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Synthesis of Complex Thermally Coupled Distillation Systems Including Divided Wall Columns.

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Abstract.

This paper deals with the design of thermally coupled distillation sequences explicitly including the possibility of divided wall columns (DWC). A DWC with a single wall can be considered thermodynamically equivalent to a fully thermally coupled sub-system formed by three separation tasks (a Petlyuk configuration in the case of three component mixtures). In this paper 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 fully thermally coupled 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. Finally, some general comments on the extension of the methodology to multi-wall columns are included.

Keywords

Distillation; Thermally coupled distillation; MINLP; Divided Wall Column; Superstructure optimization; GDP.

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. In order to get an idea of the importance of distillation, Humphrey¹ 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 al², Soave & Feliu³ calculated that distillation accounts about the 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 the evaporation steps involved. Typically more than half of the

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3 process heat distributed to a plant is dedicated to supply heat in the reboilers of distillation
4 columns ⁴. Unfortunately, this enormous amount of energy is introduced in the bottom of the
5 column and approximately the same amount of energy removed in the top, but at significantly
6 lower temperature, which renders a very inefficient process -but also one of the most effective,
7 for separation mixtures. Although distillation research is often regarded as a mature area,
8 periodically new discoveries in the design and/or operation renew the interest in distillation,
9 because improvements can translate into very large economic benefits.

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13 Renewed interest in Thermally Coupled Distillation (TCD) appeared in the last 15-20 years, due
14 the important potential savings in energy, with typical values around 10% to 40% (in some
15 cases even larger) that have been reported ⁵⁻¹⁰ when compared to conventional distillation
16 sequences. Although the interest in TCD is relatively recent the first apparatus that uses TCD
17 concepts was due to Wright in 1947 ¹¹, although the theoretical basis of TCD was developed in
18 the sixties by Petlyuk and coworkers ¹². Petlyuk and coworkers noticed that separation
19 sequences using conventional columns (a single feed with two product streams, a condenser,
20 and a reboiler) suffer from an inherent inefficiency produced by the thermodynamic irreversibility
21 during the mixing of streams at the feed, top, and bottom of the column. This remixing is
22 inherent to any separation that involves an intermediate boiling component and can be
23 generalized to an *N*-component mixture. The theoretical studies developed by Petlyuk and co-
24 workers showed that this inefficiency can be improved by removing some heat exchangers and
25 introducing thermal coupling between columns. If a heat exchanger is removed, the liquid reflux
26 (or vapor load) is provided by a new stream that is withdrawn from another column; in this way,
27 it is possible to reduce the energy consumption, and under some circumstances, also the
28 capital costs. (See Figure 1) A fully thermally coupled (FTC) configuration is reached when the
29 entire vapor load is provided by a single reboiler and all the reflux by a single condenser.
30 Halvorsen & Skogestad ¹³⁻¹⁵ proved that the minimum energy consumption for an ideal *N*-
31 component mixture is always obtained for the FTC configuration.

