC. The other systems are only intermediate for the synthesis

procedure. Thus, the detailed analysis will be focused on these systems. Cooling and heating requirements are presented in Table 5. It is observed that the total condenser duty (1603.61 kW) and the total reboiler duty (1,763.17 kW) of the CDS are lower than those for the QDDWC by 5.38% and 8.18%, respectively. However, it is important to recall that the vapor split fractions for the dividing wall system is not necessarily the adequate, it has only been assumed and adjusted to reach the desired purities. Due to the various degrees of freedom and the high interaction among the variables of the system, the QDDWC is optimized by a rigorous strategy to determine if it can indeed provide energy savings in comparison with the conventional sequence.

4.2. Optimization of the QDDWC

The computational time for the optimization problem was approximately 60 hours to carry out approximately 12,000 simulations. The metaheuristic approach obtained 9 solutions as optimal points, which have been used to plot the Pareto front, Figure 6. The Pareto front shows that the reboiler duty decreases when the total stages number increases, which indicates the conflict between these objectives. Of course, increasing the number of stages implies a higher capital cost.

The optimal point selected (red point in Figure 6) has a total number of stages of 53 and reboiler duty of 1,511.15 kW. The mole recuperations reached for this scheme are R_{Butane}= 0.989, $R_{pentane}$= 0.988, R_{hexane}= 0.988, and $R_{heptane}$= 0.988. About mole purities, it was possible to get 99.99 mol% of butane, 95.32 mol% of pentane, 94.57 mol% of hexane, and 99.83 mol% of heptane. The achieved purities have slight variations in comparison to the expected purities. This is associated to the relaxation on the recoveries, which has been necessary to allow the convergence of the optimization algorithm.

The design variables for optimized QDDWC are summarized in Table 6. It is important to mention that all configurations (CDS, QDDWC, and optimized QDDWC) accomplish the recovery constraints. Table 7 compares CDS, QDDWC, and the optimized QDDWC. Analyzing the data about the simulation base (QDDWC) and the optimized QDDWC, this last one has 21.31 % less reboiler duty than QDDWC. The condenser duty is less 22.54 % than QDDWC; however, the optimized scheme has 35.9% more stages in the column. The increment in the stages explains the decrement in reboiler and condenser duties. The diminution in the energy demand would represent a reduction in total annual cost since the operational cost is related to the energy consumption.

Comparing the CDS and the optimized QDDWC, the optimized intensified scheme has 14.3% and 18.1 % less reboiler and condenser duties, respectively, than CDS. However, it is important to notice that the temperature levels change because of the modification of the pressure profile. Besides, it exits a reduction of 14.52 % in the total number of stages; therefore, it is possible to claim that the optimized QDDWC allows obtaining the same product recovery by using smaller equipment with less energy. In this sense, both the capital and the operational costs are reduced, as will be discussed in section 4.3.

Figure 7 shows a comparison of the composition profiles for the optimized and the non-optimized QDDWC. It is observed that, in both cases, the streams deviated to the corresponding dividing wall section have a high composition of the desired component, i.e. n-pentane for the first dividing wall section and n-hexane for the second one. However, for the optimized system the stream entering to the dividing wall section has a composition close to the peak in the profile of n-pentane of the main column, and the dividing wall section requires a lower number of stages in comparison with the non-optimized scheme. Moreover, n-pentane has a better distribution in the optimized system,

reaching a higher maximum composition in the main column (approximately 54.55 mol%) in comparison with the peak for the non-optimized system (approximately 43.49 mol%).

4.3. Economic and environmental assessment

Table 8 presents the main dimensions of the separation sequences, including the diameter, the height and the areas of the heat exchangers. It is observed that, although the main condenser of the optimized QDDWC has a higher area in comparison with the not optimized scheme, the other two condensers compensate with a considerably smaller area. This occurs since the duties for Condenser 2 and Condenser 3 are considerably lower in the optimized scheme, approximately by 47 and 37%, respectively. The estimated costs for the conventional sequence and the QDDWC are presented in Table 9. It is observed that the design of the QDDWC directly obtained from the synthesis methodology has an increasing of 4.6% in capital costs and 12.8% in operational costs in comparison to the conventional sequence. The main contribution to the increase in capital cost is given by the higher energy requirements. In the case of the optimized QDDWC, its capital costs are 3% higher than the conventional scheme. However, the operational costs of the intensified system are 9.7% lower than the CDS, leading to a reduction in TAC of 6.3%. The increase in the capital costs for the intensified system is mainly associated to the operating pressure along the column, since the QDDWC operates at pressures higher than 4.5 bar, while for the conventional system the columns C2 and C3 operate at pressures lower than 2 bar. However, since operational costs contribute with 70-75% to the total annual cost, the reduction in the heat duty for the optimized QDDWC compensates the slightly higher capital cost.

