Synthesis of Complex Thermally Coupled Distillation Systems Including Divided Wall Columns

José A. Caballero
Dept. Chemical Engineering, University of Alicante, Ap. Correos 99, 03080 Alicante, Spain

Ignacio E. Grossmann
Dept. Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

The design of thermally coupled distillation sequences explicitly including the possibility of divided wall columns (DWC) is described. A DWC with a single wall can be considered thermodynamically equivalent to a fully thermally coupled (FTC) subsystem formed by three separation tasks (a Petlyuk configuration in the case of three-component mixtures). It is shown how to systematically identify all the sequences of separation tasks that can produce configurations that include at least a DWC. Feasible sequences that explicitly include DWCs are enforced through a set of logical relationships in terms of Boolean variables. These logical relationships include as feasible alternatives from conventional columns (each column must have a condenser and a reboiler) to FTC systems (only one reboiler and one condenser in the entire system). A comprehensive disjunctive programming formulation for finding the optimal solution is presented. The model is based on the Fenske, Underwood Gilliland equations. However, the disjunctive formulation allows easily the use of any other shortcut, aggregated or even rigorous model without modifying much the structure of the model. Two illustrative examples illustrate the procedure. © 2012 American Institute of Chemical Engineers AIChE J, 59: 1139–1159, 2013
Keywords: distillation, thermally coupled distillation, mixed integer nonlinear programming problem, divided wall column, superstructure optimization, disjunctive programming problem

Introduction

Distillation is one of the most studied unit operations in chemical engineering. This effort is amply justified because distillation is the most widely used separation technique in process industries, and this trend is unlikely to change in the near future. To get an idea of the importance of distillation, Humphrey[1] estimated that in the United States there are 40,000 distillation columns in operation that handle more than 90% of separations and purifications. The capital investment for these distillation systems is estimated to be 8 billion US\$. Using data by Mix et al.,[2] Soave and Feliu[3] calculated that distillation accounts about 3% of the total US energy consumption, which is equivalent to 2.87×10^{18} J (2.87 million TJ) per year, or to a power consumption of 91 GW, or 54 million tons of crude oil.

The distillation research is motivated by its major limitations. Distillation columns use very large amounts of energy because of the evaporation steps involved. Typically more than half of the process heat distributed to a plant is dedicated to supply heat in the reboilers of distillation columns.[4] Unfortunately, this enormous amount of energy is introduced in the bottom of the column and approximately the same amount of energy removed in the top, but at significantly lower temperature, which renders a very inefficient process, but also one of the most effective, for separation mixtures. Although distillation research is often regarded as a mature area, periodically new discoveries in the design and/or operation renew the interest in distillation, because improvements can translate into very large economic benefits.

Renewed interest in thermally coupled distillation (TCD) appeared in the last 15–20 years, due the important potential savings in energy, with typical values around 10–40% (in some cases even larger) that have been reported[5–10] when compared to conventional distillation sequences. Although the interest in TCD is relatively recent, the first apparatus that uses TCD concepts was due to Wright in 1947,[11] although the theoretical basis of TCD was developed in the 1960s by Petlyuk et al.[12] Petlyuk et al. noticed that separation sequences using conventional columns (a single feed with two product streams, a condenser, and a reboiler) suffer from an inherent inefficiency produced by the thermodynamic irreversibility during the mixing of streams at the feed, top, and bottom of the column. This remixing is inherent to any separation that involves an intermediate boiling component and can be generalized to an *N*-component mixture. The theoretical studies developed by Petlyuk et al. showed that this inefficiency can be improved by removing some heat exchangers and introducing thermal coupling between columns. If a heat exchanger is removed, the liquid reflux (or vapor load) is provided by a new stream that is withdrawn from another column; in this way, it is possible

Correspondence concerning this article should be addressed to J. A. Caballero at caballer@ua.es.
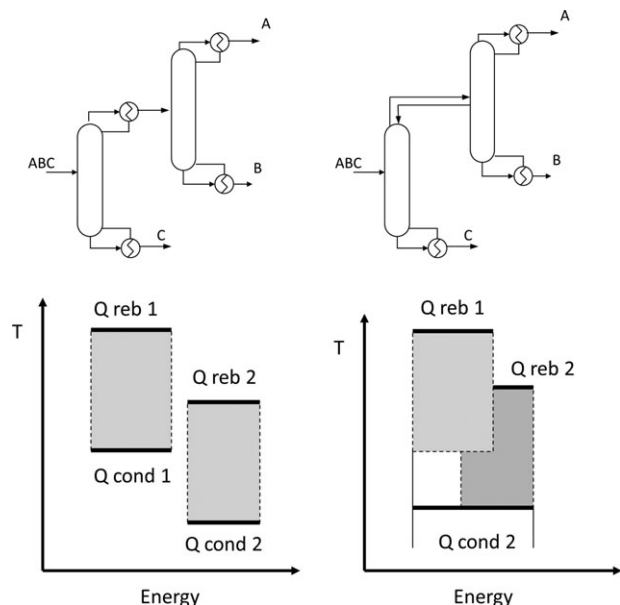
Figure 1. Sequence of conventional columns (left) and thermal couple (right) by removing the condenser in the first column.

to reduce the energy consumption, and under some circumstances, also the capital costs (see Figure 1). A fully thermally coupled (FTC) configuration is reached when the entire vapor load is provided by a single reboiler and all the reflux by a single condenser. Halvorsen and Skogestad[13–15] proved that the minimum energy consumption for an ideal *N*-component mixture is always obtained for the FTC configuration.

Despite the reduction in energy consumption, there is a price to be paid when using thermally coupled systems:

1. The energy must be supplied under the worst conditions, namely at the highest temperature in the reboiler, and removed at the lowest temperature in the condenser, preventing in most cases the use of lower cost utilities such as medium- or low-pressure steam.

2. When using conventional columns, it is common to constrain the alternatives to sharp separations. For example, in a three-component mixture (ABC), sorted by volatilities, we postulate initially separations A from BC (A/BC) and AB from C (AB/C). However, in FTC distillation, we introduce sloppy separations—an intermediate product is allowed to distribute along the column—and, therefore, we increase the number of column sections. This increase does not imply an increase in the number of columns, but usually an increase in the total number of trays. A detailed discussion on the number of column sections needed for a given separation can be found in Agrawal[16] and in Caballero and Grossmann.[5,6,17]

3. In FTC systems, the minimum vapor flow is that of the most difficult separation[14,15] and, therefore, some column sections will have large diameters.

4. Operation is also more difficult due to the large number of interconnections between the columns.

Therefore, it cannot be concluded that complex configurations are always superior, compared to sequences of simple columns. Instead, the optimum configuration will be dependent on the specific mixture and feed conditions.

Besides the energy savings in TCD, there are also possibilities of important investment savings. First, the reduction

in energy consumption is due to a reduction of the liquid and vapor flow rates, and therefore, the lower energy consumption, the smaller the diameters required for the distillation column. Second, an important saving in investment can be obtained by using divided wall columns (DWC). A FTC configuration for a three-component mixture, like that in Figure 2a, (also known as Petlyuk configuration in honor to F. Petlyuk, who discovered it) formed by two columns, can be rearranged in a single shell using an internal wall (as shown in Figure 2b). Both configurations in Figure 2, the Petlyuk and the DWC, are thermodynamically equivalent because all the flows, temperatures, and compositions are the same in both configurations. In practice, there are small differences due to the pressure differences needed to control the external streams in the Petlyuk configurations, but in a preliminary design these differences can be neglected. Detailed discussion about thermodynamically equivalent configurations can be found in the works of Caballero and Grossmann,[18] Agrawal and Fidkowski,[19,20] or Rong et al.[21,22] In this way, the separation of a three-component mixture that usually requires two distillation columns can be performed using a single column with an internal wall. The investment savings are evident because we are only using a single column, reducing the land requirements, the pumps, and piping. However, the design of TCD systems including DWC involving mixtures with more than three components is not straightforward and it is the objective of this work.

Depending on the number of distillation columns used to separate an *n*-component mixture into n product streams, the sequence can be classified as more than n-1 columns configurations, as exactly n-1 columns, and less than n-1 columns configurations.

For the case of zeotropic mixtures, sequences with exactly n-1 columns, named basic configurations by Agrawal,[23] are characterized by the following three features:

1. Mixtures (or states) with the same components are transferred only once from one distillation column to another.

2. A final product is obtained in a single location of the sequence

3. The feed stream and all the intermediate mixtures are split into exactly two product streams by two columns sections.

Configurations that violate the first two features that define a basic configuration and obey only the third one produce
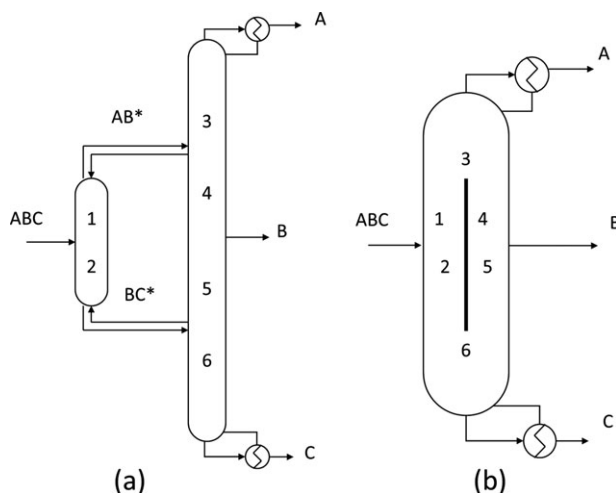

Figure 2. (a) Petlyuk configuration. (b) DWC.

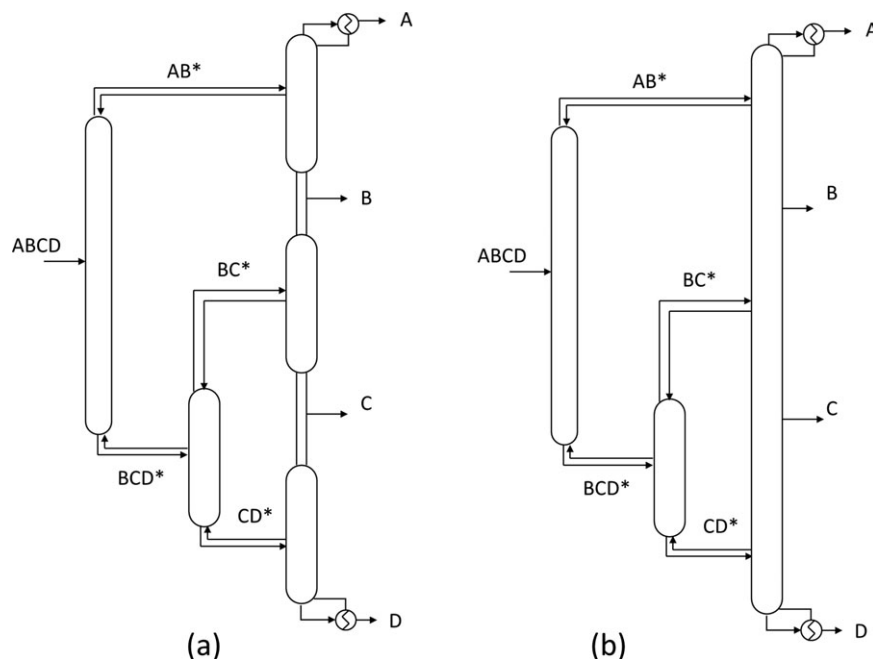Both are thermodynamically equivalent.

Figure 3. (a) Separation sequence using five columns and (b) one out of the 16 possibilities rearrangement using three distillation columns.

sequences with more than n-1 columns. These configurations, also referred as nonbasic, have higher operating cost than the best basic configuration.[6,24] Nonbasic configurations also tend to have higher capital cost due to the additional distillation columns, and, therefore, nonbasic configurations can be removed from the search space.

Configurations that violate the third feature have higher operating cost than the best basic configuration due to increased heat duty, especially for obtaining high purity products, (i.e., it is the case of trying to get near pure A, B, and C in a ABC mixture, using a single conventional column with a lateral sidestream with near pure B). However, the reduced number of columns in some situations could compensate the extra energy consumption. In the literature, some of these cases can be found, for example, those due to Brugma,[25] or Kaibel,[26] Kim and Wankat,[27] or Errico and Rong.[28] However, in this article, we focus only on basic configurations and we will study the case of fewer than n-1 columns sequences in a future work.

It is important to make some remarks on the previous features and classification.

1. Previous classification (sequences with less, exactly and more than n-1 columns) is referred to as configurations without internal walls.

2. Sequences obeying the three distinguishing features that define basic configurations can always be arranged into n-1 columns, although the total number of separation tasks can be larger. Consider the following example. We want to separate a four-component mixture ABCD where the components are sorted by decreasing volatilities (A is the most volatile component and D the least volatile). Assume we perform the following separation tasks: AB/BCD—that means separate A from CD letting the B component to be optimal distributed between distillate and bottoms—A/B; BC/CD; B/C and C/D. In this example, we can identify five separation tasks, and this sequence can be performed using five distillation columns, but this sequence can be easily arranged in

three distillation columns (see Figure 3). In fact, it can be rearranged in 16 thermodynamically equivalent configurations using three distillation columns.[18]

3. A sequence including DWC, or a single DWC like the one shown in Figure 2, is a thermodynamically equivalent configuration without walls that uses exactly n-1 columns and obeys the three distinguish features. In that sense, although strictly speaking DWC uses less than n-1 columns, it can be considered that DWCs are basic configurations.