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

- 44 (1) The energy must be supplied under the worst conditions, namely at the highest
45 temperature in the reboiler, and removed at the lowest temperature in the condenser,
46 preventing in most cases the use of lower cost utilities such as medium- or low-pressure
47 steam.
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50 (2) When using conventional columns, it is common to constrain the alternatives to sharp
51 separations. For example, in a three-component mixture (ABC), sorted by volatilities, we
52 postulate initially separations A from BC (A/BC) and AB from C (AB/C). However, in FTC
53 distillation, we introduce sloppy separations -an intermediate product is allowed to
54 distribute along the column- and, therefore, we increase the number of column sections.
55 This increase does not imply an increase in the number of columns, but usually an
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3 increase in the total number of trays. A detailed discussion on the number of column
4 sections needed for a given separation can be found in Agrawal¹⁶ and in Caballero &
5 Grossmann.^{5,6,17}
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8 (3) In FTC systems the minimum vapor flow is that of the most difficult separation^{14,15} and,
9 therefore, some column sections will have large diameters.
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12 (4) Operation is also more difficult due to the large number of interconnections between the
13 columns.
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15 Therefore, it cannot be concluded that complex configurations are always superior, compared to
16 sequences of simple columns. Instead, the optimum configuration will be dependent on the
17 specific mixture and feed conditions.
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20 Besides the energy savings in TCD, there are also possibilities of important investment savings.
21 First, the reduction in energy consumption is due to a reduction of the liquid and vapor flow
22 rates, and therefore, the lower energy consumption, the smaller the diameters required for the
23 distillation column. Second, an important saving in investment can be obtained by using Divided
24 Wall Columns. A FTC configuration for a three component mixture, like that in Figure 2a, (also
25 known as Petlyuk configuration in honor to F. Petlyuk, who discovered it) formed by two
26 columns, can be rearranged in a single shell using an internal wall (as shown in Figure 2b).
27 Both configurations in Figure 2, the Petlyuk and the Divided Wall Column (DWC), are
28 thermodynamically equivalent since all the flows, temperatures, compositions are the same in
29 both configurations. In practice there are small differences due to the pressure differences
30 needed to control the external streams in the Petlyuk configurations, but in a preliminary design
31 these differences can be neglected. Detailed discussion about Thermodynamically Equivalent
32 configurations can be found in the works of Caballero & Grossmann¹⁸ Agrawal and coworkers
33^{19,20} or Rong et al^{21,22}. In this way the separation of a three component mixture that usually
34 requires two distillation columns, can be performed using a single column with an internal wall.
35 The investment savings are evident since we are only using a single column, reducing the land
36 requirements, the pumps, and piping.. However, the design of TCD systems including DWC
37 involving mixtures with more than three components is not straightforward and it is the objective
38 of this work.
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47 Depending on the number of distillation columns used to separate an n component mixture into
48 n product streams, the sequence can be classified as more than n-1 columns configurations, as
49 exactly n-1 columns, and less than n-1 columns configurations.
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52 For the case of zeotropic mixtures, sequences with exactly n-1 columns, named basic
53 configurations by Agrawal²³, are characterized by the following three features: (1) Mixtures (or
54 states) with the same components are transferred only once from one distillation column to
55 another; (2) a final product is obtained in a single location of the sequence; (3) the feed stream
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3 and all the intermediate mixtures are split into exactly two product streams by two columns
4 sections.

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6 Configurations that violate the first two features and obey only the third one produce sequences
7 with more than $n-1$ columns. These configurations, also referred as non-basic, have higher
8 operating cost than the best basic configurations^{6,24}. Non-basic configurations also tend to have
9 higher capital cost due to the additional distillation columns, and therefore non-basic
10 configurations can be removed from the search space.

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14 Configurations that violate the third feature have higher operating cost than the best basic
15 configuration due to increased heat duty, especially for obtaining high purity products. However,
16 the reduced number of columns in some situations could compensate the extra energy
17 consumption. In the literature some of these cases can be found, for example those due to
18 Brugma,²⁵ or Kaibel²⁶, Kim et al²⁷ or Errico & Rong²⁸. However, in this paper, we focus only on
19 basic configurations and we will study the case of fewer than $n-1$ columns sequences in a future
20 work.

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

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27 (1). Previous classification (sequences with less, exactly and more than $n-1$ columns) is
28 referred to as configurations without internal walls.
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30 (2). Sequences obeying the three distinguishing features can always be arranged into $n-1$
31 columns, although the total number of separation tasks can be larger. Consider the
32 following example. We want to separate a four component mixture ABCD where the
33 components are sorted by decreasing volatilities (A is the most volatile component, D
34 the least volatile). Assume we perform the following separation tasks: AB/BCD -that
35 means separate A from CD letting the B component to be optimal distributed between
36 distillate and bottoms- A/B; BC/CD; B/C and C/D. In this example we can identify 5
37 separation tasks, and this sequence can be performed using 5 distillation columns, but
38 this sequence can be easily arranged in three distillation columns (See Figure 3). In
39 fact it can be rearranged in 16 thermodynamically equivalent configurations using
40 three distillation columns¹⁸.
- 41
42 (3) A Sequence including divided wall columns, or a single DWC like the one shown in
43 Figure 2, is a thermodynamically equivalent configuration without walls that uses
44 exactly $n-1$ columns and obeys the three distinguish features. In that sense, although
45 strictly speaking DWC uses less than $n-1$ columns, it can be considered that DWCs
46 are basic configurations.

