Process synthesis and intensification framework for the separation of ternary mixtures

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Abstract

Typically, the synthesis problem starts from a set of preestablished connections between steams and unit operations resulting in distillation sequences, which can be included into superstructure representations and reformulated as mathematical programming problems. Nevertheless, in the last decades novel approaches to process synthesis that depart from the concept of unit operation and are based on phenomenological approaches have been proposed. This work decomposes distillation structures into distillation modules where a module is equivalent to a vapor-liquid equilibrium stage in which input and output material and heat flows connect modules. Also, a process synthesis an intensification (PS+I) framework is proposed for the synthesis of distillation structures separating ternary mixtures. The proposed framework has the following steps: database generation of distillation modules, optimization, solution interpretation, validation, and post-optimization. The separation of the BTX ternary mixture was taken as case study and several interpretation guidelines have been proposed.
1. Introduction

Distillation is a widely used technology for separating liquid ternary mixtures in Chemical processes. Thus, distillation sequencing and optimization have been researched over several decades. The early works related to separating ternary mixtures consisted of numerical analyses and optimization of the direct and indirect distillation sequences, and the Petlyuk thermally coupled structure. Fidkowski and Krolikowski studied several ternary mixtures with different relative volatilities and feed compositions, in all cases the Petlyuk structure realized the minimum vapor flow rates in the columns. Then, thermally coupled columns with a side stripper or rectifier were included as candidates to separate ternary mixtures. However, the Petlyuk structure attained the lowest energy requirement. Since the remarkable energy-saving potential of thermally coupled distillation was demonstrated, later works proposed Petlyuk-like structures with modified topologies and reduced number of thermal couplings to eliminate the vapor bidirectionality issue of the Petlyuk Column. After calculations at steady-states, an optimization methodology was proposed by solving the dynamic model for the Petlyuk structure to find the optimal vapor and liquid connecting flows that minimize the reboiler energy consumption. Finally, the control properties of side stripper, side rectifier thermally coupled distillation, and the Petlyuk column were studied, and it was found that in most cases there is a trade-off between economic and controllability criteria. A comparison between conventional and thermally coupled distillation columns was performed, and under some feed and relative volatility conditions, thermally coupled alternatives have better control properties. In the aforementioned works, the drawback is that the best solution is known after all possible candidates are simulated and optimized one by one.

Superstructure representations have been proposed for synthesizing distillation structures to separate ternary mixtures. Yeomans and Grossmann proposed a state-equipment network superstructure for the synthesis of distillation sequences. In their work, two ternary mixtures were considered and conventional sequences were the best solutions. In a later work, Grossmann and coworkers included thermally coupled distillation columns in a superstructure. The Petlyuk structure and a Petlyuk-like structure with modified topology were the best solutions. The considered superstructures included distillation structure alternatives at a unit operation level. It still depends on the selection of the initial candidate structures.

The works mentioned above started from a known set of pre-established candidate distillation structures. However, in this work, the synthesis problem is solved the other way around: It finds an unknown optimal distillation structure that will become known after a solution interpretation step.

This work proposes a Process Synthesis and Intensification (PS+I) framework in which the synthesis problem is represented by module-based low aggregation superstructure for synthesizing optimal distillation structures to separate ternary mixtures. Furthermore, the derived optimal distillation structures do not rely on any a priori pre-established process structures.

Since the economy of distillation processes is largely dominated by its utility cost, in the first step, the synthesis problem for separating the ternary mixture is solved to obtain the optimal process structure with minimum utility cost. Later, once the optimal distillation structure is known, another optimization problem is solved to find the values of operating (e.g., reflux ratio, interconnection flow rates) and structural variables (e.g., number of stages, feed stage, and interconnection stages in each column) that minimize the Total Annual Cost (TAC).