The emissions of carbon dioxide for each system are presented in Table 10. These emissions are reported in kg/s, as obtained from Equation (8). However, the equivalent in

tons per year is also presented to better appreciate the differences among the purification schemes. The optimized QDDWC has emissions 21.3% lower than the non-optimized system, and 9.8% lower than the conventional scheme. This is consistent with the lower heating requirements of the intensified system after the optimization. Such result is an indicator of the potential of the structure to reduce the environmental impact of the separation associated to the use of energy for heating.

5. Conclusions

In this work, a double wall column system has been proposed for the separation of quaternary mixtures. The sequence was obtained through a synthesis sequence using as starting point the conventional direct distillation sequence and by introducing thermal couplings and redistributing the column sections, the quaternary double dividing wall column (QDDWC) was obtained. Through the proposed synthesis strategy, a design that accomplishes with the required recoveries and purities is obtained and further optimized. Through the optimization, the intensified system allowed reducing heat duty in 14.3%, total annual cost in 6.3% and emissions of CO_2 in 9.8%, in comparison with the conventional sequence. Thus, the proposed system has been shown to have potential for reducing the costs for the separation and the environmental impact. However, future research must be performed to identify the feed compositions that for which the column allows obtaining reductions in energy requirements, costs and environmental impact. Moreover, other kinds of mixtures must be tested. Additionally, it is relevant to verify the mechanical design of the structure and its dynamic performance.

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Symbols used

B_{C5} [] boil-up ratio in column 5

C% [] carbon content of the fuel used to produce steam

CC [USD] capital cost

$[CO_2]_{em}$ [kg/s] emissions of carbon dioxide

D [m] diameter of the tray

D_{C1} [kmol/h] distillate rate in column 1

D_{C2} [kmol/h] distillate rate in column 2

D_{C4} [kmol/h] distillate rate in column 4

FS [] feed stage

FV_1 [kmol/h] vapor molar flow from column 3 to column 2 in QDDWC

FV_2 [kmol/h] vapor molar flow from column 5 to column 4 in QDDWC

G [kg/s] flowrate of the vapor across the tray

H_c [m] height of the column

h_{proc} [kJ/kg] enthalpy of the steam

ṅ [kmol/h] molar flowrate

n [y] payback period

N [] number of theoretical stages

NHV [kJ/kg] net heating value of fuel

OC [USD/y] operational cost

Q [kJ/s] heat duty of the quaternary double dividing wall column

Q_{fuel} [kJ/s] heat duty of fuel burnt to produce steam

Q_{proc} [kJ/s] heat duty required by the process

R [] molar recovery

S_{C1} [] number of stages on column 1

S_{C3} [] number of stages on column 3

S_{C5} [] number of stages on column 5

TS [] total number of stages

V_{act} [m/s] operating vapor velocity

Greek letters

λ_{proc} [kJ/kg] latent heat of steam

η [] stage efficiency

ρ_L [kg/m^3] density of the liquid

ρ_V [kg/m^3] density of the vapor

Subscripts

i [] molecular specie

o [] output stream

f [] feed stream

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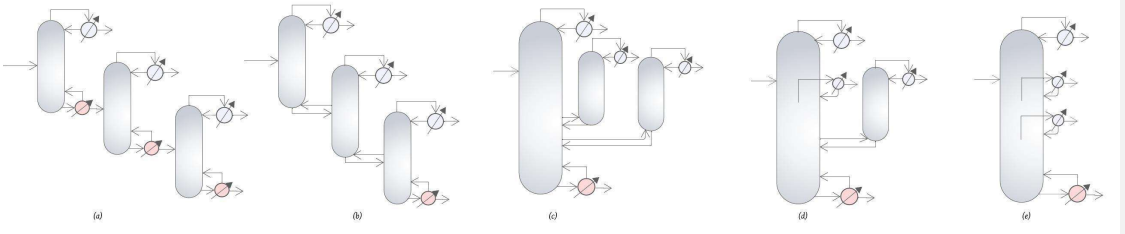


Figure 1. Synthesis procedure (a) conventional distillation sequence, CDS, (b) original thermally coupled configuration, OTC, (c) thermodynamically equivalent structure, TES, (d) quaternary dividing wall column with side rectifier, QDWC-SR, (e) quaternary double dividing wall column, QDDWC.