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54 As a final any sequence of distillation columns can be rearranged in a single column using
55 vertical partitions and various reboilers and/or condensers. In some situations they can even be
56 stacked using horizontal partitions. A detailed discussion is presented by Agrawal²⁹. In this
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work we do not consider those alternatives, but just the 'classical' divided wall columns with at most a single reboiler and a single condenser.

In this paper 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. In order 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 paper 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, non conventional and explicitly divided wall columns 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 in order 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 non-key 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 divided wall columns, 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 Agrawal²³. Following this line, later Ivakpour & Kasiri³⁰ proposed a formulation in which

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3 distillation configurations are presented mathematically as upper triangular matrices.
4 Independently, Shah & Agrawal³¹ presented an alternative matrix formulation in which
5 distillation configurations are generated by exploring all possible instances of the presence or
6 absence of transfer streams. This last approach is very efficient for generating the full set of
7 basic configurations. All these rule based approaches have proved to be effective when
8 generating alternatives, but the enumeration of all the alternatives is, except in the case of a
9 reduced number of possibilities, an inefficient strategy. While these approaches can be easily
10 adapted for metaheuristic optimization (i.e genetic algorithms, Particle Swarm Optimization,
11 etc.), it is not clear how to adapt them to a deterministic mathematical programming formulation.
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16 Based on the observations in the seminal paper by Agrawal¹⁶, Caballero & Grossmann^{5,6,17}
17 proposed a complete set of logical rules in terms of Boolean variables that implicitly include all
18 the basic column configurations. These logical equations can be transformed into linear
19 equations in terms of binary variables, and integrated in a mathematical programming
20 formulation. The objective in those works was not to generate explicitly all the basic
21 configurations, but to develop a set of logic equations that ensure a strong relaxation when
22 solving the resulting MINLPs that include all the performance equations of the distillation
23 columns, for extracting the optimal configuration without an explicit enumeration of all the
24 alternatives. It is interesting to note that Shah & Agrawal³¹ proposed a valid set of equations in
25 terms of binary variables that can be integrated in a mathematical programming framework.
26 However, their focus was on checking quickly if a given alternative is a basic one (with excellent
27 performance) and not when those equations are integrated with the model of the columns in a
28 mathematical programming framework (i.e. some of their equations can be obtained from the
29 aggregation of some of the logic relations presented by Caballero & Grossmann^{5,6}, and
30 therefore a worse relaxation is expected)
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38 If we try to synthesize a sequence of distillation columns, the concept of basic configuration is
39 not enough. Consider, for example, the Figures 4a, 4b and 4c. These three sequences of
40 columns correspond to the same basic sequence. The difference between Figures 4a and 4b is
41 that they differ in the existence of the internal heat exchangers. An internal heat exchanger is a
42 condenser or reboiler associated to any internal mixture. In other words, a heat exchanger
43 associated to a stream connecting two different columns. Note that the final heat exchangers,
44 that are associated to final products, are the same in the three configurations of Figure 4. In
45 general, a given basic configuration can differ in the existence or not of internal heat
46 exchangers, but the heat exchangers associated to final products are the same. A detailed
47 discussion about this point can be found in the work by Caballero & Grossmann⁶. In the case of
48 Figure 4c is not so obvious that this configuration corresponds to the same basic configuration.
49 But if we look at the sequence of separation tasks, we observe that the three sequences are
50 performing the same sequence of tasks (see Figure 4d). Figures 4b and 4c are
51 thermodynamically equivalent.
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Figures 4a and 4b 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; i.e. 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 & 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.

In order 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, i.e. 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).

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 column¹⁸.