Problem statement

The synthesis problem for separating a ternary mixture was solved under the following assumptions:

1. The operating pressure is given in advance, and the pressure drop is negligible.
2. The feed conditions (flow rate, composition, temperature, and enthalpy) are given in advance.
3. All products are withdrawn as saturated liquid.
4. The molar recovery and purity of each product are specified at the lower bound of its key component.
5. Vapor-liquid equilibrium (VLE) is reached in each stage of distillation structures.
6. Heat integration among distillation structures is not considered.
7. Utility costs per unit amount of heating and cooling are given in advance.
8. The optimization criterion is based only on the utility costs.
9. The process is at steady state.

These assumptions are considered when proposing the low aggregation superstructure and its mathematical reformulation. Next section explains in detail the proposed $PS+I$ framework.

**PS+I Framework**

The proposed $PS+I$ framework departs from synthesizing process structures at the unit operation level and focuses on the functions a chemical process can perform. Thus, chemical processes can be broken into different *functional modules* \(^9\). The proposed framework consists of the following steps that will be discussed in detail in later subsections.

A low aggregation superstructure of functional distillation modules is proposed. It comprises all possible combinations among modules. The liquid and vapor molar compositions in equilibrium and phase molar enthalpy of each *functional module* are stored in a database. These values are calculated by discretizing the liquid composition space. Then, the superstructure is reformulated as an optimization problem. Its solution is interpreted into a realistic intensified distillation process structure. The interpretation is validated through rigorous simulations for the distillation process. Finally, once the feasibility of the interpreted distillation structure is confirmed, post optimization is done to find their optimal operating and structural variables.

In short, the $PS+I$ framework is divided into two parts: a process synthesis problem to derive the optimal distillation structure, and then, when the distillation structure becomes known, to optimize it using well-established optimization algorithms. Figure 1 summarizes the proposed $PS+I$ framework.

![Fig. 1. Steps in the $PS+I$ framework](image)

**Superstructure representation of functional modules**

The use of superstructures is one of the most widely used approaches to solve synthesis problems dealing with distillation sequencing and optimization. However, most of these superstructures solve synthesis problems at the unit operation level, which poses an intrinsic limitation because the obtained solution depends on the unit operations considered in the superstructure \(^10\). This work proposes a low aggregation superstructure based on functional modules. Drake and Manousiouthakis \(^11\) proposed a distillation network synthesis problem based on the Infinite Dimensional State-space (IDEAS) approach, which included all possible process configurations. Later, Takase and Hasebe modified this approach for the synthesis of heat-integrated distillation columns \(^12\), the separation of zeotropic ternary mixtures \(^13\), and a reactive distillation column \(^14\). In previous research the optimal process structure with minimum energy consumption is interpreted at a condition near the minimum reflux, which implies that many stages are necessary in the columns. This work proposes a new mathematical relaxation, interpretation guidelines, and expands the previous research by proposing a post optimization step which finds the best process structure with minimum Total Annual Cost (TAC).
The proposed PS+I framework uses a reformulation, where the equality constraints are relaxed to solve the problem with a smaller number of modules and a less computational time. Also, the optimal structure is known once it has been interpreted and validated. Therefore, any optimization algorithm (stochastic or deterministic) can be used to find the detailed optimal structure at a post-optimization step.

A distillation module is a liquid composition subspace in which VLE is attained when vapor and liquid streams contact each other, and it resembles a distillation stage. Since the liquid composition, module pressure and its thermodynamic state (i.e., saturated liquid) are known, the vapor composition and the molar enthalpy in each phase are uniquely calculated. Therefore, the optimization variables are only in terms of material flows (i.e., liquid and vapor) and heat flows. Figures 2 shows the conceptual representations of a distillation module.

![Input and Output of a Distillation Module](image)

**Fig. 2.** Representation of a distillation module

As it can be seen in the figure, a distillation module has liquid flow, vapor flow, and heat flow inputs and outputs. Moreover, the distillation modules included in a superstructure represent the set of all possible material and heat flow connections among modules. Figure 3 shows the proposed superstructure representation in this work.