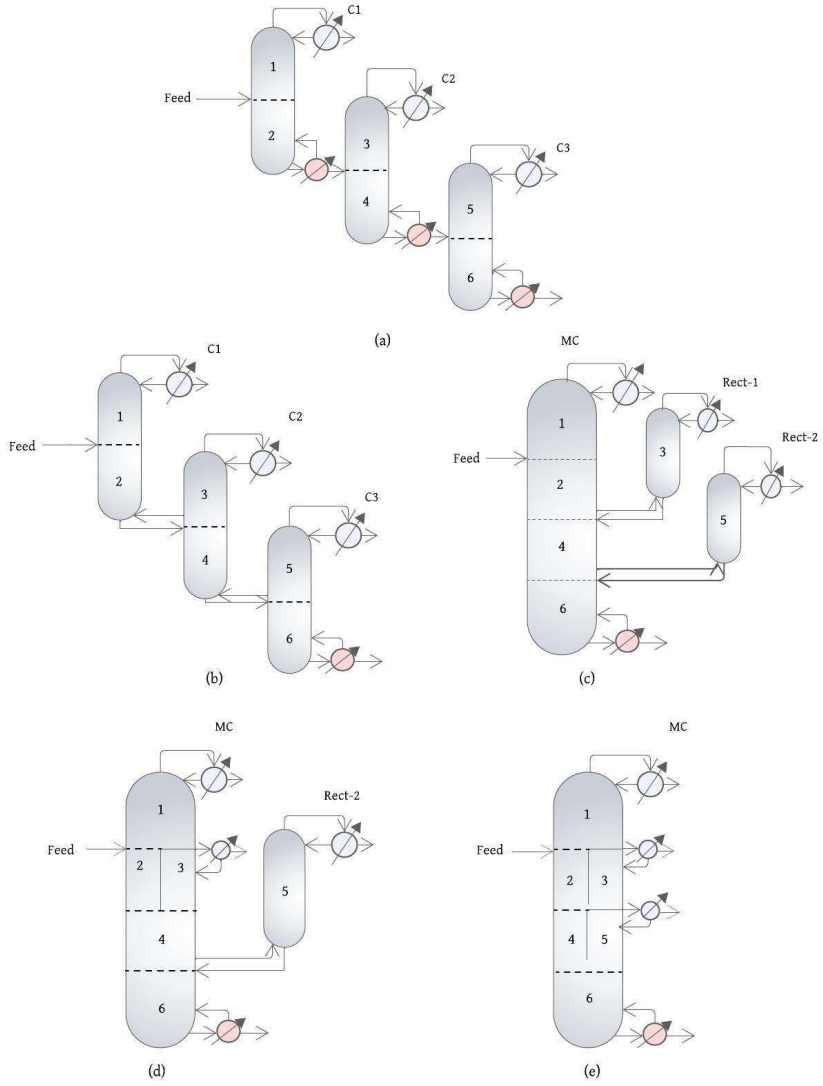


Figure 2. Distribution and rearrangement of sections (a) conventional distillation sequence, CDS, (b) thermodynamically equivalent structure, TES, (c) quaternary dividing wall column with side rectifier, QDWC-SR, (d) quaternary double dividing wall column, QDDWC.