Using the STN formalism, Caballero & 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

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3 tasks). Although from a theoretical point of view it is possible to generate a multi-wall column
4 that in the extreme case separates all the components in a single column, nowadays only
5 columns with one wall have been built and operate, so we constrain ourselves to a maximum of
6 one wall in a given column. At the end of the paper we have included a small section with an
7 outline of how to systematically generate multi-wall columns.
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10 A divided wall column is formed by the union of three separation tasks or by four states: a feed
11 state, the two states produced by the first separation task and the intermediate product state.
12 For example, Figure 5 shows the different sequences of states that produce DWCs in a five
13 component mixture.
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16 To generate the logical relations that ensure that all alternative DWC are taken into account, it is
17 necessary first to identify which combinations of states (or tasks) are able to generate a DWC.
18 The next conditions assure that all the DWCs are taken into account:
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- 21 1. All intermediate states (those that do not include a component with extreme volatility)
22 can form part of a DWC; i.e. according to the definition in previous paragraph, the states
23 A and E cannot be part of the 4 states that define a DWC (See Figure 5).
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- 26 2. The intermediate product state in the DWC must be produced by two different states. i.e
27 in the Figure 5.(c1) state C is produced by BC and CD. In Figure 5b.(c2), state C is
28 produced by states ABC and CDE.
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- 31 3. Each one of the two states that produce the intermediate product in the DWC must be
32 generated by a single contribution; i.e. in Figure 5.(c1) the two states that produce C are
33 BC and CD. Both BC and CD are generated from a single state: BC from BCD and CD
34 from BCD.
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- 37 4. The state that generates intermediate states in the DWC must be produced by the
38 same state; i.e. in Figure 5.(c1) the two states that produce C are BC and CD. These
39 two states are generated from the same state BCD. In Figure 5.c2 the two states that
40 produce C are ABC and CDE; both, ABC and CDE are produced from ABCDE.
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45 With the 4 previous rules, it is straightforward to generate all the possible DWC. For example, in
46 a 5 component mixture there are 15 DWCs (3 with B as intermediate product; 4 with C as
47 intermediate product; 3 with D; 2 with BC; 2 with CD and 1 with BCD. See Figure 5)
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49 In order to explicitly include DWC in a GDP or MINLP model, it is necessary to add some logical
50 relationships that ensure the feasibility of the sequence. Therefore, to the set of logical rules
51 previously developed by Caballero & Grossmann^{5,6,17} -See appendix- we must add the logical
52 relationships shown in next paragraphs.
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55 First let us define the following index sets:
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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}

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

1.- The first logical relationship simple relates the DWCs with the states:

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

where the Boolean 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.

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

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

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

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 its 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 the DWCs to have reboiler and condenser, and maybe to force the feed to the DWCs to be a single stream.

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}

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

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

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 formalism³⁴. 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 pseudo-column. (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 flowrate (and minimum liquid flowrate) in each pseudo-column (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:

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

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:

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

equation (5) can be written as follows:

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

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

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

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 non-convex equation.

In order 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. $IM_S = \{s \mid s \text{ is an intermediate state. All but initial and final products}\}$
 - e.g. $IM_S = \{(ABC), (BCD), (AB), (BC), (CD)\}$
4. COMP = {i | i is a component to be separated in the mixture}
 - e.g. COMP = {A, B, C, D}
5. $FS_T = \{t \mid t \text{ is a possible initial task; Task that receives the external feed}\}$
 - e.g. TASK = {(A/BCD), (AB/BCD), (AB/CD), (ABC/BCD), (ABC/CD), (ABC/D)}
6. $TS_s = \{\text{tasks } t \text{ that the state } s \text{ is able to produce}\}$
 - e.g. $TS_{ABCD} = \{(AB/BCD), (ABC/BCD), (ABC/CD)\}$

$$TS_{ABC} = \{(AB/BC), (AB/C)\}$$

$$TS_{BCD} = \{(B/CD), (BC/CD)\}$$

7. $ST_s = \{\text{tasks } t \text{ that are able to produce state } s\}$

$$\text{e.g. } ST_{ABC} = \{(ABC/CD), (ABC/BCD)\}$$

$$ST_{BCD} = \{(AB/BCD), (ABC/BCD)\}$$

$$ST_{AB} = \{(AB/BCD), (AB/BC), (AB/C)\}$$

$$ST_{BC} = \{(AB/BC), (BC/CD)\}$$

$$ST_{CD} = \{(ABC/CD), (B/CD), (BC/CD)\}$$

8. $RECT_s = \{\text{task } t \text{ that produces state } s \text{ by a rectifying section}\}$