The squares are distillation modules numbered from 1 to $N$, and as the number of discretized subspaces increases, $N$ also increases. Thus, two squares with the same number correspond to the same module. In addition to distillation modules, there are four types of modules: 1) a feed module, 2) product modules, 3) a heating module, and 4) a cooling module. Moreover, the feed and heating modules have only material and heat outputs. Contrarily, the products and cooling modules have only material and heat inputs. Finally, solid lines are liquid and vapor connections between modules, and dotted lines are heating and cooling connections with modules. Thus, there will be optimal material and heat connection paths between modules which result in the optimal process structure.
Fig. 3. Low aggregation superstructure representation

Mathematical formulation

The superstructure shown in Figure 3 is reformulated as a mathematical programming problem for solving the synthesis problem. The objective function is the minimization of the Utility Cost (UC) as shown in Equation 1 since the total cost of distillation processes is largely dominated by the utility cost in most cases. Equation 2 shows the feed material balance. Equations 3, 4 and 5 show the overall mass balance, the component mass balance for the light key components and the heat balance for each distillation module. Equations 6 and 7 show the molar purity and recovery constraints for each product.
\[
\begin{align*}
\min \text{UC} &= \sum_{i \in S_N} (C_H Q^H_i + C_C Q^C_i) \\
\text{s.t.} & \\
\sum_{i \in S_N} L^F_i - F &= 0 \quad (1) \\
\sum_{j \in S_N} (L_{ji} + V_{ji}) + L^F_i - \sum_{j \in S_N} (L_{ij} + V_{ij}) - L^F_i &= 0 \quad (2) \\
\sum_{p \in S_p} L^P_{ip} &= 0 \quad i \in S_N \quad i \neq j \quad (3) \\
\sum_{j \in S_N} (x_{jk} L_{ji} + y_{jk} V_{ji}) + x_k^F L^F_i - \sum_{j \in S_N} (x_{ik} L_{ij} + y_{ik} V_{ij}) - L^F_i &= 0 \quad i \neq j \quad (4) \\
x^P_p \sum_{i \in S_N} L^P_{ip} - \sum_{i \in S_N} x_{ip} L^P_{ip} &\leq 0 \quad p \in S_p \quad (5) \\
\eta_p x_k^F L^F_i - \sum_{i \in S_N} x_{ip} L^P_{ip} &\leq 0 \quad p \in S_p \quad (6) \\
L^F_i, L_{ij}, V_{ij}, L^P_{ip}, Q^H_i, Q^C_i &\geq 0 \quad (7)
\end{align*}
\]

where \( S_N \), \( S_p \) and \( LK \) are the sets of the distillation modules, products, and light key components, respectively. The parameters in the optimization problem are: the cost per unit amount of heating and cooling (\( c_H \) and \( c_C \)), the composition, molar enthalpy, and inlet flow of the feed (\( x^F_k \), \( h^F_i \), and \( L^F_i \)), the lower bound of the composition of each product (\( x^P_k \)), the molar recovery of each product (\( \eta_p \)), and the phase compositions in equilibrium and their molar enthalpy (\( x_{ik} \), \( y_{jk} \), \( h^L_i \), and \( h^V_i \)) for distillation modules.

It should be observed that liquid or vapor material flows between the same module are not allowed. Thus, \( L_{ii} = V_{ii} = 0 \), \( i \in S_N \). Therefore, Equation 2 and 3 exclude these material flows.

The optimization variables are: heating and cooling (\( Q^H_i \) and \( Q^C_i \)) in distillation modules, liquid and vapor flow rates from distillation module \( i \) to distillation module \( j \) (\( L_{ij} \) and \( V_{ij} \)), feed flow rate to a distillation module \( i \) (\( L^F_i \)), and the liquid flow rate from distillation module \( i \) to product stream \( p \) (\( L^P_{ip} \)).