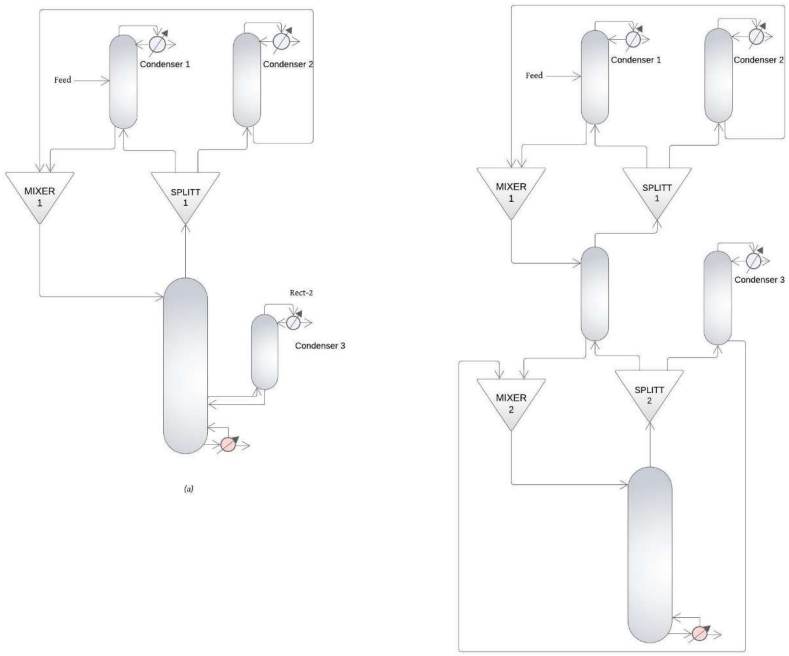


Figure 3. Representation of the dividing-wall configurations in the simulation environment (a) quaternary dividing wall column with side rectifier, QDWC-SR, (b) quaternary double dividing wall column, QDDWC.

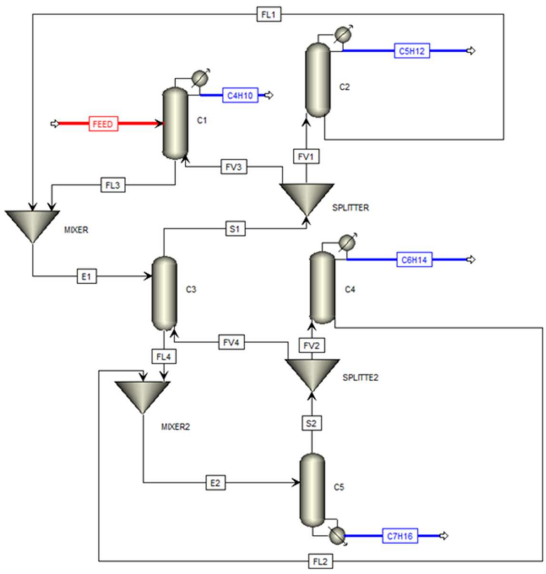


Figure 4. Detailed process diagram of the QDDWC employed as base simulation for the optimization procedure.

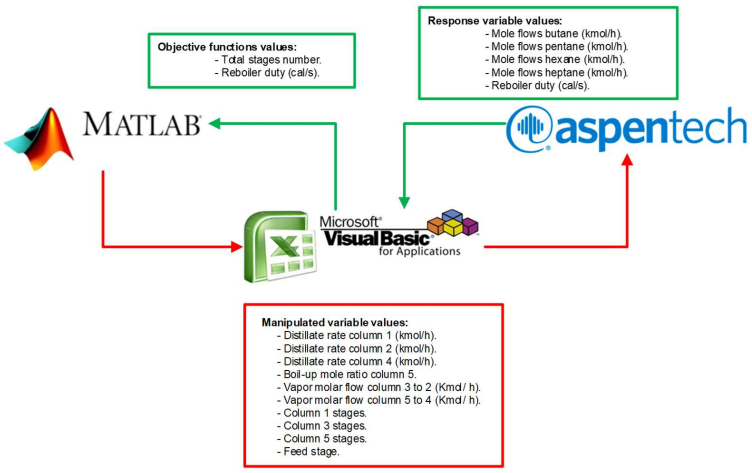


Figure 5. Multiobjective metaheuristic optimization strategy.