$$\text{e.g. } RECT_{ABC} = \{(ABC/CD), (ABC/BCD)\}$$

$$RECT_{AB} = \{(AB/BCD), (AB/BC), (AB/C)\}$$

$$RECT_{BC} = \{(BC/CD)\}$$

9. $STRIP_s = \{\text{task } t \text{ that produces state } s \text{ by a stripping section}\}$

$$\text{e.g. } STRIP_{BCD} = \{(AB/BCD), (ABC/BCD)\}$$

$$STRIP_{BC} = \{(AB/BC)\}$$

$$STRIP_{CD} = \{(ABC/CD), (B/CD), (BC/CD)\}$$

10. $FP_s = \{s \mid s \text{ is a final state (pure products)}\}$

$$\text{e.g. } FP = \{(A), (B), (C), (D)\} \text{ do not confuse with components, although the name is the same.}$$

11. $PRE_i = \{\text{tasks } t \text{ that produce pure product } i \text{ through a rectifying section}\}$

$$\text{e.g. } PRE_A = \{(A/B)\}$$

$$PRE_B = \{(B/CD), (B/C)\}$$

$$PRE_C = \{(C/D)\}$$

12. $PST_i = \{\text{tasks } t \text{ that produce pure product } i \text{ through a stripping section}\}$

$$\text{e.g. } PST_B = \{(A/B)\}$$

$$PST_C = \{(AB/C), (B/C)\}$$

$$PST_D = \{ (C/D) \}$$

13. $UR = \{r \mid r \text{ is Underwood root}\}$

e.g. $\{r_1, r_2, r_3, r_4\}$

14. $AUR_t = \{r \text{ is an active Underwood root in task } t\}$

e.g. $AUR_{A/BCD} = \{r_1\}$

$AUR_{AB/BCD} = \{r_1, r_2\}$

$AUR_{ABC/BCD} = \{r_1, r_2, r_3\}$

$AUR_{AB/CD} = \{r_2\}$ etc.

We introduce the following continuous variables:

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
$f_{i,i}$	Molar flow of component i the enters in the separation task t
$d_{i,i}$	Molar flow of component i that exits from rectifying section of task t
$b_{i,i}$	Molar flow of component i that exits from the stripping section of task t
LI_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

and the following Boolean variables.

Y_t	True if the separation task t exists. False otherwise.
Z_s	True if the state s exists. False, otherwise
W_s	True if the heat exchanger associated to the state s exists. False, otherwise

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

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

where the capital cost 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; i.e. 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:

1. *Disjunctions related with the existence or not of a given separation task:*

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

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 sub-cooled liquid stream (a detailed discussion can be found in the works by Carlberg & Westerberg^{37,38} and Navarro et al³⁹). 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:

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

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:

$$\begin{aligned} V1 &= F_V + V2 \\ L2 &= F_L + L1 \end{aligned} \quad (11)$$

the liquid fraction is defined as:

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

and therefore,

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

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 or from a thermal couple).

2. *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.

2.1. *Mass balance in the feed to the system:*

$$\begin{aligned}
 F_0 &= \sum_{t \in FS_t} F_t \\
 f_{0i} &= \sum_{t \in FS_t} f_{t,i}
 \end{aligned}
 \tag{14}$$

2.2. *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 relationship between a sequence of tasks and a sequence of states. Therefore, the introduction of the new boolean variables Z_s 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).

The second term in the main disjunction (when the boolean Z_s 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 task 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 W_s 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 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 if 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.

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3 If the heat exchanger does not exist ($-W_s$), but the state exists, then we have a
4 thermal couple. Equations inside this term of the disjunction are simply mass
5 balances to ensure the correct liquid and vapor flow transfer between columns.
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8 Figure 9a, 9b shows a conceptual graphical description of disjunction D-2 that
9 helps to understand the meaning of each term.
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2.3. 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.

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

2.4. Recovery of final products

$$\sum_{t \in PRE_s} d_{i,t} + \sum_{t \in PSE_s} b_{i,t} \geq rec_i f_{0,i} \quad \forall i \in COMP, s \in FP \quad (15)$$

$$\sum_{t \in PRE_s} D_t + \sum_{t \in PSE_s} B_t = P_s \quad s \in FP$$

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.