Moreover, Equations 1 to 7 are expressed as linear relationships of optimization variables. Thus, the optimization problem can be solved as a linear programming (LP) problem. In addition, all optimization variables are non-negative. Next subsection explains in detail the solution procedure in the proposed \( PS+I \) framework.
Mathematical relaxation

As the number of distillation modules \((N)\) increases, the value of the objective function decreases until it reaches an asymptotic minimum\(^{13}\). Theoretically, an infinite number of distillation modules is necessary to cover all possible compositions in the ternary diagram, as the number of modules tend to infinity, the LP problem becomes an infinite linear program (ILP) in which the value of the objective function tends to its minimum value. The IDEAS framework approximates the ILP problem by finite-dimensional linear programs of ever-increasing size \(^{15}\). Therefore, the synthesis problem must be solved within a finite number of modules. Takase and Hasebe proposed the relaxation of liquid compositions with lower and upper bounds (i.e., \(x_{ik}^{lo} \leq x_{ik} \leq x_{ik}^{up}\)) to cover any possible liquid composition outside the set of \(N\) modules. Also, they proposed a convergence criterion represented by an inequality constraint.

In this work, the liquid composition is not relaxed, but material and heat balance equality constraints are relaxed into inequality constraints. By doing this, the process operating lines are relaxed. Mathematically, the LP problem, summarized in Equation 8 was reformulated as shown in Equation 9 as follows:

\[
\begin{align*}
\text{min} & \quad UC \\
\text{s.t.} & \quad h(X) = 0 \\
& \quad g(X) \leq 0 \\
& \quad X \geq 0
\end{align*}
\]

\[
\begin{align*}
\text{min} & \quad UC \\
\text{s.t.} & \quad -\varepsilon \leq h(X) \leq \varepsilon \\
& \quad g(X) \leq 0 \\
& \quad X \geq 0
\end{align*}
\]

where \(h(X)\) and \(g(X)\) are equality and inequality constraints, \(X\) is the vector of optimization variables, and \(\varepsilon\) is the acceptable tolerance needed to satisfy material and energy balances.

Figure 4 shows graphically the differences between the previous relaxation\(^{13}\) and the proposed relaxation.

**Fig. 4.** Graphical interpretation of mathematical relaxation

In Figure 4a, the molar composition of modules is relaxed between upper and lower bounds, which allows covering any composition that is not explicitly included in the modules. Contrarily, Figure 4b relaxes the
values of liquid flows that satisfy the material balance. In other words, if there is a feasible path of material and energy flows, there will be a solution for the synthesis problem. Although liquid compositions and flows are shown, the same logic is applied to vapor flows and heat flows.

As it can be inferred from Figure 4b, if $\varepsilon$ takes a large value, the solution will lack of meaning and the trivial solution of $\text{UC} = 0$ will be obtained. Oppositely, there is a minimum tolerance value ($\varepsilon_{\text{min}}$) that can find a feasible path of flows and heat for which UC tends to infinity. The selection of the tolerance must be higher than this value (i.e., $\varepsilon > \varepsilon_{\text{min}}$).

Before solving the synthesis problem, the value for $\varepsilon_{\text{min}}$ must be known in order to get feasible solutions because otherwise (i.e., $\varepsilon_{\text{min}} > \varepsilon$), there will not be an operation line that can connect modules on the other hand if epsilon value is too big (i.e., $\varepsilon \gg \varepsilon_{\text{min}}$) the necessity of connecting modules become less relevant and the material balance becomes too loose that it starts to lack of meaning. Therefore, the value of epsilon will affect the solution and its objective function. A detailed analysis will be presented in the next section.

**Solution procedure**

This section explains the procedure to solve the synthesis problem for any number of modules $N$ and tolerance $\varepsilon$.

1. Set the feed flow rate ($F$) and its liquid composition ($x^F_k$), molar purity ($x^P_p$) and recovery ($\eta_p$) of products, and the process operating pressure ($P$).
2. Calculate $h^F$ for the feed.
3. Discretize the liquid molar composition ($x_{ik}$) of the ternary diagram into $N$ subspaces and assign them to a distillation module for each subspace $i \in S_N$, $i = \{1, \ldots, N\}$.
4. Given $x_{ik}$ and $P$ for all $N$, calculate $y_{ik}$, $h^L_i$, and $h^V_i$ for each subspace $i \in S_N$.
5. Input the values of the intensive properties calculated in steps 2 to 4 as parameters in the optimization problem.
6. Solve the following optimization problem to find $\varepsilon_{\text{min}}$

$$
\begin{align*}
\min_{\varepsilon_{\text{min}}} & & \varepsilon_{\text{min}} \\
\text{s.t.} & & UC \geq 0 \\
& & -\varepsilon \leq h(X) \leq \varepsilon \\
& & g(X) \leq 0 \\
& & X \geq 0
\end{align*}
$$