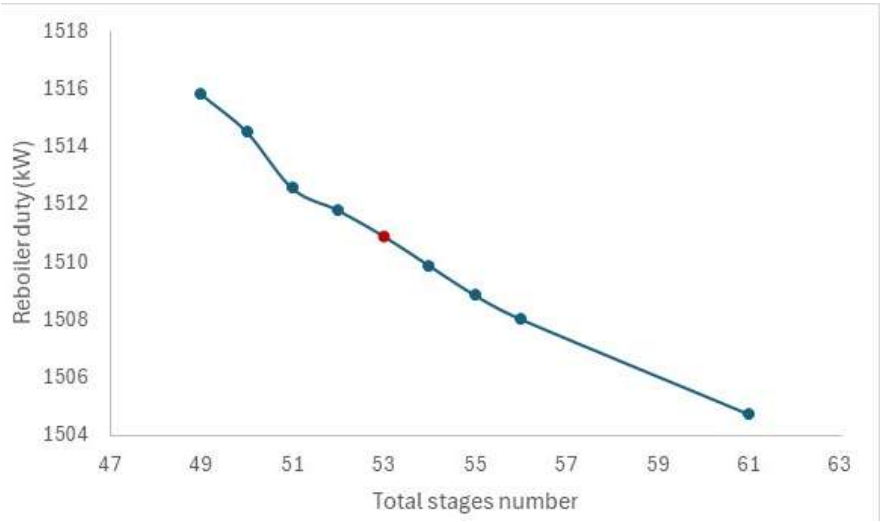
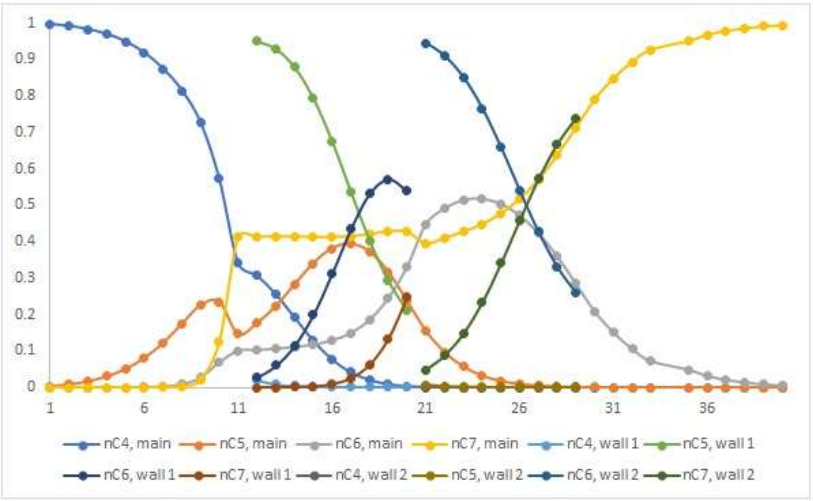
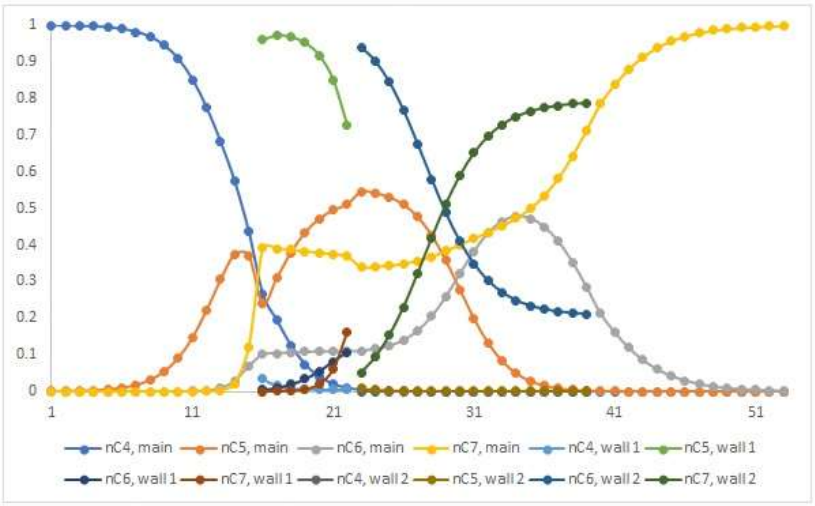


Figure 6. Pareto front for the optimization of the QDDWC.



(a)



(b)

Figure 7. Composition profiles, (a) non-optimized QDDWC, (b) optimized QDDWC.

Table 1. Manipulated variables and their bounds for genetic algorithm.

Manipulated variable	**Lower bound**	**Upper bound**
Distillate rate column 1 (kmol/ h)	39.2	39.9
Distillate rate column 2 (kmol/ h)	10.1	10.8
Distillate rate column 4 (kmol/ h)	10.1	10.8
Boil-up mole ratio column 5	3	7.5
Vapor molar flow from column 3 to column 2 (kmol/ h)	27	41
Vapor molar flow from column 5 to column 4 (kmol/ h)	55	72
Number of stages in column 1	4	40
Number of stages in column 3	4	30
Number of stages in column 5	4	30
Feed stage number	4	39

Table 2. Unitary costs for utilities (Turton et al., 2012).