As a final, any sequence of distillation columns can be rearranged in a single column using vertical partitions and various reboilers and/or condensers. In some situations, they can even be stacked using horizontal partitions. A detailed discussion is presented by Agrawal.[29] In this work, we do not consider those alternatives, but just the "classical" DWC with at most a single reboiler and a single condenser.

In this article, we propose a mathematical programming approach that takes the form of a mixed integer nonlinear programming problem (MINLP) or general disjunctive programming problem (GDP) to search for the optimal sequence among all the basic configurations, explicitly including DWCs. To accomplish this objective, we first develop a set of logic relationships that can be used in a mathematical programming environment in terms of Boolean (GDP) or binary (MINLP) variables that allow only feasible basic sequences and explicitly include DWCs. We will show that basic configurations do not take into account heat exchangers (reboilers and condensers) but in systems with DWCs these heat exchangers can be explicitly taken into account. Finally, several examples are presented.

Problem Statement

The problem addressed in this article can be stated as follows: given is a mixture of M components that do not form azeotropes. The objective is to generate the best sequence of distillation columns, including conventional, nonconventional,

and explicitly DWC to completely separate N ($N \leq M$) components.

With "complete separation," we are referring to the sharp separation of those N key components (i.e., high recovery of any of the M components). The rest of the components are allowed either to distribute in all the final streams to perform the separation with the minimum energy consumption, or if the components are previously classified by groups (i.e., C3s, C4s, etc.), the separation is performed in such a way that all the components in a group exit from the system all together. In any case, the nonkey components do not add complexity to the system, and therefore, without loss of generality we can assume that we have an N-component mixture that must be separated into their N pure components.

Finally, although we are assuming a final sharp separation between all the key components, this does not exclude some sloppy separations (a component is distributed among distillate and bottoms) in any of the intermediate columns.

Logic Approach to TCD Sequences with DWCs

As pointed out in the introduction, a sequence of distillation columns that includes conventional, thermally coupled, and DWC, must include the space of all the basic configurations (recall that a DWC can be considered as two columns sharing a single shell). The first rule based algorithm for generating the full set of basic configurations was proposed by Agrawal.[23] Following this line, later Ivakpour and Kasiri[30] proposed a formulation in which distillation configurations are presented mathematically as upper triangular matrices. Independently, Shah and Agrawal[31] presented an alternative matrix formulation in which distillation configurations are generated by exploring all possible instances of the presence or absence of transfer streams. This last approach is very efficient for generating the full set of basic configurations. All these rule-based approaches have proved to be effective when generating alternatives, but the enumeration of all the alternatives is, except in the case of a reduced number of possibilities, an inefficient strategy. Although these approaches can be easily adapted for metaheuristic optimization (i.e., genetic algorithms, Particle Swarm Optimization, etc.), it is not clear how to adapt them to a deterministic mathematical programming formulation.

Based on the observations in the seminal paper by Agrawal,[16] Caballero and Grossmann[5,6,17] proposed a complete set of logical rules in terms of Boolean variables that implicitly include all the basic column configurations. These logical equations can be transformed into linear equations in terms of binary variables, and integrated in a mathematical programming formulation. The objective in those works was not to generate explicitly all the basic configurations but to develop a set of logic equations that ensure a strong relaxation when solving the resulting MINLPs that include all the performance equations of the distillation columns, for extracting the optimal configuration without an explicit enumeration of all the alternatives. It is interesting to note that Shah and Agrawal[31] proposed a valid set of equations in terms of binary variables that can be integrated in a mathematical programming framework. However, their focus was on checking quickly if a given alternative is a basic one (with excellent performance) and not when those equations are integrated with the model of the columns in a mathematical programming framework (i.e., some of their equations can be obtained from the aggregation of some of the logic

relations presented by Caballero and Grossmann,[5,6] and therefore, a worse relaxation is expected).

If we try to synthesize a sequence of distillation columns, the concept of basic configuration is not enough. Consider, for example, the Figures 4a–c. These three sequences of columns correspond to the same basic sequence. The difference between Figures 4a and b is that they differ in the existence of the internal heat exchangers. An internal heat exchanger is a condenser or reboiler associated to any internal mixture. In other words, a heat exchanger associated to a stream connecting two different columns. Note that the final heat exchangers, that are associated to final products, are the same in the three configurations of Figure 4. In general, a given basic configuration can differ in the existence or not of internal heat exchangers, but the heat exchangers associated to final products are the same. A detailed discussion about this point can be found in the work by Caballero and Grossmann.[6] In the case of Figure 4c, it is not so obvious that this configuration corresponds to the same basic configuration. But if we look at the sequence of separation tasks, we observe that the three sequences are performing the same sequence of tasks (see Figure 4d). Figures 4b, c are thermodynamically equivalent.

Figures 4a, b are the same basic configuration but are not equivalent. One would expect that their behavior (and the total cost) be similar in both configurations, but the different structure of internal heat exchangers can produce important differences; that is, it is known that given a basic configuration the arrangement in columns with minimum energy consumption is that with the maximum possible thermal coupling (that arrangement without internal heat exchangers). However, this reduced numbers of heat exchangers must provide vapor flow to the entire system, and therefore, it is likely that some column sections must be designed with larger diameters. So, the internal structure of heat exchangers is important and must also be optimized. Based on these observations, Caballero and Grossmann[5,6,32] proposed a sequential algorithm in which first the search was constrained to basic configurations with the maximum thermal coupling. Then for the best basic configuration obtained in the first step the structure of internal heat exchangers is optimized, and finally the optimal column rearrangement is performed taken into account the thermodynamically equivalent alternatives.

The sequential approach cannot guarantee the global optimal solution, but a good solution. However, DWCs introduce an important reduction in the investment costs, and therefore, the search space should not be constrained only to the basic configurations but to the internal structure of heat exchangers that must be simultaneously optimized. However, differences in thermodynamically equivalent alternatives are expected to be very small, mainly due to operational considerations, and therefore, thermodynamically equivalent configurations should not be included in the search space.

To develop a set of logical relationships that allow to generate TCD sequences with DWCs, we use the State Task Network (STN) formalism.[33,34] A state is a stream (or a set of streams) that are characterized by a minimum set of relevant features. These can be qualitative, that is, composition (ABC mixture inside some specifications), phase liquid or vapor, or quantitative if necessary. A task is a chemical or physical transformation between adjacent states (i.e., separate A from BC in a mixture ABC).
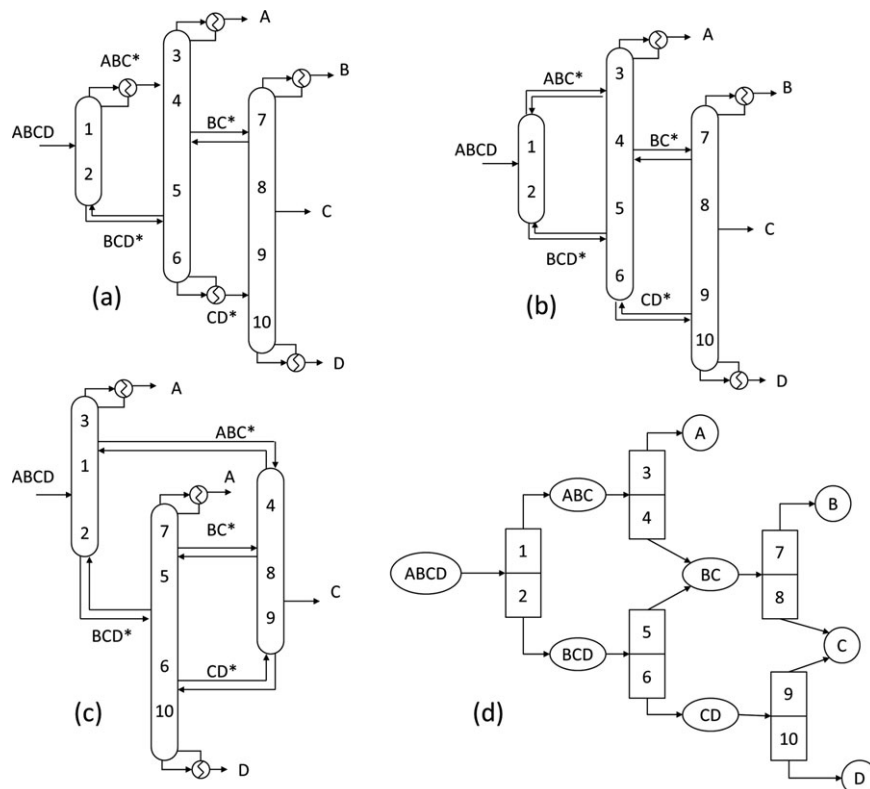
Figure 4. Three sequences of columns with the same basic sequence.

(a) And (b) differ in the internal heat exchangers and they are not equivalent. (b) And (c) are thermodynamically equivalents. (d) Sequence of separation tasks common to the three column arrangements.

In the case of TCD, it is interesting to note that a separation task is performed always by two column sections (a column section is a portion of a distillation column which is not interrupted by entering or exiting streams or heat flows). But these two column sections do not necessarily belong to the same final distillation column.[18]

Using the STN formalism, Caballero and Grossmann[5,6,17] presented a set of logical relations between separation tasks that ensure feasible sequences. The first step is then to extend those logical equations to take into account the possibility of including DWCs. For a detailed description of these logical relationships, the interested reader is referred to the original works. However, for the sake of clarity, an outline of those relationships is included in the Appendix.

It is important to note that exists a one-to-one relationship between the sequence of separation tasks and the states formed by those tasks. Therefore, we can take advantage of this relationship and express the logical relations to include DWCs in terms of states (instead of tasks). Although from a theoretical point of view it is possible to generate a multi-wall column that in the extreme case separates all the components in a single column, nowadays only columns with one wall have been built and operate, so we constrain ourselves to a maximum of one wall in a given column.

A DWC is formed by the union of three separation tasks or by four states: a feed state, the two states produced by the first separation task, and the intermediate product state. For example, Figure 5 shows the different sequences of states that produce DWCs in a five-component mixture.

To generate the logical relations that ensure that all alternative DWC are taken into account, it is necessary first to identify which combinations of states (or tasks) are able to generate a DWC. The next conditions assure that all the DWCs are taken into account:

1. All intermediate states (those that do not include a component with extreme volatility) can form part of a DWC; that is, according to the definition in previous paragraph, the States A and E cannot be part of the four states that define a DWC (see Figure 5).

2. The intermediate product state in the DWC must be produced by two different states; that is, in the Figure 5 (c1) State C is produced by BC and CD. In Figure 5b (c2), State C is produced by states ABC and CDE.

3. Each one of the two states that produce the intermediate product in the DWC must be generated by a single contribution; that is, in Figure 5.(c1), the two states that produce C are BC and CD. Both BC and CD are generated from a single state: BC from BCD and CD from BCD.

4. The state that generates intermediate states in the DWC must be produced by the same state; that is, in Figure 5.(c1) the two states that produce C are BC and CD. These two states are generated from the same state BCD. In Figure 5.c2, the two states that produce C are ABC and CDE; both, ABC and CDE are produced from ABCDE.

With the four previous rules, it is straightforward to generate all the possible DWC. For example, in a five-component mixture, there are 15 DWCs (three with B as intermediate product; four with C as intermediate product; three with D; two with BC; two with CD and one with BCD. see Figure 5).

To explicitly include DWC in a GDP or MINLP model, it is necessary to add some logical relationships that ensure the feasibility of the sequence. Therefore, to the set of logical rules previously developed by Caballero and
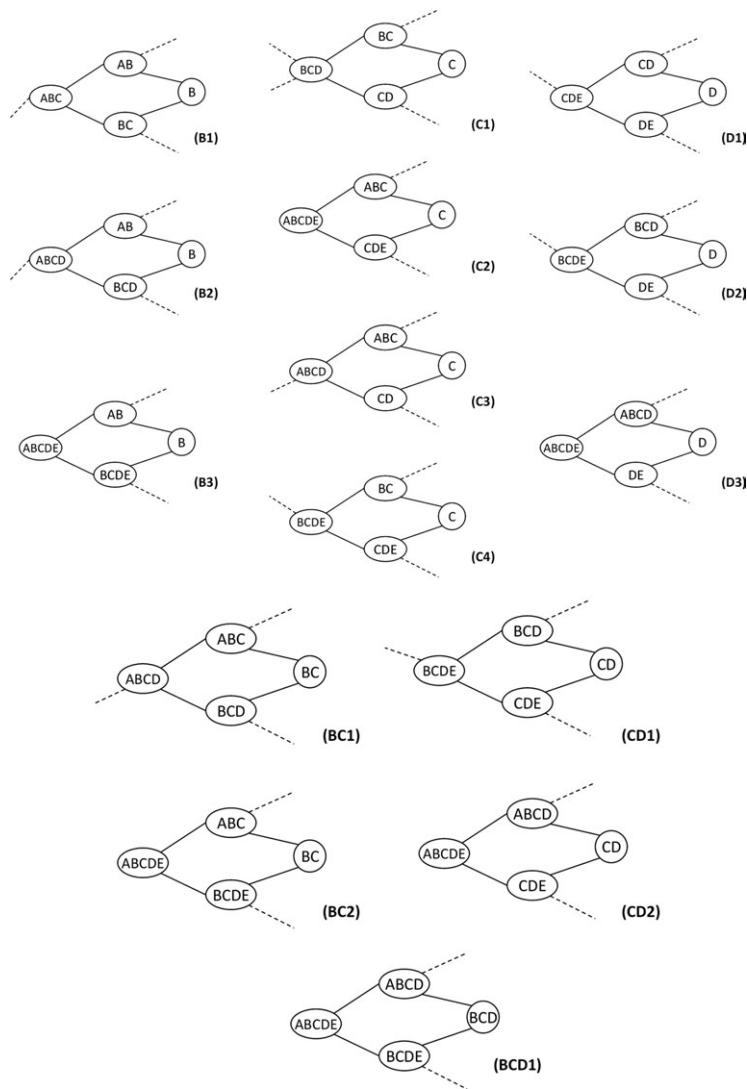
Figure 5. Sequences of states that can produce a DWC in a five-component mixture.