1. Set $\varepsilon > \varepsilon_{\text{min}}$ and solve the relaxed optimization problem in Equation 9.
2. Increase $N$ and repeat steps 3 to 7 until there is not much improvement in the objective function.
3. Given the optimal solution, plot the modules with liquid and vapor flows higher than zero in ternary diagrams.
4. Calculate the liquid and vapor flows distributions.
5. If interpretation of the plotted solution in step 9 is not possible, increase the flows lower bound value until interpretation is possible (e.g., liquid and vapor flows higher than the median, or another percentile for the histogram in step 10).
6. Interpret the optimal solution and translate it into an intensified, task-integrated structure.
7. Simulate the interpreted solution at step 12 and validate it by comparing the utility cost of the final solution and that obtained at step 7 by the LP problem.

The process simulation software Aspen Plus V11® was used to calculate all the parameters for each module. However, any simulation software commercial or open source can be used. Also, the thermodynamic model can be coded in Excel VBA® or any numerical analysis software, such as MATLAB®, or PYTHON®. In
addition, the used optimization software was IBM ILOG CPLEX Optimization Studio 12.8.0. Similarly, another optimization software can be used. To solve the synthesis problem, a macro was used to link Aspen Plus V11® and Excel VBA to store all modules data. Then, the optimization software and Excel were linked to read the modules data and to write the optimization solution.

Results and Discussion
This section explains the PS+I framework through the solution of a case study.

Case study
The separation of a benzene, toluene, and o-xylene mixture has been widely researched for distillation sequencing and optimization\textsuperscript{13,16,17}. In this research, the Peng-Robinson Equation of State was used to calculate the intensive properties of modules. Table 1 shows the additional information to solve the optimization problem, which was adopted from previous research\textsuperscript{13}.

Table 1. Additional information to solve the optimization problem

<table>
<thead>
<tr>
<th>Parameter (Units)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (kPa)</td>
<td>101.3</td>
</tr>
<tr>
<td>L\textsuperscript{F} (kmol/h)</td>
<td>300</td>
</tr>
<tr>
<td>x\textsuperscript{F} (-)</td>
<td>(0.333,0.333,0.334)</td>
</tr>
<tr>
<td>x\textsuperscript{P} (-)</td>
<td>(0.900, 0.900, 0.900)</td>
</tr>
<tr>
<td>η\textsuperscript{P} (-)</td>
<td>(0.900, 0.900, 0.900)</td>
</tr>
<tr>
<td>C\textsubscript{H} ($/GJ)</td>
<td>11.00</td>
</tr>
<tr>
<td>C\textsubscript{C} ($/GJ)</td>
<td>0.25</td>
</tr>
<tr>
<td>N (-)</td>
<td>{231, 351, 595, 861, 1326}</td>
</tr>
</tbody>
</table>

Optimization results
A uniform discretization of the liquid composition with a width between 0.05 and 0.02 was taken to generate the distillation modules. Figure 5 shows the results of the objective function for the considered N values shown in Table 1. The optimization problem was solved for the following tolerance values: \(0.1 \epsilon_{\text{min}} \leq \epsilon \leq 1.25 \epsilon_{\text{min}}\).
From the figure, as the number of modules increases, UC decreases because the solution gets closer to the minimum reflux condition since more connections between distillation become possible. Also, circles correspond to several solutions for $\varepsilon$, but it is more apparent for low values of $N$ because few distillation modules exist. The line represents the solution for $\varepsilon = 1.01\varepsilon_{\text{min}}$. For few distillation modules ($N = 231$), the solution approximates the optimal structure at the minimum number of stages condition. Oppositely, for many distillation modules ($N = 1326$), the solution approximates the optimal structure at the minimum reflux condition. The optimal distillation structure is always obtained between these two extreme conditions. In the next section, the results are taken for interpretation and validation.