Utility	**Unitary cost**	**Units**
Cooling water	0.354	USD/GJ

(25°C)		
Low pressure steam (5 barg, 160°C)	14.05	USD/GJ
Medium pressure steam (10 barg, 184°C)	14.83	USD/GJ
High pressure steam (41 barg, 254°C)	17.70	USD/GJ

Table 3. Designs for the CDS, the OTC configuration and the TES.

	CDS			**OTC**			**TES**		
	C-1	**C-2**	**C-3**	**C-1**	**C-2**	**C-3**	**MC**	**REC1**	**REC2**

Number of stages	20	20	22	20	20	22	39	11	12
Feed stage	11	11	12	11	11	12	11, 20, 29	12	13
Operating pressure (bar)	4.575	1.578	1.0	4.575	1.578	1.0	4.575	4.923	5.079
Distillate flowrate (kmol/h)	39.7	10.09	10.31	39.7	10.37	10.23	39.83	10.24	10.16
Reflux ratio	1.387	4.987	8.2737	1.482	1.962	2.893	1.651	2.938	9.493
FV1 (kmol/h)	--	--	--	--	86.5	--	35	--	--
FV2 (kmol/h)	--	--	--	--	--	110.5	101	--	--

Table 4. Designs for the dividing-wall systems.

	QDWC-SR				**QDDWC**				
	1-2	**3**	**5**	**4-6**	**1-2**	**3**	**4**	**5**	**6**
Number of stages	20	11	12	19	20	11	9	12	10
Feed stage	11	--	--	30	11	--	--	--	--
Operating pressure (bar)	4.575	4.766	4.992	--	4.575	4.766	--	4.992	--

Distillate flowrate (kmol/h)	39.88	10.17	10.11	--	39.84	10.324	--	10.16	--
Reflux ratio	1.56	3.943	10.343	--	15	7.2	--	11	--
FV1 (kmol/h)	--	--	--	43	--	--	60	--	--
FV2 (kmol/h)	--	--	--	106	--	--	--	--	98

Table 5. Heating and cooling duties for the CDS and the QDDWC.

	CDS			**QDDWC**
	C-1	**C-2**	**C-3**	
Q_C (kW)	506.51	407.07	690.03	531.68 (Condenser 1) 436.89 (Condenser 2) 726.23 (Condenser 3)
Q_R (kW)	737.73	293.32	732.12	1,920.30

Table 6. Design for the optimized QDDWC.

	QDDWC (Optimized)				
	1-2	**3**	**4**	**5**	**6**
Number of stages	22	7	17	17	14
Feed stage	15	--	--	--	--
Operating pressure (bar)	4.71	4.965	5.084	5.084	5.373
Distillate flowrate (kmol/h)	39.57	10.37	--	10.45	200.40

Reflux ratio	1.96	2.62	--	5.39	1.23
FV1 (kmol/h)	--	33.87	--	--	--
FV2 (kmol/h)	--	--	--	61.13	--

Table 7. Comparison between the separation schemes.

	CDS	**QDDWC**	**QDDWC (Optimized)**
Condenser heat duty (kW)	1,603.61	1,694.8	1,312.8
Reboiler heat duty (kW)	1,763.17	1,920.3	1,511.15

Total number of stages	62	39	53

Table 8. Dimensions for the analyzed systems.

	CDS			**QDDWC**	**QDDWC (Optimized)**
	C-1	**C-2**	**C-3**		
D (m)	0.72	0.73	1.08	1.35	1.19
H_C (m)	15.25	15.25	16.47	26.84	35.38
Condenser area (m^2)	31.89	22.71	20.31	33.79 (Condenser 1) 8.23 (Condenser 2)	38.05 (Condenser 1) 4.31 (Condenser 2)

				8.31 (Condenser 3)	5.10 (Condenser 3)
Reboiler area (m^2)	27.76	6.47	15.44	94.21	88.68

Table 9. Estimated costs for the studied systems.

	CDS	**QDDWC**	**QDDWC (Optimized)**
CC (USD)	1,428,419.95	1,496,702.69	1,472,949.61
OC (USD/y)	784,536.14	900,255.13	708,210.42
TAC (USD/y)	1,070,220.13	1,199,595.67	1,002,800.34

Table 10. Estimated CO_2 emissions for the studied systems.

	CDS	**QDDWC**	**QDDWC (Optimized)**
CO_2 emissions (kg/s)	0.1149	0.1317	0.1036
CO_2 emissions (t/y)	3,558.62	4,076.29	3,207.76