Grossmann[5,6,17]—see Appendix—we must add the logical relationships shown in next paragraphs.

First let us define the following index sets

DWC = {w | w is a DWC}; i.e., In a five-component mixture, one out of the 15 possibilities commented above.

STATES = {s | s is a state; i.e., A, B, C... AB, BC, CD... ABC, BCD, etc

$DWY_{w,s}$ = { States s that form part of the DWC w}

$DWN_{w,s}$ = {States that cannot appear simultaneously to the DWC w}

$INC_{w,s}$ = { Set of DWCs w sharing the state s}

$DWCINT_{w,s}$ = {internal states s that form part of the DWC w}

1) The first logical relationship simple relates the DWCs with the states

$$
\begin{aligned}
CW_w &\Rightarrow Z_s & \forall w, s \in DWY_{w,s} \\
CW_w &\Rightarrow \neg Z_s & \forall w, s \in DWN_{w,s}
\end{aligned}
\tag{1}
$$

where the Boolen variable CW_w takes the value true if the DWC w exists, and False otherwise. And the Boolean variable Z is True if the state s exists and zero otherwise.

2) If two or more DWCs share a state, at most one of those columns can be selected

$$
\text{at most one}_{w \in INC_{w,s}} (DW_w) \; \forall s \; \left(\sum_{w \in INC_{w,s}} dw_w \leq 1 \quad \forall s \right) \tag{2}
$$

For example, among the following configurations: B1; C1; C4; BC1; BC2—referred to Figure 5—that share the state BC we can select at most one.

3) Any heat exchanger associated to an internal state in a DWC must not be selected

$$
CW_w \Rightarrow \bigwedge_{s \in DWCINT_{s,w}} (\neg W_s) \tag{3}
$$

where the Boolean variable W_s makes reference to a heat exchanger associated to the state s.

One of the characteristics of this logic based approach is it flexibility for including any other constraints. For example, it is of interest not to allow thermally coupled between the DWC and the rest of the system. In other words, we can force to the DWCs to have reboiler and condenser, and maybe to force the feed to the DWCs to be a single stream.
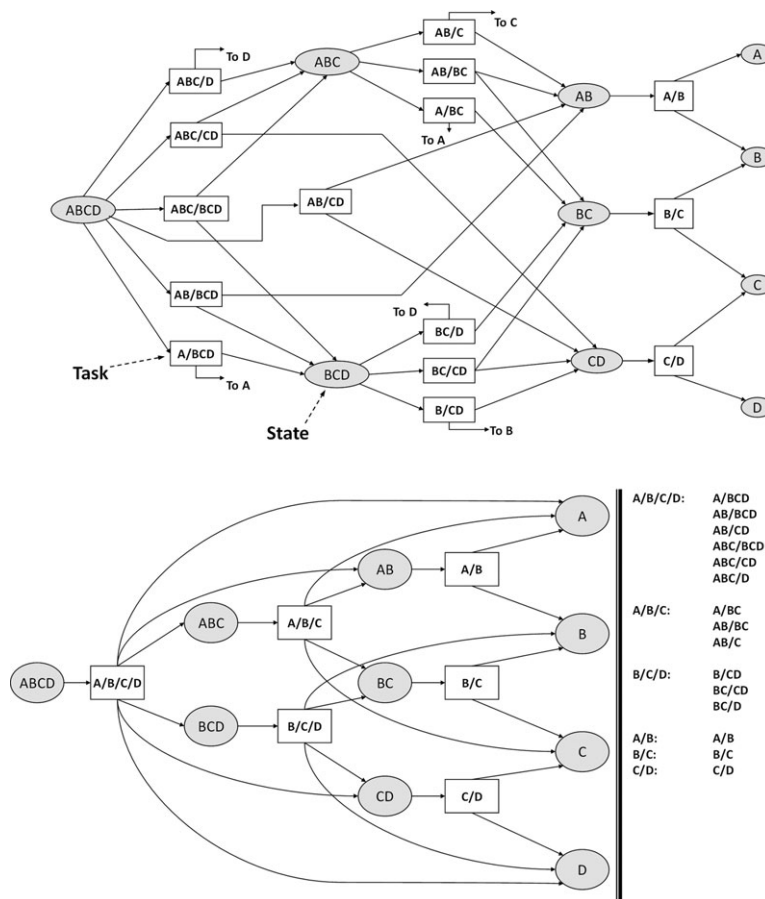
Figure 6. Two equivalent superstructures for a four component separation.

To do this, we add the following index set and constraint:

$DWCOND_{w,s}$ = { State s that form part of the DWC w and could have a condenser}

$DWREB_{w,s}$ = { State s that form part of the DWC w and could have a reboiler}

$$CW_w \Rightarrow WC_s \wedge WR_{ss} \quad s \in DWCOND_{w,s}$$
$$ss \in DWREB_{w,ss} \quad \forall w \in DWC \quad (4)$$

Model

In this section, we present a comprehensive description of the model. The first step is to generate a superstructure that includes all the alternatives. In this case, as indicated above, we will follow the STN formalism.[34] Generating the superstructure is straightforward: we only need to generate all possible separation tasks and all the states and join the tasks with the states that the task produces and vice versa. However, the visualization of this superstructure is not easy. Fortunately, there is a one to one relationship between the sequence of states and the sequence of separation tasks. Therefore, we will use only the states, only the tasks, or both to get the maximum clarity, (see Figure 6).

A separation task is formed by two column sections that are named, by similarity with conventional columns, rectifying and stripping sections. However, in the final configuration of the actual columns, these two sections are not necessarily placed in the same column. In that sense, we can consider a task as a pseudocolumn. (Figure 7 helps to clarify this point and shows some important variables used in the model).

In this work, we use the Underwood, Gilliland, Fenske equations[35,36] to calculate the minimum vapor flow rate (and minimum liquid flow rate) in each pseudocolumn (task). We use the following heuristics that at the same time simplify the problem:

a) The reflux ratio is assumed to be 1.2 times the minimum.

b) Each separation is performed assuming a fixed recovery of key components, typically greater than 0.95. In this way, it is possible to estimate *a priori* the minimum number of separation trays. According to the Fenske equation, the minimum number of trays is given by

$$N_{\min} = \frac{Ln\left[\left(\frac{x_i}{x_j}\right)_D \left(\frac{x_j}{x_i}\right)_B\right]}{Ln(\alpha_{i,j})} \quad (5)$$

where i and j make reference to the light key and heavy key components, respectively. Subscript D and B make reference to the distillate and bottoms streams, respectively, and α is the relative volatility of the light key respect to the heavy key.

If we write previous equation in terms of molar flow rates of key components, and taking into account that

$$f_i = d_i + b_i; \quad d_i = \varepsilon_i f_i; \quad b_i = (1 - \varepsilon_i)f_i \quad i \text{ is the light key}$$
$$f_j = d_j + b_j; \quad d_i = (1 - \varepsilon_j)f_j; \quad b_j = \varepsilon_j f_j \quad j \text{ is the heavy key}$$
$$(6)$$

$$D = V1-L1$$

V1
L1

Rectifying section

V1
L1

$$F_V$$

$$F_L$$

V2
L2

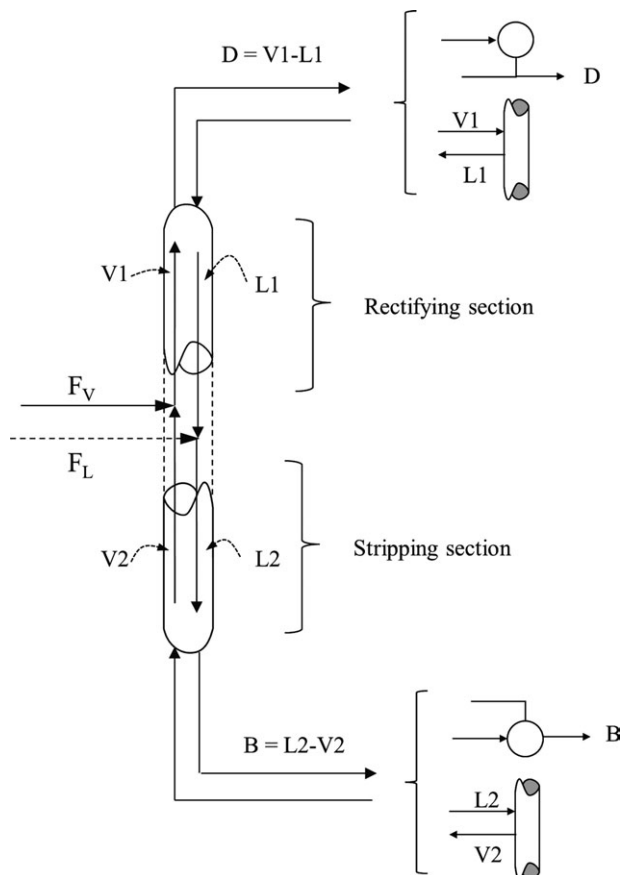Stripping section

$$B = L2-V2$$

L2
V2

Figure 7. Equivalence of a separation task with a pseu-docolumn.

Some relevant nomenclature is included for clarity.

Eq. 5 can be written as follows

$$N_{\min} = \frac{Ln\left[\left(\frac{x_i}{x_j}\right)_D \left(\frac{x_j}{x_i}\right)_B\right]}{Ln(\alpha_{i,j})} = \frac{Ln\left[\left(\frac{d_i}{d_j}\right)\left(\frac{b_j}{b_i}\right)\right]}{Ln(\alpha_{i,j})} = \frac{Ln\left[\left(\frac{\varepsilon_i}{1-\varepsilon_i}\right)\left(\frac{\varepsilon_j}{1-\varepsilon_j}\right)\right]}{Ln(\alpha_{i,j})} \tag{7}$$

c. The actual number of trays can then be calculated using the Gilliland correlation

$$\frac{N_{act} - N_{\min}}{N_{act} + 1} = 0.75\left[1 - \left(\frac{RR - RR_{\min}}{RR + 1}\right)^{0.5688}\right] \tag{8}$$

where RR is the reflux ratio. Using the heuristic that RR = $1.2 \cdot RR_{\min}$, the right hand side of the equation varies between 0.6 and 0.5 for minimum reflux ratios between 0.5 and 5. In this way, we do not introduce too much error if we assume a constant value around 0.53. Of course, the equation can be included in the model but this avoids including a nonlinear and nonconvex equation.

To develop the model, the following index sets must be defined:

1. TASK = {t | t is a given task}
   e.g. TASK= {(ABC/BCD), (AB/BCD), (ABC/CD), (AB/BC), (AB/C) (B/CD), (BC/CD), (A/B), (B/C), (C/D)}
2. STATES = {s | s is a state}
   e.g. STATES= {(ABCD), (ABC), (BCD), (AB), (BC), (CD), (A), (B), (C), (D)}

3. IM_S = {s | s is an intermediate state. All but initial and final products}
   e.g. IMS= {(ABC), (BCD), (AB), (BC), (CD)}
4. COMP = { i | i is a component to be separated in the mixture}
   e.g. COMP = { A, B, C, D}
5. FS_T = { t | t is a possible initial task; Task that receives the external feed}
   e.g. TASK {(A/BCD), (AB/BCD), (AB/CD), (ABC/BCD), (ABC/CD), (ABC/D)}
6. TS_s= {tasks t that the state s is able to produce}
   e.g. TS_{ABCD}= {(AB/BCD), (ABC/BCD) ,(ABC/CD)}
   TS_{ABC} = {(AB/BC), (AB/C)}
   TS_{BCD}= {(B/CD), (BC/CD)}
7. ST_s= {tasks t that are able to produce state s}
   e.g ST_{ABC} = { (ABC/CD), (ABC/BCD) }
   ST_{BCD} = { (AB/BCD), (ABC/BCD)}
   ST_{AB} = { (AB/BCD), (AB/BC), (AB/C) }
   ST_{BC} = { (AB/BC), (BC/CD) }
   ST_{CD} = { (ABC/CD), (B/CD), (BC/CD) }
8. $RECT_s$= {task t that produces state s by a rectifying section}
   e.g. $RECT_{ABC}$ = { (ABC/CD), (ABC/BCD) }
   $RECT_{AB}$ = { (AB/BCD), (AB/BC), (AB/C) }
   $RECT_{BC}$ = { (BC/CD) }
9. $STRIP_s$= {task t that produces state s by a stripping section }
   e.g. $STRIP_{BCD}$ = { (AB/BCD), (ABC/BCD) }
   $STRIP_{BC}$ = { (AB/BC) }
   $STRIP_{CD}$ = { (ABC/CD), (B/CD), (BC/CD) }
10. FP_s = {s | s is a final state (pure products) }
    e.g. FP = {(A), (B), (C), (D)} do not confuse with components, although the name is the same.
11. PRE_i = {tasks t that produce pure product i through a rectifying section}
    e.g. PRE_A = { (A/B) }
    PRE_B = { (B/CD), (B/C) }
    PRE_C = { (C/D) }
12. PST_i = { tasks t that produce pure product i through a stripping section}
    e.g. PST_B = { (A/B) }
    PST_C = { (AB/C), (B/C) }
    PST_D = { (C/D) }
13. UR = {r | r is Underwood root}
    e.g. {r1, r2, r3, r4}
14. AUR_t = {r is an active Underwood root in task t}
    e.g. $AUR_{A/BCD}$ ={r1}
    $AUR_{AB/BCD}$ ={r1,r2}
    $AUR_{ABC/BCD}$ ={r1, r2, r3}
    $AUR_{AB/CD}$ ={r2} etc.