Solution interpretation and validation

Once the solution of the optimal structure is known, the next steps are interpretation and validation. Interpretation depends on the user’s knowledge in distillation processes and ternary diagrams. Therefore, several interpretation guidelines are proposed.

Ternary diagrams in Figure 6 show the liquid and vapor composition paths connecting distillation modules, and these connections will be translated into distillation structures. In the figure the empty the squares represent the selected distillation modules, the lines denote the connected liquid or vapor flows between distillation modules, the blue circles represent cooling, and the red circles represent heating. Figures 6a and 6c show the liquid flow connections and Figure 6b and 6d show the vapor flows connections when the synthesis problem was solved for 231 modules. For interpretation, Figures 6a and 6b shows meaningful molar flows higher than the 50th percentile (28.75 kmol/h and 29.39 kmol/h) while Figure 6c and 6d shows meaningful molar flows higher than the 90th percentile (248.6 kmol/h and 258.6 kmol/h). It can be seen when many modules are plotted it is difficult to make an interpretation. However, as the number of plotted modules decreases, the interpretation becomes easier, but some valuable information of connections can be lost. Therefore, the user should explore several limit values of meaningful flows and based on some criteria, alongside with the subsequent steps of interpretation, validation, and post-optimization.
Fig. 6. Liquid and vapor flows for the optimal solutions using 231 distillation modules: many modules plotted (top), few modules plotted (bottom).

Figures 7a and 7b show the liquid and vapor flow connections when the synthesis problem was solved for 1326 modules. In this case, the meaningful liquid and vapor molar flows are those higher than 248.6 kmol/h and 258.6 kmol/h, respectively.
Interpretation guidelines

The following guidelines to interpret the ternary diagrams of molar liquid composition are:

1. A reboiler or intermediate reboiler is placed when modules have heat inlet flows.
2. A condenser or intermediate condenser is placed when modules have heat outlet flows.
3. Identify the modules with feed inlet and product outlet liquid flows.
4. Identify the clusters of connected modules, they can be regarded as a section of a distillation column.
5. Identify modules with multiple liquid flows. These modules can be interpreted as mixing or splitting of liquid flows.
6. Use the lever rule and connect points. If the modules are ordered in a straight-line, they can be regarded as stages in a distillation section separating a binary mixture.
7. Identify the regions when the connections among modules are not a straight line. These regions can be considered as complex columns (i.e., multiple feed and products streams).

The same guidelines can be applied for molar vapor flows. Understanding both ternary diagrams will help to do a better interpretation.

In this work, the Petlyuk column was chosen as the optimal structure that reflects well liquid and vapor flow paths in Figures 6 and 7. Therefore, Figure 8 shows the optimal process considering the above-mentioned guidelines. For the sake of clarity, the aim for solving the synthesis problem is to find a distillation structure. The connected modules with liquid and vapor flow paths show compositions where the optimal process structure passes, and not necessarily the actual number of stages in the process. Therefore, the presented
solutions are the Petlyuk columns in which each column section has fifty stages. The interpreted solutions are validated through rigorous simulation in Aspen Plus V11®.

Fig. 8. Simulation results of interpreted solutions: a) 231 modules, b) 231 modules, and c) 1326 modules

As it can be seen, this framework conders the use of intensified processes because they inherently represent options with less energy consumption, thus cost 18. Figure 9 shows the compositions profiles of the solutions in Figure 8.
Fig. 9. Ternary diagram for the simulation results: a) 231 modules, b) 231 modules, and c) 1326 modules

By comparing Figures 6, 7, and 9, the selected distillation modules and the composition of stages in the simulated Petlyuk columns show similar connection paths of liquid streams. Therefore, it can be concluded that the interpretation and simulation can validate the optimization result. Since at this point, the optimal structures are interpreted and validated, in the last step of the framework, a post optimization problem is applied for the known structure.

4.4. Post-optimization analysis

Once the optimal structure by the PS+I framework is interpreted, simulated, and validated, a post-optimization step that minimizes the Total Annual Cost (TAC) was done. In this step, the operating variables (e.g., recycle flows, reflux ratio, reboiler and condenser duties) and structural variables (e.g., number of stages, feed stage, dimensions of the reboiler, condensers and heat exchangers)\textsuperscript{19} are optimized.

The TAC is function of the total investment (TIC) and operating (TOC) costs, and a set payback period (pbp). These relations can be represented based on Luyben’s methodology\textsuperscript{19} as is shown in Equation 11 to 13.

\[
TAC = TIC + \frac{TOC}{pbp} \tag{11}
\]

\[
TIC = \sum_i \rhoA C_i^{shell} + C_i^{tray} + C_i^{con} + C_i^{reb} + C_i^{hx} \tag{12}
\]

\[
TOC = C_C \sum_i \rhoA Q_i^{con} + C_H \sum_i \rhoA Q_i^{reb} \tag{13}
\]

where the TIC considers the costs of columns ($C_i^{shell}$), trays ($C_i^{tray}$), condensers ($C_i^{con}$), reboilers ($C_i^{reb}$), and any heat exchanger ($C_i^{hx}$), and the TOC considers the cost of cooling in condensers ($Q_i^{con}$) and heating in reboilers ($Q_i^{reb}$) for all columns $i$ COL.

It is important to mention that the second part of the PS+I framework consists in optimizing a known
structure. Therefore, any optimization approach deterministic or stochastic can be used to optimize the structure obtained at the interpretation step.

In this work, the use of Genetic Algorithms has been chosen since a previous work has used them \(^{20}\). The minimization problem was carried out through a genetic algorithm (GA) via an interface between Matlab and Aspen Plus. The GA parameters were obtained from literature and are presented in Table 2 \(^{21–23}\).

**Table 2** Parameters for solving the GA algorithm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Generations</td>
<td>40</td>
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<tr>
<td>Individuals</td>
<td>500</td>
</tr>
<tr>
<td>Crossover factor</td>
<td>0.8</td>
</tr>
<tr>
<td>Mutation factor</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The sets of operational and structural variables that lead to unfeasible solutions were penalized with a large value of TAC, so the algorithm can discard those combinations.

Table 3 shows the comparison between the pre- and post-optimization results for the three interpreted solutions shown in Fig. 8. Although the distillation structures are simulated as thermally coupled distillation columns, in the post-optimization step Dividing Wall Columns (DWC) are optimized because they are thermodynamically equivalent and the latter are the standard for commercial applications\(^{20}\).

**Table 3** Post-optimization results

<table>
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<td>20</td>
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<td>Diameter [m]</td>
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<td>2.36</td>
<td>2.21</td>
<td></td>
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<td>Condenser duty [kW]</td>
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<td>3519</td>
<td>3593</td>
<td>4019</td>
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<tr>
<td>Reboiler duty [kW]</td>
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<td>3668</td>
<td>3687</td>
<td>3761</td>
<td>4185</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UC [$/h]</td>
<td>148.28</td>
<td>148.4</td>
<td>149.17</td>
<td>152.15</td>
<td>169.34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOC [M$/y]</td>
<td>1.3</td>
<td>1.300</td>
<td>1.31</td>
<td>1.333</td>
<td>1.48</td>
<td></td>
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<tr>
<td>TIC [M$]</td>
<td>2.76</td>
<td>1.007</td>
<td>2.78</td>
<td>1.060</td>
<td>2.78</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>TAC [M$/y]</td>
<td>2.22</td>
<td>1.635</td>
<td>2.23</td>
<td>1.686</td>
<td>2.41</td>
<td></td>
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</tr>
</tbody>
</table>

where, NT1 and NT2 denote the total number of stages in the prefractirotator column (PF) and in the main column (MC), NF is the feed stage in PF, NL and NV are stages in MC from where liquid and vapor interconnection flows leave the column (wall size), and NS is the side stream product.