The objective of the model is to minimize the total annualized cost. Therefore, the objective function is as follows

$$\min : TAC = \frac{r(1+r)^L}{(1+r)^L - 1}[\text{Capital costs}] + \text{Operating costs} \tag{9}$$

where the capital costs are annualized assuming a depreciation interval of $L = 8$ years in this work and an interest rate ($r = 0.09$ in this work −9%-). This corresponds to a capital charge factor of 0.18; that is, 18% of the capital costs are charged annually to cover interest on spent capital and depreciation. The rest of the model includes the following equations:

$$\begin{bmatrix} Y_t \\ F_t = D_t + B_t \\ f_{t,i} = d_{t,i} + b_{t,i} \ i \in COMP \\ V1_t = D_t + L1_t \\ L2_t = B_t + V2_t \\ F_t + V2_t + L1_t = V1_t + L2_t \\ F_t = \sum_{i \in COMP} f_{t,i} \\ D_t = \sum_{i \in COMP} d_{t,i} \\ B_t = \sum_{i \in COMP} b_{t,i} \\ \left. \begin{array}{l} \sum_{i \in COMP} \frac{\alpha_i f_{t,i}}{\alpha_i - \phi_r} = V1_t - V2_t \\ \sum_{i \in COMP} \frac{\alpha_i d_{t,i}}{\alpha_i - \phi_r} \leq V1_t \\ -\sum_{i \in COMP} \frac{\alpha_i b_{t,i}}{\alpha_i - \phi_r} \leq V2_t \end{array} \right\} r \in AUR_t \\ Task \ cost_t = f(V1, V2, L1, L2, \ldots) \end{bmatrix} \vee \begin{bmatrix} \neg Y_t \\ F_t = 0 \\ D_t = 0 \\ B_t = 0 \\ \left. \begin{array}{l} f_{t,i} = 0 \\ d_{t,i} = 0 \\ b_{t,i} = 0 \end{array} \right\} i \in COMP \\ V1_t = 0 \\ V2_t = 0 \\ L1_t = 0 \\ L2_t = 0 \\ Task \ cost_t = 0 \end{bmatrix} \qquad (D\text{-}1)$$

The second term of the disjunction ensures that if a task does not exist all the flows and costs are forced to be zero. Note also that the Underwood root (ϕ_r) is left free in that case.

The first five equations in the first term of the disjunction are, respectively, the total mass balance in the task, component mass balance in the task, mass balances in condenser, reboiler, and feed tray. The next three equations are Underwood equations and the last is to calculate the task cost.

Related to the Underwood equations, there are several important remarks to take into account:

The second and third Underwood equations are written as inequalities. The reason is that the original Underwood equations calculate the minimum reflux, or minimum internal vapor flows. But in a thermally coupled system, it is possible that some columns cannot operate at minimum (or 1.2 times the minimum) due to the vapor (and liquid) transfer between columns. Therefore, the "dominant" column will force the other to increase the vapor and liquid flows. Figure 8 clarifies this point.

In a TCD system is not correct to assume that the feed to a given column is liquid at its bubble point. In fact, if we connect the rectifying section of a task with another task through a thermal couple, these two streams are equivalent to a single superheated vapor stream whose flow is the net flow. If we connect the stripping section of a task with another task through a thermal couple, these two streams are equivalent to a subcooled liquid stream (a detailed discussion can be found in the works by Carlberg and Westerberg[37,38] and Navarro et al.[39]). This fact is explicitly taken into account in the model because we maintain the two streams (liquid and vapor) that form a thermal couple, instead of calculating the equivalent thermal state of the feed. Usually, the right hand side of the first Underwood equation is written in terms of the feed thermal state as follows
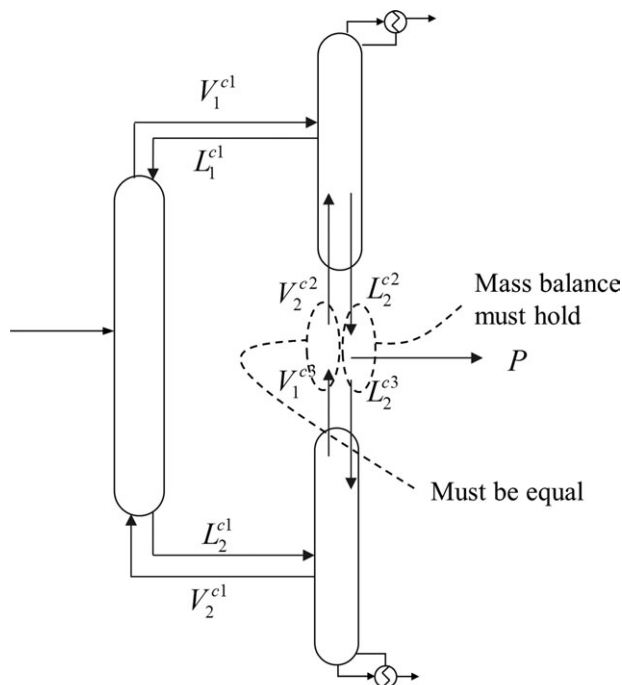
Flows in column 2 or/and column 3 must be adjusted to assure that:

$$V_2^{c2} = V_1^{c3} \ ; \ L_2^{c2} = L_1^{c3} + P$$

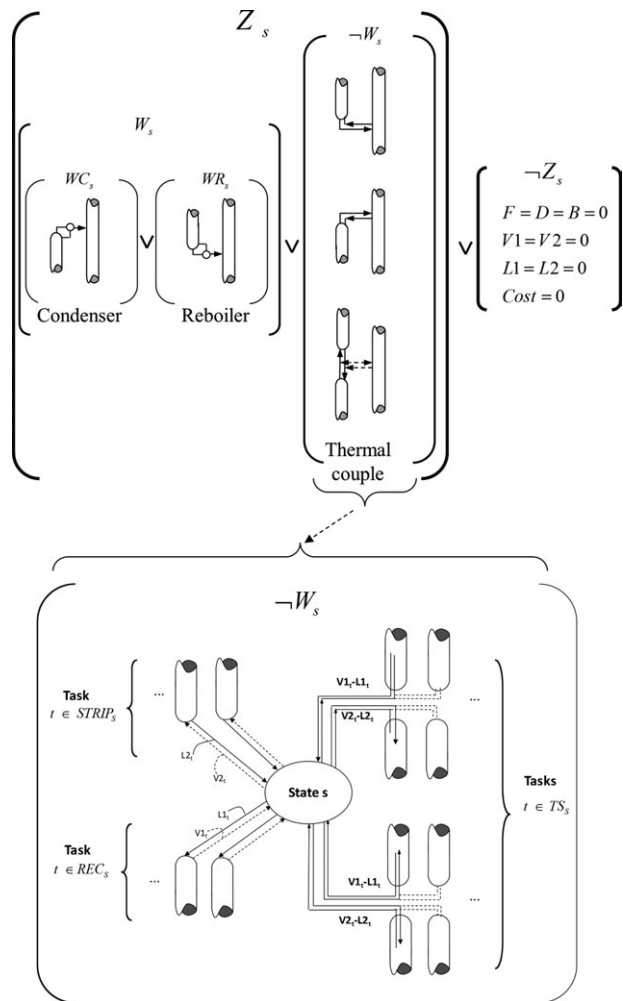**Figure 8. Example of how the flows in some sections must be modified to satisfy the mass balances.**

Figure 9. Conceptual graphical description of disjunction D-2 (see text).

$$\sum_{i \in COMP} \frac{\alpha_i f_i}{\alpha_i - \phi_r} = F(1 - q) \qquad (10)$$

But a simple mass balance in the feed tray (see Figure7) allows removing the variable q (liquid fraction), and at the same time to remove a nonlinear and nonconvex term

$$V1 = F_V + V2$$
$$L2 = F_L + L1 \qquad (11)$$
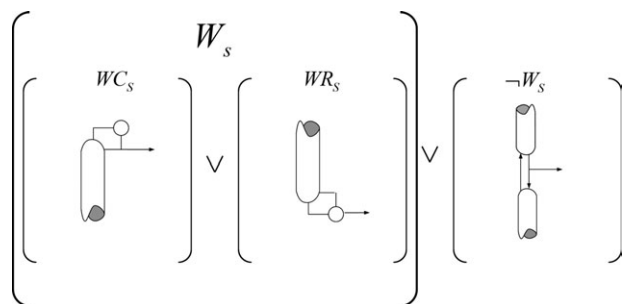
the liquid fraction is defined as

Figure 10. Conceptual graphical representation of disjunction D-3 (see text).
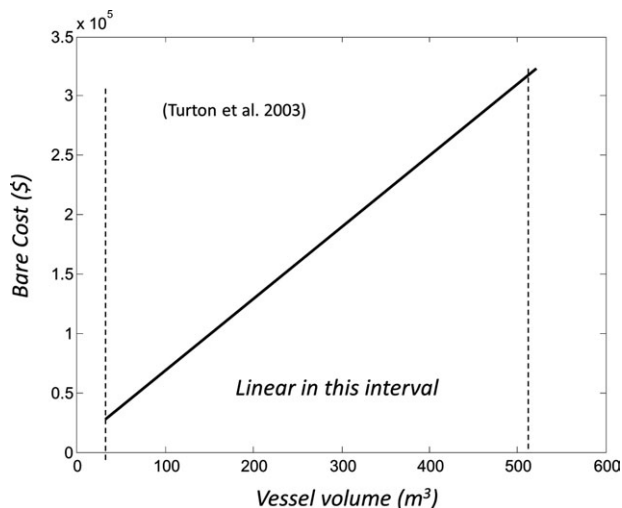
Figure 11. Bare cost module of the vertical vessel as a function of its volume.

$$q = \frac{F_L}{F} = \frac{L2 - L1}{F}; \quad \text{or} \quad 1 - q = \frac{V1 - V2}{F}; \qquad (12)$$

and, therefore,

$$F(1 - q) = V1 - V2 \qquad (13)$$

It is worth noting also that the previous disjunction does not take into account the existence or not of heat exchangers (reboiler and/or condenser). In other words, the task requires reflux and a vapor load streams, but for the disjunction it is not relevant where those streams come from (i.e., from a heat exchanger of from a thermal couple).

Connectivity equations and equations related to the existence or not of a given state

Connectivity equations are flow relations between tasks. They can be modeled by admitting that a state generates a mixer and a splitter. The connectivity equations depend also on the existence or not of a heat exchanger. If a heat exchanger does not exist, the connectivity between two tasks must also take into account the transfer of vapor and liquid streams that form a thermal couple.

Mass Balance in the Feed to the System

$$F_0 = \sum_{t \in FS_t} F_t$$
$$f_{0i} = \sum_{t \in FS_t} f_{t,i} \qquad (14)$$

Intermediate States: Mass and Energy Balances and Cost Calculations. In disjunction D2, the variable Z_s takes the value true if the state s exists and false otherwise. It is important to recall that there is a one-to-one relationship between a sequence of tasks and a sequence of states. Therefore, the introduction of the new Boolean variables Zs do not increase the combinatorial complexity of the model. Even more, if the problem is solved using a MINLP reformulation, it is necessary to define as binary variables those that are either related to tasks, or those that are related to states (the other can be defined as a continuous variables bounded between 0 and 1). The logical relationships will force the other set of variables to take the correct integer values. (see Appendix).

Component	Feed Composition (mol fraction)	$\alpha_{i,j}$*	ΔH_{vap} (kJ/mol)	MW
(A) Benzene	0.3	10.5	30.77	78
(B) Toluene	0.2	4.04	33.19	92
(C) Ethylbencene	0.1	1.76	35.58	106
(D) Styrene	0.2	1.31	36.83	104
(E) α-Methyl styrene	0.2	1	38.30	118
Total flow		200 kmol/h		
Pressure		0.1 atm		
Steam cost		5.00 \$/GJ (8000 h/year of operation)		
Cold water cost		0.19 \$/GJ		
Recovery		0.98 of light and heavy key in each separation		

*Relative volatility of component i, with respect to the heaviest one [α-methyl styrene (component j)].

The second term in the main disjunction (when the Boolean Zs takes the value of false) is introduced for the sake of completeness, but it is redundant. Note that if a given state does not exists, the logical relationships will force that all the tasks that could be generated by the state, and all the tasks that could generate the state, do not exist as well. Therefore, the second term in disjunction D-1 also forces the variables related with those tasks to be all zero.