As it can be seen, at the post-optimization step, TAC decreased because the columns need fewer stages than those at near minimum reflux conditions in Fig. 8.

Figures 10a and 10b show the optimal distillation structure after solving the post-optimization step and the composition of stages in a ternary diagram. The presented optimized structure corresponds to the one with the lowest TAC in Table 3.
Table 4 summarizes the comparison between the synthesis problem solution, simulated solution, and post-optimization solution for the optimal process.

<table>
<thead>
<tr>
<th></th>
<th>UC [$/h]</th>
<th>TAC [M$/y]</th>
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</thead>
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<tr>
<td>Optimization</td>
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<td>LP 231 modules</td>
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<td>LP 1326 modules</td>
<td>126.00</td>
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<td>Simulation</td>
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<td>149.17</td>
<td>2.230</td>
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<td>1326 modules</td>
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<td>2.410</td>
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<td>Post-optimization</td>
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<td>148.40</td>
<td>1.635</td>
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<td>231 modules</td>
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<tr>
<td>1326 modules</td>
<td>161.23</td>
<td>1.753</td>
</tr>
</tbody>
</table>

For the synthesis problem, as the number of considered distillation modules increases, the utility cost decreases, because the optimal structure approximates the minimum reflux condition. However, if simulations are at near minimum reflux conditions, the values of UC do not differ much. Thus, there is a set of simulations that can satisfy the design specifications because the interconnection liquid and vapor flows are optimization variables. Finally, at the post-optimization step, the detailed design is considered where structural and operation variables are optimized. At the post-optimization step, for the simulations where 231 modules were considered, the UC slightly increases, but the TAC decreased. For the simulation where 1326 modules were considered, the UC and TAC decreased. Finally, the optimality gap between the LP solution at 1326 modules (126.0 $/h) and the best post-optimization solution (148.40 $/h) was 17.8%. There is always a gap with LP solution because this mathematical solution is unrealistic due to the complexity of connections between modules. Therefore, UC worsens as the solution is simplified and translated into a realistic process and when TIC is also considered in the optimization problem.
Data Availability and Reproducibility Statement

The numerical data from Figure 5 is summarized in an Excel file including the number of modules, $\varepsilon$, value of the objective function, material balance tolerance, and computation time. The numerical raw data from Figures 6 and 7 are available as Excel files including the intensive properties of modules, all needed input shown in Table 1, and all liquid, vapor, and heat flows connecting modules. The numerical data from Figure 8 is available in three .bkp files generated by Aspen Plus V11® and that from Figure 9 can be taken directly from those files. Finally, the numerical data from Figure 10 is available in a .bkp file generated by Aspen Plus V11®. All files supporting the data in figures are included as a .7z file in the Supplementary Material. The histograms in Figure S1 are generated only by taking all non-zero values of $L_{ij}$ and $V_{ij}$ from Excel files with the raw data.

5. Conclusions

This work proposed a new reformulation for the synthesis and intensification of distillation process for the separation of ternary mixtures. The proposed method consisted of five steps: module generation and superstructure formulation, optimization, solution interpretation, simulation and validation, and post-optimization. The separation of a Benzene Toluene and O-Xylene mixture was taken as case study to evaluate the performance of the proposed framework.

The synthesis problem proposes a superstructure formulation based on functional modules and it is reformulated as a linear programming problem. The mathematically optimal solution is an unknown distillation structure; therefore, an interpretation step is needed. Then, the interpretation was validated through process simulation. Finally, when the optimal structure is known, a stochastic optimization problem was implemented to find the optimal structural and operation variables. To ease the interpretation step, several guidelines were proposed. The obtained solutions were better than those obtained by previous methods. Also, our findings showed that it is not necessary to use too many modules to find optimal structures. The presented framework can be applied to the separation of any ternary mixture without loose of generality. Also, other types of modules can be added for the synthesis and intensification of distillation-based optimization process.

References