The disjunction inside the first term in D-2 is related to the existence or not of a heat exchanger in a state (if Ws is True heat exchanger is selected). Again, it is worth noting that there is a one-to-one relationship between assigning heat exchangers to states or to tasks. The logical relationships
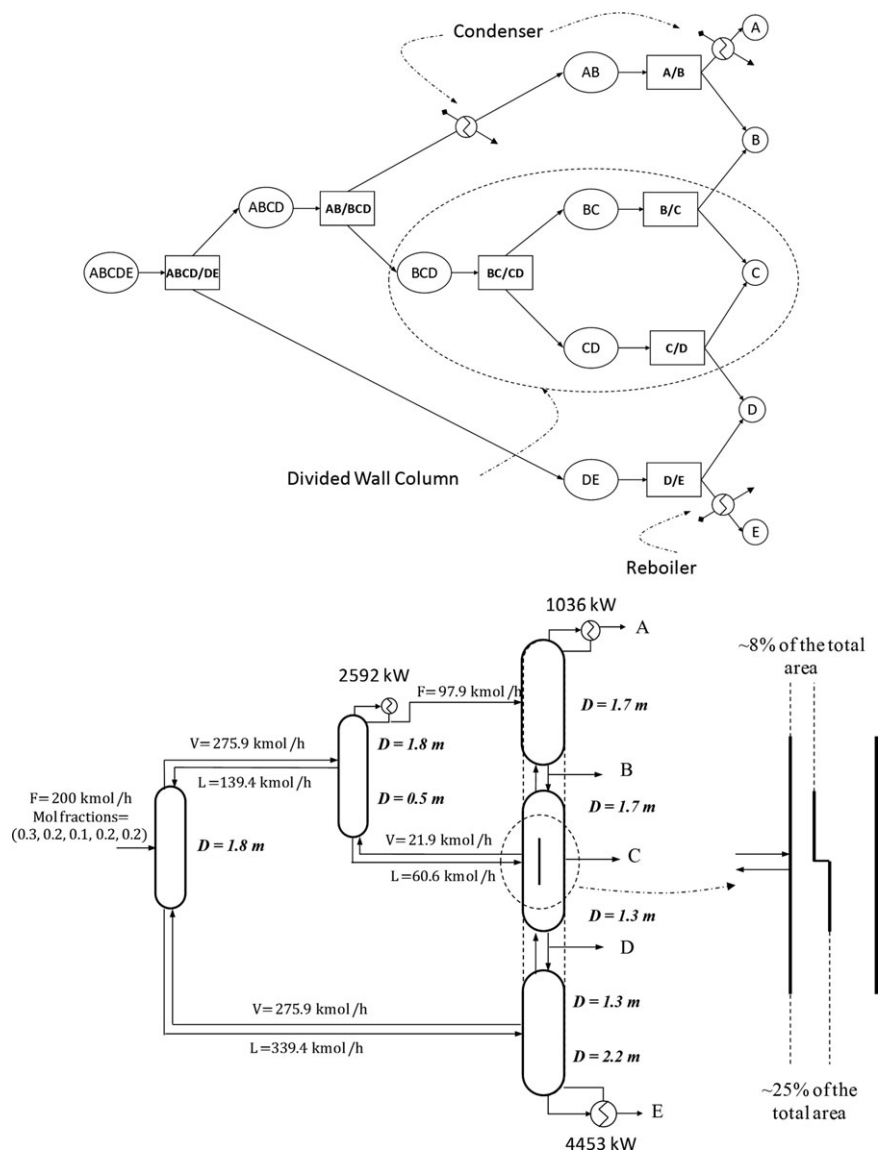

Figure 12. Best solution for Example 1 (Sol 1.1).

Sequence of tasks and states and one out of the four thermodynamically equivalent possible arrangements in actual columns.

force that if one is selected (i.e., tasks), the corresponding correct state is selected and vice versa. If the heat exchanger is selected, the equations are different depending on whether the heat exchanger is a condenser or a reboiler. The inner most disjunction (those related to WCs—True if heat exchanger is a condenser—or WRs—True if heat exchanger is a reboiler) includes the energy balance in condenser or reboiler and the cost equations.

If the heat exchanger does not exist ($\neg W_s$), but the state exists, then we have a thermal couple. Equations inside this term of the disjunction are simply mass balances to ensure the correct liquid and vapor flow transfer between columns.

Figures 9a,b show a conceptual graphical description of disjunction D-2 that helps to understand the meaning of each term.

$$
\left[
\begin{array}{c}
Z_s \\
\sum_{t\in TS_s} F_t - \sum_{t\in RECT_s} D_t - \sum_{t\in STRIP_s} B_t = 0 \\
\sum_{t\in TS_s} f_{t,i} - \sum_{t\in RECT_s} d_{t,i} - \sum_{t\in STRIP_s} b_{t,i} = 0 \quad i\in COMP \\[2mm]
\left[
\begin{array}{c}
W_s \\
\left[\begin{array}{c} WC_s \\ QCond_t\, D_t = \sum_{i\in COMP} H_i d_{t,i} V1_t \quad t\in REC_s \\ \text{Cost Cond}_t = f(QCond_t,\ Area) \end{array}\right]
\vee
\left[\begin{array}{c} WR_s \\ QReb_t\, B_t = \sum_{i\in COMP} H_i b_{t,i} V2_t \quad t\in STRIP_s \\ \text{Cost Reb}_t = f(QReb_t,\ Area) \end{array}\right]
\end{array}
\right]
\vee
\left[
\begin{array}{c}
\neg\, W_s \\
\sum_{t\in TS_s}(V1_t - V2_t) - \sum_{t\in REC_s} V1_t + \sum_{t\in STRIP_s} V2_t \\
\sum_{t\in TS_s}(L1_t - L2_t) - \sum_{t\in REC_s} L1_t + \sum_{t\in STRIP_s} L2_t \\
QCond_t = 0 \quad t\in REC_s \\
QReb_t = 0 \quad t\in STRIP_s
\end{array}
\right]
\\[4mm]
\vee
\left[
\begin{array}{c}
\neg\, Z_s \\
F_t = 0 \quad f_{t,i}=0 \quad t\in TS_s \quad i\in COMP \\
D_t = 0 \quad d_{t,i}=0 \quad t\in RECT_s \quad i\in COMP \\
B_t = 0 \quad b_{t,i}=0 \quad t\in STRIP_s \quad i\in COMP \\
\left.\begin{array}{c} V1_t \\ V2_t \\ L1_t \\ L2_t \end{array}\right\} t\in TS_s \cup RECT_s \cup STRIP_s
\end{array}
\right] \quad s\in IM_s
\end{array}
\right] \quad (D\text{-}2)
$$

Final States: Mass and Energy Balances and Cost Calculations A final state is a state related with a pure product, or in general with a stream that leaves the system (the sequence of columns), and then these states must always exist. The most volatile product will always have a condenser and the heaviest a reboiler. However, the rest could have a condenser or a reboiler if it is produced by a single contribution, or no heat exchanger at all if produced by two contributions. In this last case, the internal liquid and vapor flows of at least one of the tasks that generate the state must be adjusted to satisfy the mass balances (see Figure 8). The following disjunction shows this situation. Figure 10 shows a conceptual representation of disjunction D-3.

$$
\left[
\left[\begin{array}{c} W_s \\ \left[\begin{array}{c} WR_s \\ \text{cost Reb} = \\ f(Qreb, Area) \end{array}\right] \vee \left[\begin{array}{c} WC_s \\ \text{cost Cond} = \\ f(Qcond, Area) \end{array}\right] \end{array}\right]
\vee
\left[\begin{array}{c} \neg W_s \\ \sum_{t\in PRE_s} V2_t = \sum_{t\in PST_s} V1_t \\ \sum_{t\in PRE_s} L2_t = \sum_{t\in PST_s} L1_t + P_s \end{array}\right]
\right] \quad \forall s\in FP_s \quad (D\text{-}3)
$$

Recovery of Final Products

$$
\sum_{t\in PRE_s} d_{i,t} + \sum_{t\in PST_s} b_{i,t} \geq rec_i f_{0,i} \quad \forall i\in COMP,\ s\in FP
$$

$$
\sum_{t\in PRE_s} D_t + \sum_{t\in PST_s} B_t = P_s \quad s\in FP \quad (15)
$$

where "rec" is the global recovery of each component typically between 0.95 and 0.999. In this way, we ensure the final desired sharp separation of each component.

Existence of a DWC

As discussed previously, a DWC is thermodynamically equivalent to a set of three FTC tasks (no internal heat exchangers). The presence or not of a condenser and a reboiler depends on the designer preferences or maybe to control considerations, but they are not strictly necessary. In any case, the only difference in the initial design is in the cost of the column. Note that any extra consideration related with the controllability, or even to the designer preferences, can easily be added through logical relationships or extra constraints.

The cost of a distillation column can be estimated by adding the costs of the trays (or the packing), the cost of the vessel, and the costs of heat exchangers (reboilers and condensers). Note that the existence or not of a heat exchanger does not depend on the existence of a task. Therefore, we
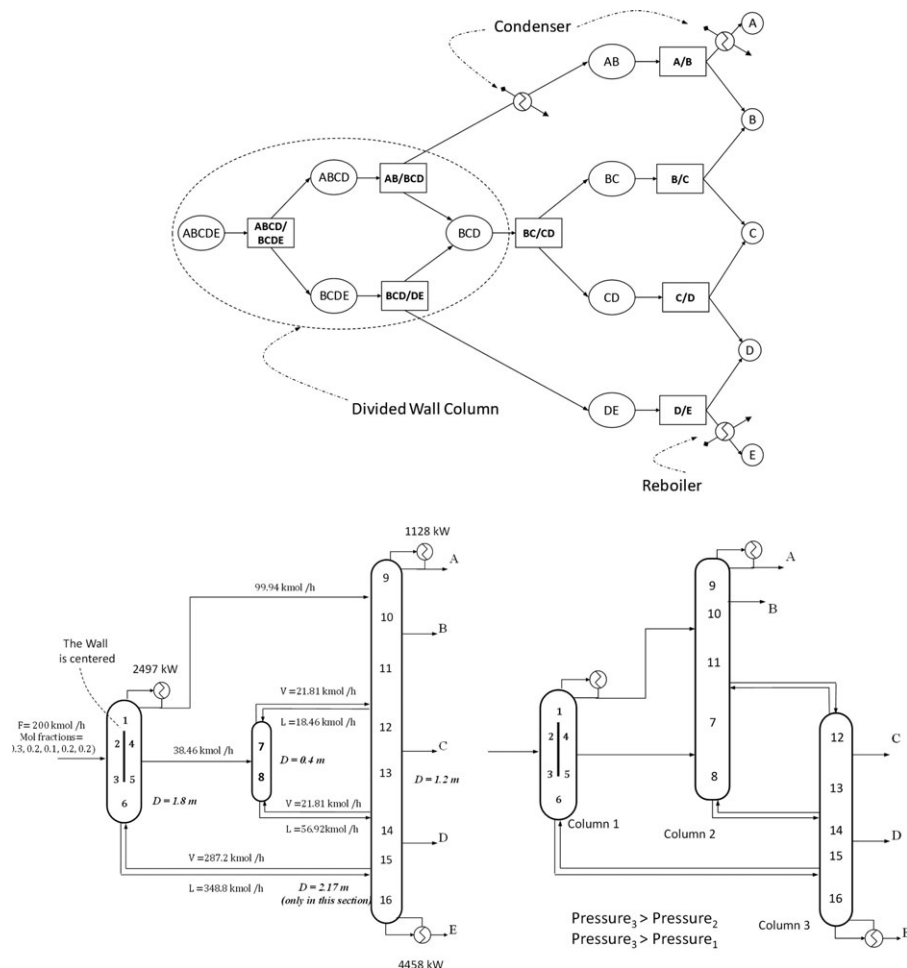
Figure 13. Second best solution for Example 1. (Sol 1.3).

Two possible arrangements in actual columns. At the left, the "most similar" to the sequence of task. In the right, a thermodynamically equivalent configuration without "reverse vapor" between columns.

can separate the vessels from the heat exchangers. It is worth remembering that a separation task can be considered as a pseudocolumn, so we can calculate the costs of trays as the addition of the costs of each task. If we want that the number of total trays in the sections that share a wall be the same in the two sides of the wall, the simplest possibility is to assume that the most restrictive situation is the dominant one. In other words, we can assume that the total number of trays in the zone of the internal wall is equal to the maximum trays in each part of the wall.

A different situation appears when we want to calculate the cost of the vessels that form the distillation columns. In general, consider a separation task as a column, and simply adding the costs of all the vessels, is not correct because the number of tasks can be greater than the number of actual columns. As mentioned above, independently of the number of tasks that form a sequence, all basic sequences can be arranged in N-1 columns. If we include the DWCs, the number of vessels decreases by one for each DWC introduced. The major difficulty in calculating the cost of the vessel is that we should know which column sections form a given column, but this is precisely something that we want to avoid because a given sequence of tasks could be rearranged in a large number of thermodynamically equivalent configurations.

A simple approach to solve this problem consists of taking advantage of the fact that according to Turton et al.[40] the

purchased cost of a vertical vessel varies linearly with its volume, see Figure 11.

$$C_p = C_f + C_v \, Vol. \quad (16)$$

where Vol is the vessel volume. Therefore, we can add the volume of all the vessels and taking into account that in a basic configuration there are (N-1) vessels minus the number of DWC the total cost of the vessels can be calculated as follows

$$\text{Total Vessels Cost} = (N-1)C_f - \sum_{w \in DWC} C_f CW_w + \sum_{t \in Task} Cv_t \, Vol_t \quad (17)$$

Before going into the examples, there are some interesting points about the proposed model.

The disjunctive model is reformulated as a MINLP problem, using a big-M formulation[41,42] and written in GAMS.[43] The problem can be solved using any standard solver. However, the nonconvexities and the large number of local solutions in this type of problem often lead to suboptimal solutions. Therefore, based on the following observations, it is possible to solve the model and get a very good solution, in most of the cases, the global optimal solution.
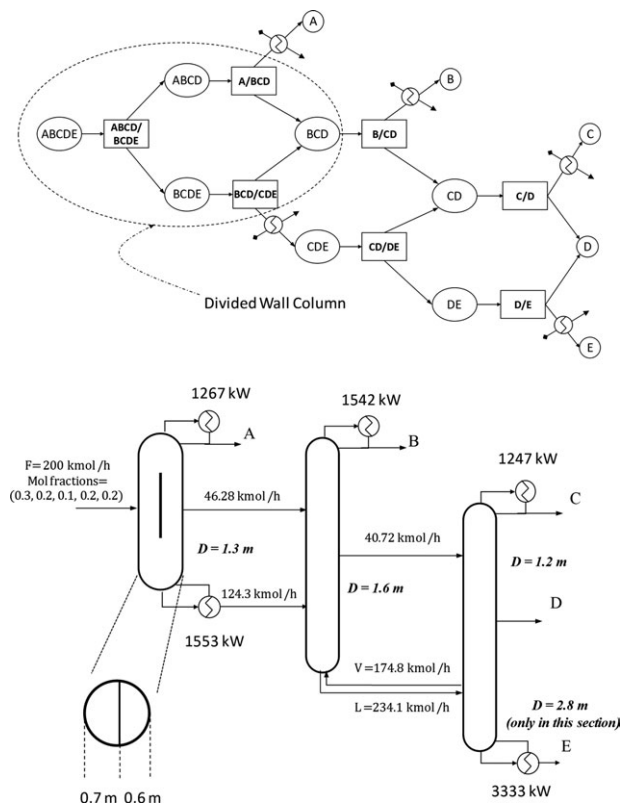
Figure 14. Best solution for Example 1 including a DWC that is not thermally coupled with the rest of the system (Sol 1.4).

a. Problems with a fixed topology (fixed binary variables) produce the optimal solution and rarely get trapped in local solutions. The same can be said for the resulting nonlinear problem (NLP) with a relaxation of the binary variables (we use the solver CONOPT[44] under GAMS). This fact can be checked comparing the results of the local optimizer with a deterministic global solver like BARON.[45]

b. For a fixed sequence of separation tasks (or states), the optimal solution tends to be a solution with a large degree of thermal couples in the internal states. In other words, the sequence without internal heat exchangers is likely to be near the optimal solution for that configuration. Remember that an internal heat exchanger is a heat exchanger associated to a stream—state—that connects two separation tasks. Heat exchangers associated to a final product (a stream that leaves the system) are fixed with the sequence of tasks.

Based on observation (a), a simple branch and bound based solver, that solves only NLPs in a tree search, like SBB[46] in GAMS, is expected to find a near global optimal solution, which in many cases we expect to be the global optimal solution. Note that although BARON is able to solve each of the nodes to global optimality, the CPU time is orders of magnitude larger than the CPU time used by a local solver, and therefore, from a computational point of view, using a global NLP deterministic optimizer inside the branch and bound search is prohibitive.

Decomposition techniques such as the Outer Approximation[47,48] or the Generalized Benders Decomposition[49] are another alternative. However, in this case, the master problem is very sensitive to the nonconvexities, cutting off important parts of the feasible region. As a result, we often get trapped in suboptimal solutions.

Figure 15. Best solution found using the heuristic algorithm in Example 1 (Sol 1.5).

Figure 16. Best solution for Example 1, using only conventional columns, "classical column sequencing" (Sol 1.6).

Table 2. Results and Model Statistics in Example 1

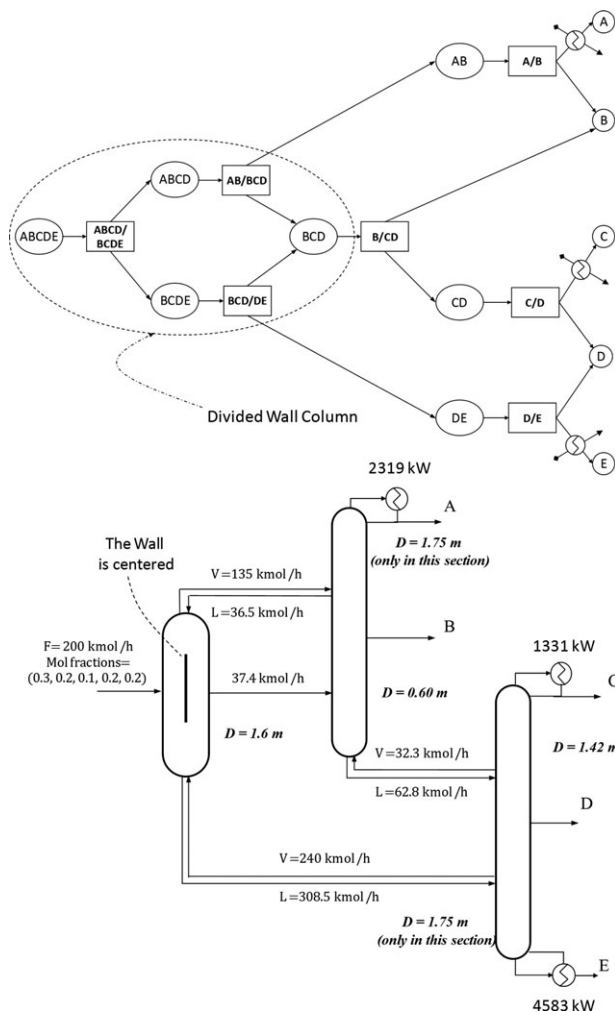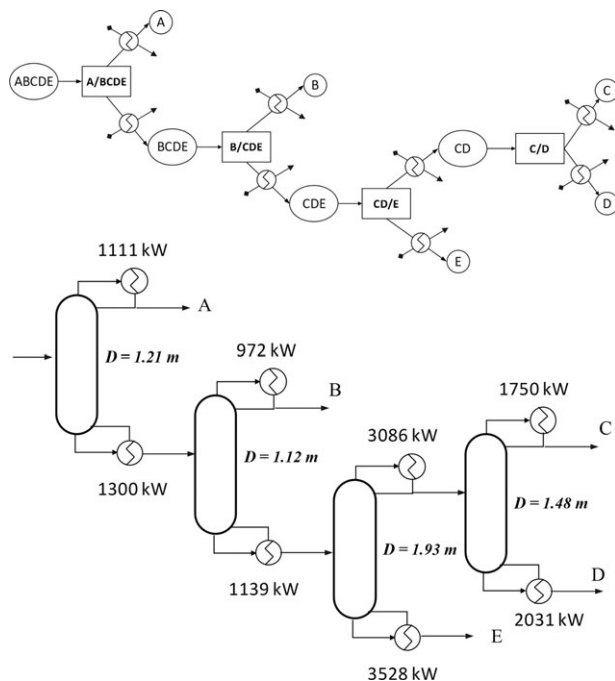|	Model					
	Sol 1.1	Sol 1.2	Sol 1.3	Sol 1.4	Sol 1.5	Sol 1.6
Total vessels cost (k$)	800.436	822.789	824.275	671.176	831.160	595.974
Total tray cost (k$)	252.165	252.165	258.261	222.114	253.896	184.000
Total reboilers cost (k$)	256.190	256.190	256.190	327.252	256.190	575.083
Total condensers cost (k$)	270.510	270.510	270.437	342.341	271.480	525.721
Total steam cost (k$/year)	642.000	642.000	642.000	700.800	642.000	1151.775
Total cooling water cost (k$/year)	19.851	19.851	19.836	22.192	19.973	37.860
Total Investment (k$)	1579.300	1601.654	1609.163	1562.883	1612.726	1880.778
TAC (charging factor = 0.18) (k$/year)	**946.134**	**950.149**	**951.485**	**1004.311**	**952.264**	**1528.175**
*Sequence of separation tasks**	ABCD/DE (38) AB/BCD^C (9) BC/CD (14) A/B^C (17) B/C (19) C/D (53) D/E$_R$ (58)	ABCD/DE (38) AB/BCD^C (9) BC/CD (14) A/B^C (17) B/C (19) C/D (53) D/E$_R$ (58)	ABCD/BCDE (7) AB/BCD^C (9) BCD/DE (28) BC/CD (14) A/B^C (17) B/C (19) C/D (53) D/E$_R$ (58)	ABCDE/BCDE (7) A/BCD^C (17) BCD/CDE$_R$ (12) B/CD^C (19) CD/DE (28) C/D^C (53) D/E$_R$ (58)	ABCDE/BCDE (7) AB/BCD (9) BCD/DE (28) B/CD (19) A/B^C (17) C/D^C (53) D/E$_R$ (58)	A/BCDE^C_R (17) B/CDE^C_R (19) CD/E^C_R (58) D/E^C_R (58)
DWCs (states in the DWC)[†]	BCD-BC-CD	No	ABCDE-ABCD-BCDE	ABCDE-ABCD-BCDE	ABCDE-ABCD-BCDE	No
CPU time (s)[†]	1727.8	1202.2	1658.2	257.6	222.0	3.4
No equations	3028	3207	3043	3208	3043 (2933)[‡]	1189
No continuous variables	1347	1347	1347	1347	1338 (1312)[‡]	661
Binary variables	65	65	65	65	56 (30)	20

Values in bold correspond to total annual costs that are the comparison parameter used in the text.
*Super-index C indicates a condenser in the task; sub-index R indicates a reboiler in the task. Number in parenthesis indicates the number of actual trays.
[†]Using SBB under GAMS in Windows 7; Processor Intel(R) Core(TM)2Q Quad CPU 2.40GHz 2.39 GHz; RAM 8.00GB.
[‡]Number out of the parenthesis correspond to the outer problem. Number in parenthesis correspond to inner problem.

Therefore, in this work, we solve the model using SBB. We sacrifice some computational performance to obtain a good solution.

Based on observation (b), it is also possible to develop a strategy that in most cases get a solution close to the best solution in a fraction of the CPU time. The algorithm is as follows:

1. Fix the value of all internal heat exchangers to False (zero).

2. Using branch and bound solve the resulting MINLP. Note that DWCs are allowed if we relax the condition that a DWC must have a reboiler and a condenser.

3. For the solution in Step 2, fix the sequence of tasks and determine the optimal distribution of internal heat exchangers. The solution of Step 3 is an upper bound to the optimal solution of the problem.

4. Repeat from Step 1 until in two consecutive iterations there is no improvement in the upper bound.

Of course, previous algorithm is based on a heuristics rule but numerical test have proved that usually get a solution very close to the optimal.

Example 1: Separation of a Mixture of Aromatic Hydrocarbons

This example illustrates some of the capabilities of the proposed model. Here, we present the separation of a five-component mixture (benzene, toluene, ethylbenzene, styrene, and alpha methyl styrene). All the relevant data for the problem are presented in Table 1. According to the previous comments in the paper, we constrain the search to basic configurations: the sequence of tasks and states can be rearranged in N-1 actual distillation columns. Each DWC reduces by one the number of actual columns. The model assumes that the possible polymerization of styrene is negligible by either controlling the temperature in the system (low pressure) and adding small amounts of inhibitors or retarders such as nitro derivatives, free radicals, and so forth. They can be added alone or in combination to take advantage of synergic effects. But in this example we consider their presence negligible.

Table 3. Data for Example 2

Component	Feed Composition (mol fraction)	$\alpha_{i,j}$*	ΔH_{vap} (kJ/mol)	MW
(A) n-hexane	0.1	17.5	29.00	86
(B) n-heptane	0.2	8.37	31.90	100
(C) n-octane	0.3	4.04	34.75	114
(D) n-nonane	0.3	1.99	37.29	128
(E) n-decane	0.1	1	39.63	142
Total Flow	200 kmol/h			
Pressure	1 atm			
Steam cost	5.00 $/GJ (8000 h/year of operation)			
Cold water cost	0.19 $/GJ			
Recovery	0.98 of light and heavy key in each separation			

*Relative volatility of component i, with respect to the heaviest one [n-decane j].
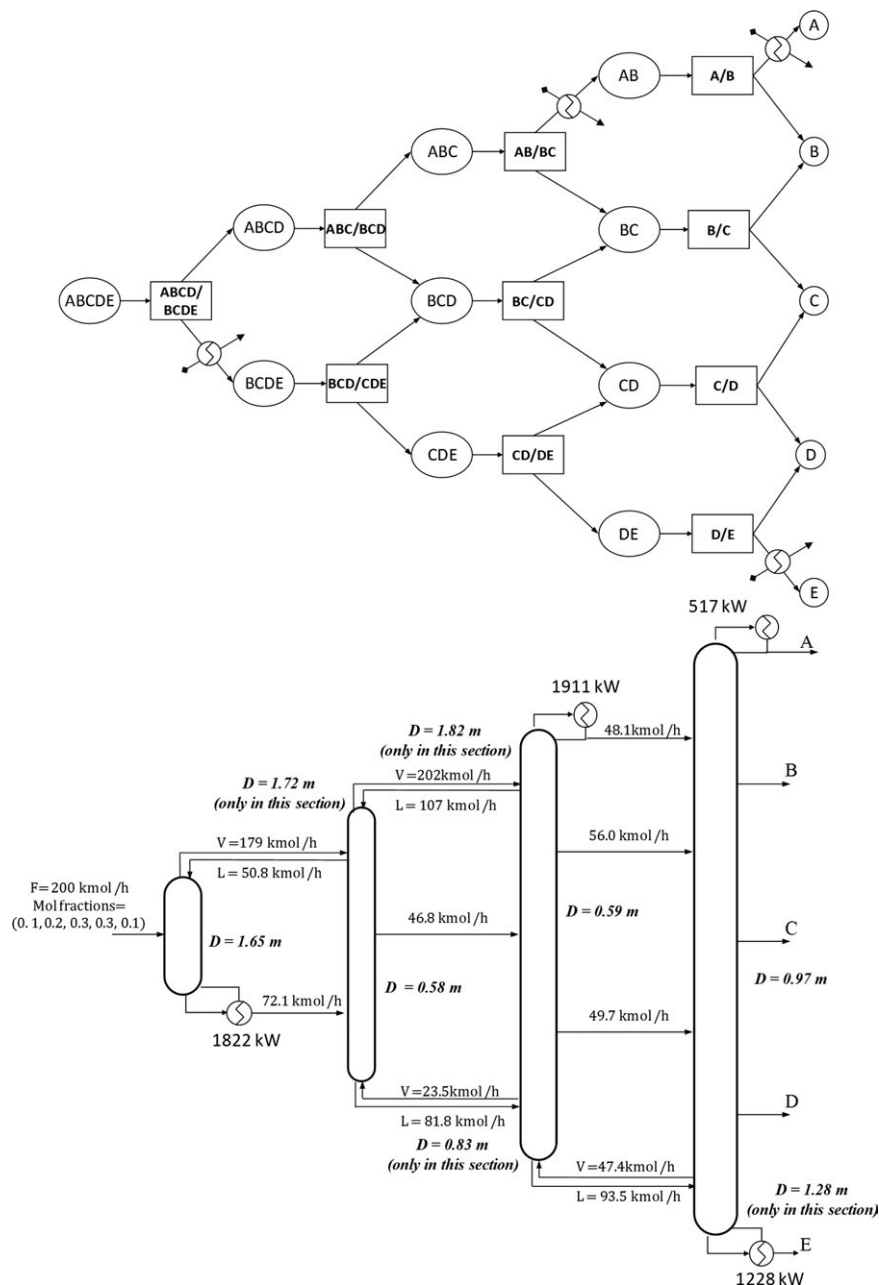
Figure 17. Solution in Example 2. (Sol 2.1).

First, we solve the model allowing all the thermal couples; that is, DWCs can be thermally coupled with the rest of the system. The best solution obtained (Sol 1.1) is shown in Figure 12, with a TAC of $946,130/year. The optimal solution includes a DWC formed by the following tasks (BC/CD; B/C, C/D). The arrangement in actual columns shown in Figure 12b is only one out of the four thermodynamically equivalent configurations that maintain the existence of the DWC. The solution obtained has two important issues related with the DWC. First, the areas in both sides of the DWC are very different, and second, the areas in the same side but different sections of the DWC are also very different. Although it is possible to build DWCs in which the wall is not centered, if the deviation is too large, hydrodynamic problems makes the DWC an invalid option. This drawback can be easily solved adding a constraint that forces DWCs to have similar areas in both sides of the wall (i.e., a maximum deviation around 20–30%). If we force the feed and the intermediate product to be saturated liquid, the vapor flow rate in different sections, but in the same side of the wall, will be equal and then the areas will also be similar. Including these constraints, the solution is the same in terms of states and tasks but without including DWCs. The total annual costs increases to $950,150/year (Sol 1.2).

In this first case, because the dominant cost is the energy, the optimal solution is almost a FTC configuration. It is remarkable, however, the presence of a heat exchanger (a condenser) in the task AB/BCD. Removing that heat exchanger and introducing a thermal link instead is likely to produce some decrease in the total energy consumption. However, the thermal links also produce an increase in the total vapor flow through the entire system increasing the diameters of some columns.

Figure 18. Best solution for Example 2 using the heuristic algorithm (Sol 2.2).

The cost correlations, the constant volatilities assumption, and some of the rules of thumb introduce some uncertainty in the model. Therefore, it is of interest to obtain not only the best

solution but also the set of solutions inside a given tolerance (i.e., 5%). This set of solutions should be evaluated with detail using rigorous models. As an example, the Figure 13 shows the second best solution (Sol 1.3) with a TAC of $951,500/year that is only 0.5% more expensive than the best configuration. In this case, the optimal solution includes a DWC.

Here, it is important to remark that the optimal solution obtained in the model is a sequence of tasks and not a configuration in actual columns. To get the optimal configuration in actual columns, the designer must select the optimal among all the thermodynamically equivalent configurations taking into account other considerations. One of the more important is related to the controllability; in particular, it is highly desirable that the vapor flows always from columns with higher to lower pressures to avoid the use of compressors and control the vapor flows just with valves. Fortunately, Caballero and Grossmann,[18] in a previous paper showed that for a given sequence of tasks with thermal couples it is always possible to get at least a configuration in actual columns (and in general more than one) in which the reverse vapor flow is avoided. As an example in Figure 13a, thermodynamically equivalent configuration with that characteristic is included. In the rest of the article, and for the sake of clarity, we will show the configuration in actual columns more similar to the sequence of separation tasks, but in all the cases, it is possible to get a thermodynamically equivalent configuration in which the vapor flows always from higher to lower pressures. Detailed algorithms of how generating all the possible alternatives with this characteristic can be found in the work of Agrawal[19] or in the previously mentioned work by Caballero and Grossmann.[18]

In both solutions (Sol 1.1 and Sol 1.3), the DWCs are extensively thermally coupled and integrated with the rest of the system. It is also of interest to force the DWCs to be not thermally coupled with the rest of the system (the DWC must have a condenser and a reboiler). This can be done by adding logical constraints (eq. 5). If we do that, and force the existence of at least a DWC, the optimal solution is shown in Figure 14 (Sol 1.4). The TAC increases to $1,004,453/year (6% more expensive).

Figure 19. Best solution for Example 2, using only conventional columns, "classical column sequencing" (Sol 2.3).

Table 4. Results and Model Statistics in Example 2

	Model					
	Sol 2.1		Sol 2.2		Sol 2.3	
Total vessels cost (k$)	413.994		468.127		361.006	
Total tray cost (k$)	123.810		135.268		96.383	
Total reboilers cost (k$)	244.198		192.704		477.674	
Total condensers Cost (k$)	215.735		266.341		438.680	
Total steam cost (k$/year)	439.376		442.061		844.981	
Total cooling water cost (k$/year)	13.290		13.081		27.442	
Total investment (k$)	997.737		1062.440		1373.743	
TAC (charging factor = 0.18) (k$/year)	**632.258**		**646.381**		**1119.697**	
Sequence of separation tasks*	$ABCD/BCDE_R$	(6)	$ABCD/BCDE$	(6)		
	ABC/BCD	(8)	ABC/BCD	(8)		
	BCD/CDE	(8)	A/BC^C	(22)	AB/CDE^C_R	(22)
	AB/BC^C	(11)	BC/CD	(11)	C/DE^C_R	(22)
	BC/CD	(11)	CD/DE	(12)	A/B^C_R	(22)
	CD/DE	(12)	B/C^C	(22)	D/E^C_R	(23)
	A/B^C	(22)	C/D	(22)		
	B/C	(22)	D/E_R	(23)		
	C/D	(22)				
	D/E_R	(23)				
DWCs (states in the DWC)	No		ABCDE- ABCD- BCDE		No	
CPU time (s)[†]	1673.7		225.1		2.4	
N° equations	3043		3043 (2933)[‡]		1189	
N° continuous variables	1347		1338 (1312)[‡]		661	
Binary variables	65		56 (30)		20	

Values in bold correspond to total annual costs that are the comparison parameter used in the text.
*Super-index C indicates a condenser in the task; sub-index R indicates a reboiler in the task. Number in parenthesis indicates the number of actual trays.
[†]Using SBB under GAMS in Windows 7; Processor Intel(R) Core(TM)2Q Quad CPU 2.40GHz 2.39 GHz; RAM 8.00GB.
[‡]Numbers out of the parenthesis correspond to the outer problem. Numbers inside the parenthesis correspond to inner problem.

All previous models take between 20 and 30 min of CPU time to solve (using SBB under GAMS version windows 7, 64 bit in a machine with a processor Intel Core2 Quad 2.40 GHz and 8 GB of RAM). If instead of using a branch and bound search over the original model, we use the heuristic algorithm proposed in previous section (maintaining the constraints to assure feasible walls) we obtain a solution involving a DWC with a TAC $952,270/year (Sol 1.5)—see Figure 15—just a 0.08% larger than the best solution in only 3.7 min of CPU time.

It should be noted that there are a relatively large number of alternatives with similar TAC, but important structural differences, which adds an extra degree of freedom that can be used to select a good alternative taking into account other considerations (controllability, environmental considerations, etc.).

The potential of TCD is clear if we compare it to the optimal solution using conventional columns (each column is forced to have a condenser and a reboiler) and sharp separation in each column—classical column sequencing-. The optimal configuration in this case is shown in Figure 16, (Sol 1.6) with a TAC $1,528,174/year which is 61.5% more expensive!

Finally, to establish the numerical performance or the model and solution algorithms, Table 2 shows some statistics about the models.

Example 2: Separation of a Mixture of Linear Hydrocarbons

In this example, we separate a mixture of five linear hydrocarbons (from n-hexane to n-decane) in which the relative volatilities between two consecutive components is similar, and the separations are easier than in the previous example. Table 3 shows all the relevant data of this problem.

In this case, the optimal solution has a TAC of $632,258/year (Sol 2.1) and includes the maximum number of column

sections[16] [N(N+1)]. Also it is almost a FTC configuration with only an internal condenser in state AB and an internal reboiler in state BCDE, (see Figure 17). In this example, the flows between internal states with two contributions (BCD, BC, CD) have been forced to be saturated liquid. Although from a theoretical point of view, we can save some energy allowing thermal couples in this situation; this could produce important control problems and column section with very different diameters. Constraints mentioned in the first example about feasibility in DWCs are maintained. In this case, the optimal solution does not include a DWC showing that DWCs are not always the best alternative. In some situations, the DWCs are not even feasible. But one interesting conclusion is that it is likely that there are solutions not involving DWCs with similar performance.

If instead of solving the full model, we use the two stage algorithm, the optimal solution increases to a TAC of $646,381/year (Sol 2.2) that is only a 2.2% larger than the best obtained solution (see Figure 18), confirming that usually thermally coupled systems have a large number of solutions with similar TAC, which provides the designer with an extra degree of freedom to select the best configuration taking into account any other extra considerations.

Again, if we consider the sequence formed only by conventional columns, the best sequence has a TAC of $1,119,697/year (Sol 2.3) that is 77% more expensive than the best solution (Figure 19).

Finally, Table 4 shows the main results and some statistics of the example.

Conclusions and Final Remarks

This article has introduced a methodology for the design of distillation columns sequences of zeotropic mixtures explicitly including DWC. Some remarkable characteristics of the proposed approach are the following:

1. The model is very flexible, and includes from sharp conventional sequences (each column has a reboiler and a condenser—classical column sequencing) to fully thermally couple configurations (a single reboiler and a single condenser for all the sequence of columns), going through all the intermediate possibilities, and explicitly including DWCs.

2. Constraining the search to any of the extreme cases presented in the previous paragraphs, or including any preference of the designer is very straightforward by just including or removing some logical constraints in the model.

3. The search is constrained to basic configurations. A DWC can be included if we take into account that a DWC can be considered thermodynamically equivalent to a FTC subsystem formed by three separation tasks. However, the particularities of the DWCs make necessary the explicit identification of these substructures. Again, the model proved to be very flexible and logical relationships easily control the possibility of decoupling or not (through heat exchangers) the DWC from the rest of the sequence.

4. In this work, we presented a shortcut model approach based on the Underwood–Fenske equations. However, the disjunctive representation of the model accommodates any other aggregated or even rigorous model. In any case, the approach presented here is enough for the preliminary design. It allows identifying some promising alternatives for a latter detailed simulation.

5. When we consider thermally coupled systems with DWCs, it is common that there are a good number of alternatives with similar economic performance, but the best solution not necessarily includes a DWC. Although these alternatives increases the difficulty of the system, at the same time it provides an extra degree of freedom to the designer that could take into account other considerations (i.e., controllability, environmental considerations, safety, etc.) in the final design.

6. Even though the DWCs are explicitly taken into account, the model is based on a tasks approach instead of a column approach. The reason is that when a thermal couple appears, it introduces two thermodynamic equivalent configurations. In a preliminary design, all these thermodynamic equivalent alternatives must be avoided to avoid a large redundancy (i.e., large number of equivalent configurations with the same performance from the total annual cost point of view).

A final remark could be of interest. Any sequence of distillation columns can be rearranged in a single column using vertical partitions and various reboilers and/or condensers. In some situations, they can even stacked using horizontal partitions. A detailed discussion was presented by Agrawal.[29] In this work, we do not consider those alternatives but just the "classical" DWC with at most a single reboiler and a single condenser.

Acknowledgments

Notation

F_t = feed molar flow that enters in the separation task t
D_t = molar flow that exits from rectifying section of task t
B_t = molar flow that exits from the stripping section of task t
$f_{t,i}$ = molar flow of component i the enters in the separation task t
$d_{t,i}$ = molar flow of component i that exits from rectifying section of task t

$b_{t,i}$ = molar flow of component i that exits from the stripping section of task t
$L1_t$ = liquid molar flow in rectifying section of task t
$L2_t$ = liquid molar flow in stripping section of task t
$V1_t$ = vapor molar flow in rectifying section of task t
$V2_t$ = vapor molar flow in stripping section of task t
Ps = molar flow of a stream that leaves the system (final product)
$QCond_t$ = heat load in the condenser in task t
$QReb_t$ = heat load in the reboiler of task t

Boolean variables

Y_t = True if the separation task t exists. False otherwise
Zs = True if the state s exists. False, otherwise
Ws = True if the heat exchanger associated to the state s exists. False, otherwise

Literature Cited

1. Humphrey J. Separation processes: playing a critical role. *Chem Eng Prog*. 1995;91:43–54.
2. Mix T, Dweck J, Weinberg M, Armstrong R. Energy conservation in distillation. *Chem Eng Prog*. 1978;74:49–55.
3. Soave G, Feliu JA. Saving energy in distillation towers by feed splitting. *Appl Therm Eng*. 2002;22:889–896.
4. Kunesh J, Kister H, Lockett M, Fair JR. Distillation: still towering over other options. *Chem Eng Prog*. Oct. 1995;43–54.
5. Caballero JA, Grossmann IE. Design of distillation sequences: from conventional to fully thermally coupled distillation systems. *Comput Chem Eng*. 2004;28:2307–2329.
6. Caballero JA, Grossmann IE. Structural considerations and modeling in the synthesis of heat-integrated-thermally coupled distillation sequences. *Ind Eng Chem Res*. 2006;45:8454–8474.
7. Fidkowski ZT. Distillation configurations and their energy requirements. *AIChE J*. 2006;52:2098–2106.
8. Fidkowski ZT, Agrawal R. Multicomponent thermally coupled systems of distillation columns at minimum reflux. *AIChE J*. 2001;47:2713–2724.
9. Rudd H. Thermal coupling for energy efficiency. *Chem Eng-London*. 1992;27:S14–S15.
10. Triantafyllou C, Smith R. The design and optimization of fully thermally coupled distillation-columns. *Chem Eng Res Des*. 1992;70:118–132.
11. Wright RO, Inventor. Fractionation apparatus. U.S. Patent 1949;2471134. Standard Oil Development Company (Delaware).
12. Petlyuk FB, Platonov VM, Slavinsk DM. Thermodynamically optimal method for separating multicomponent mixtures. *Int Chem Eng*. 1965;5:555–561.
13. Halvorsen IJ, Skogestad S. Minimum energy consumption in multicomponent distillation. 1. V-min diagram for a two-product column. *Ind Eng Chem Res*. 2003;42:596–604.
14. Halvorsen IJ, Skogestad S. Minimum energy consumption in multicomponent distillation. 2. Three-product Petlyuk arrangements. *Ind Eng Chem Res*. 2003;42:605–615.
15. Halvorsen IJ, Skogestad S. Minimum energy consumption in multicomponent distillation. 3. More than three products and generalized Petlyuk arrangements. *Ind Eng Chem Res*. 2003;42:616–629.
16. Agrawal R. Synthesis of distillation column configurations for a multicomponent separation. *Ind Eng Chem Res*. 1996;35:1059–1071.
17. Caballero JA, Grossmann IE. Generalized disjunctive programming model for the optimal synthesis of thermally linked distillation columns. *Ind Eng Chem Res*. 2001;40:2260–2274.
18. Caballero JA, Grossmann IE. Thermodynamically equivalent configurations for thermally coupled distillation. *AIChE J*. 2003;49:2864–2884.
19. Agrawal R. More operable fully thermally coupled distribution column configurations for multicomponent distillation. *Chem Eng Res Des*. 1999;77:543–553.
20. Agrawal R, Fidkowski ZT. More operable arrangements of fully thermally coupled distillation columns. *AIChE J*. 1998;44:2565–2568.
21. Rong BG, Kraslawski A, Turunen I. Synthesis and optimal design of thermodynamically equivalent thermally coupled distillation systems. *Ind Eng Chem Res*. 2004;43:5904–5915.
22. Rong BG, Turunen I. A new method for synthesis of thermodynamically equivalent structures for Petlyuk arrangements. *Chem Eng Res Des*. 2006;84:1095–1116.
23. Agrawal R. Synthesis of multicomponent distillation column configurations. *AIChE J*. 2003;49:379–401.

24. Giridhar A, Agrawal R. Synthesis of distillation configurations: I. Characteristics of a good search space. *Comput Chem Eng*. 2010; 34:73–83.
25. Brugma AJ. Process and device for fractional distillation of liquid mixtures. U.S. Patent 2.295.256. 1942.
26. Kaibel G. Distillation columns with vertical partitions. *Chem Eng Techol*. 1987;10:92–98.
27. Kim JK, Wankat PC. Quaternary distillation systems with less than N-1 columns. *Ind Eng Chem Res*. 2004;43:3838–3846.
28. Errico M, Rong B-G. Modified simple column configurations for quaternary distillations. *Comput Chem Eng*. 2012;36:160–173.
29. Agrawal R. Multicomponent distillation columns with partitions and multiple reboilers and condensers. *Ind Eng Chem Res*. 2001;40:4258–4266.
30. Ivakpour J, Kasiri N. Synthesis of distillation column sequences for nonsharp separations. *Ind Eng Chem Res*. 2009;48:8635–8649.
31. Shah VH, Agrawal R. A matrix method for multicomponent distillation sequences. *AIChE J*. 2010;56:1759–1775.
32. Caballero JA, Grossmann IE. Logic Based Methods for Generating and Optimizing Thermally Coupled Distillation Systems. Paper Presented at the European Symposium on Computer Aided Process Engineering-12. 2002; The Hague, The Netherlands.
33. Kondili E, Pantelides CC, Sargent RWH. A General algorithm for short-term scheduling of batch-operations .1. Milp Formulation. *Comput Chem Eng*. 1993;17:211–227.
34. Yeomans H, Grossmann IE. A systematic modeling framework of superstructure optimization in process synthesis. *Comput Chem Eng*. 1999;23:709–731.
35. King CJ. *Separation Processes*. New York: McGraw-Hill, 1980.
36. Underwood A. Fractional distillation of multicomponent mixtures. *Chem Eng Prog*. 1948;44:603–614.
37. Carlberg NA, Westerberg AW. Temperature heat diagrams for complex columns .2. underwoods method for side strippers and enrichers. *Ind Eng Chem Res*. 1989;28:1379–1386.
38. Carlberg NA, Westerberg AW. Temperature heat diagrams for complex columns. 3. underwoods method for the petlyuk configuration. *Ind Eng Chem Res*. 1989;28:1386–1397.
39. Navarro MA, Javaloyes J, Caballero JA, Grossmann IE. Strategies for the robust simulation of thermally coupled distillation sequences. *Comput Chem Eng*. 2012;36:149–159.
40. Turton R, Bailei RC, Whiting WB, Shaeiwitz JA. *Analysis Synthesis and Design of Chemical Processes*. New York: McGraw-Hill, 2003.
41. Grossmann IE. Review of nonlinear mixed-integer and disjunctive programming techniques. *Optim Eng*. 2002;3:227–252.
42. Vecchietti A, Lee S, Grossmann IE. Modeling of discrete/continuous optimization problems: characterization and formulation of disjunctions and their relaxations. *Comput Chem Eng*. 2003;27:433–448.
43. Rosenthal RE. *GAMS - A User's Guide*. Washington, DC: GAMS Development Corporation, 2012.
44. Drud AS. *CONOPT: A System for Large Scale Nonlinear Optimization. Reference Manual*. Bagsvaerd, Denmark: ARKI Consulting and Development A/S, 1996.
45. Sahinidis NV. BARON: A general purpose global optimization software package. *J Global Optim*. 1996;8:201–205.
46. Bussieck MR, Drud AS. *A new solver for mixed integer nonlinear programming*. In: *Recent Advances in Nonlinear Mixed Integer Optimization*. INFORMS. Invited Talk, 2000.
47. Duran MA, Grossmann IE. A Mixed-integer nonlinear-programming algorithm for process systems synthesis. *AIChE J*. 1986;32:592–606.
48. Yuan X, Pibouleau L, Domenech S. Experiments in process synthesis via mixed integer programming. *Chem Eng Process* 1989;25: 99–116.
49. Geofrion AM. Generalized benders decomposition. *J Optim Theory Appl*. 1972;10:237–259.

Appendix

Here, we present the logical relationships to ensure a feasible basic column sequence. Besides the index sets included in the text, we must include the following.

P_REC_S = {task t that produces final product s through a rectifying section.}

P_STR_S = {task t that produces final product s through a stripping section.}

The rest of index sets are variables were defined in the text.

1. A given state s can give rise to at most one task

$$\underset{t \in \overline{TS_t}}{\vee} Y_t \quad \underline{\vee} \quad K \quad ; \quad s \in COL \qquad (A1)$$

where K is a dummy Boolean variable that means "do not choose any of the previous options."

2. A given state can be produced at most by two tasks: one must come from the rectifying section of a task and the other from the stripping section of a task

$$\left. \begin{array}{l} \underset{t \in \overline{RECT_s}}{\vee} Y_t \underline{\vee} K \\ \underset{t \in \overline{STRIP_s}}{\vee} Y_t \underline{\vee} K \end{array} \right\} \quad s \in STATES \qquad (A2)$$

where K has the same meaning than in eq. 1. Note that if we want only systems with the minimum number of column sections at a given state, except products, it should be produced at most by one contribution. Note also that when at least a state is produced by two contributions, the number of separation tasks is not the minimum.

3. All the products must be produced at least by one task

$$\underset{t \in (P\_REC_s \cup P\_STR_s)}{\vee} Y_t \; ; \quad s \in FP \qquad (A3)$$

4. If a given final product stream is produced only by one task, the heat exchanger associated with this state (product stream) must be selected

$$\left. \begin{array}{l} \neg \left(\underset{t \in P\_REC_s}{\vee} Y_t \right) \Rightarrow W_s \\ \neg \left(\underset{t \in P\_STR_s}{\vee} Y_t \right) \Rightarrow W_s \end{array} \right\} \quad s \in FP \qquad (A4)$$

5. If a given state is produced by two tasks (a contribution coming from a rectifying section and the other from a stripping section of a task), then there is not a heat exchanger associated to that state (stream)

$$(Y_t \wedge Y_k) \Rightarrow \neg W_s \quad \begin{cases} t \in RECT_s \\ k \in STRIP_s \\ s \in STATES \end{cases} \qquad (A5)$$

6. Connectivity relationships between tasks in the superstructure

$$\left. \begin{array}{l} Y_t \Rightarrow \underset{k \in TS_s}{\vee} Y_k; \quad t \in ST_s \\ Y_t \Rightarrow \underset{k \in ST_s}{\vee} Y_k \; ; \quad t \in TS_s \end{array} \right\} \quad s \in STATES \qquad (A6)$$

7. If a heat exchanger associated to any state is selected, then a task which generates that state must also be selected

$$W_s \Rightarrow \underset{ST_s}{\vee} Y_t \; ; \quad s \in STATES \qquad (A7)$$

8. If a separation task t produces a state s by a rectifying section, and that state has a heat exchanger associated, then it must be a condenser. If the state is produced by a stripping section, then it must be a reboiler

$$\begin{array}{l} Y_t \wedge W_s \Rightarrow WC_s \quad t \in RECT_s \\ Y_t \wedge W_s \Rightarrow WR_s \quad t \in STRIP_s \end{array} \qquad (A8)$$

It is convenient to complete the pervious rule adding that:

9. If a given state does not have a heat exchanger, then both WC and WR associated to that state must be False

$$\neg W_s \Rightarrow \neg WC_s \wedge \neg WR_s \quad s \in STATES \quad \text{(A9)}$$

It is important to note that if the problem is solved as an MI(N)LP or GDP, the variables wc and wr do not need to be declared as binary and they can be considered as continuous with values between 0 and 1. Previous eqs. A8 and A9 force wc and wr to take integer values as far as y and w are integer. Therefore, variables wr and wc do not increase the combinatorial complexity of the problem.

10. It is worth mentioning that the set of logical rules previously presented in terms of separation tasks could be easily rewritten in terms only of states: "There is a one to one correspondence between the sequence of tasks and the sequence of states and vice-versa." The relationship between tasks and states is as follows

$$Y_t \Rightarrow Z_s ; \quad t \in ST_S \quad \text{(A10)}$$

$$Z_s \Rightarrow \bigvee_{t \in TS_s} Y_t \quad \text{(A11)}$$

Equation A10 could be read as: "if the task t, that belongs to the set of task produced by the state s, exits then the state s must exist." And eq. A11 as: "If the state s exists at least one of the tasks that the state s is able to produce must exist"

We should note that if the problem is solved as an MI(N)LP, it is only necessary declare as binary either yt or zs, but not both. Whether yt is declared as binary zs can be declared as continuous between zero and one and vice-versa.