3. Existence of a Divided Wall Column

As discussed previously, a divided wall column is thermodynamically equivalent to a set of three fully thermally coupled 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 can separate the vessels from the heat exchangers. It is worth remembering that a separation task can be considered as a pseudo-column, 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 divided wall columns the total cost of the vessels can be calculated as follows:

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

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

The disjunctive model is reformulated as a mixed integer non-linear programming (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 non-convexities and the large number of local solutions in this type of problem often lead to suboptimal solutions. However, based on the following observations it is possible solve the model and get a very good solution, in most of the cases, the global optimal solution.

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3 a. Problems with a fixed topology (fixed binary variables) produce the optimal solution
4 and rarely get trapped in local solutions. The same can be said for the resulting
5 nonlinear problem (NLP) with a relaxation of the binary variables (we use the solver
6 CONOPT⁴⁴ under GAMS). This fact can be checked comparing the results of the local
7 optimizer with a deterministic global solver like BARON⁴⁵.
8
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10 b. For a fixed sequence of separation tasks (or states), the optimal solution tends to be
11 a solution with a large degree of thermal couples in the internal states. In other words,
12 the sequence without internal heat exchangers is likely to be near the optimal solution
13 for that configuration. Remember that an internal heat exchanger is a heat exchanger
14 associated to a stream -state- that connects two separation tasks. Heat exchangers
15 associated to a final product (a stream that leaves the system) are fixed with the
16 sequence of tasks.
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21 Based on observation (a) a simple branch and bound based solver, that solves only NLPs in a
22 tree search, like SBB⁴⁶ in GAMS, is expected to find a near global optimal solution, which in
23 many cases we expect to be the global optimal solution. Note that although BARON is able to
24 solve each of the nodes to global optimality, the CPU time is orders of magnitude larger than
25 the CPU time used by a local solver, and therefore, from a computational point of view, using a
26 global NLP deterministic optimizer inside the branch and bound search is prohibitive.
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30 Decomposition techniques like the Outer Approximation^{47,48} or the Generalized Benders
31 Decomposition⁴⁹ are another alternative. However, in this case the Master problem is very
32 sensitive to the nonconvexities, cutting off important parts of the feasible region. As a result we
33 often get trapped in suboptimal solutions.
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37 Therefore in this work we solve the model using SBB. We sacrifice some computational
38 performance in order to obtain a good solution.
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41 Based on observation (b), it is also possible to develop a strategy that in most cases get a
42 solution close to the best solution in a fraction of the CPU time. The algorithm is as follows:
43

- 44 1. Fix the value of all internal heat exchangers to False (zero).
- 45 2. Using branch and bound solve the resulting MINLP. Note that DWCs are allowed if we
46 relax the condition that a divided wall column must have a reboiler and a condenser.
- 47 3. For the solution in step 2, fix the sequence of tasks and determine the optimal
48 distribution of internal heat exchangers. The solution of step 3 is an upper bound to the
49 optimal solution of the problem.
- 50 4. Repeat from step 1 until in two consecutive iterations there is no improvement in the
51 upper bound.
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3 Of course, previous algorithm is based on a heuristics rule but numerical test have proved that
4 usually get a solution very close to the optimal.
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8 **Example 1. Separation of a mixture of aromatic Hydrocarbons**

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10 This example illustrates some of the capabilities of the proposed model. Here we present the
11 separation of a five component mixture (Benzene, Toluene, EthylBenzene, Styrene, alpha
12 methyl styrene). All the relevant data for the problem is presented in Table 1. According to the
13 previous comments in the paper, we constrain the search to basic configurations: the sequence
14 of tasks and states can be rearranged in N-1 actual distillation columns. Each DWC reduces by
15 one the number of actual columns.
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20 First, we solve the model allowing all the thermal couples. i.e. DWCs can be thermally coupled
21 with the rest of the system. The best solution obtained (sol 1.1) is shown in Figure 12, with a
22 TAC of \$946,130 /year. The optimal solution includes a DWC formed by the following tasks
23 (BC/CD; B/C, C/D). The arrangement in actual columns shown in Figure 12b is only one out of
24 the four thermodynamically equivalent configurations that maintain the existence of the DWC.
25 The solution obtained has two important issues related with the DWC. First, the areas in both
26 sides of the DWC are very different, and second, the areas in the same side but different
27 sections of the DWC are also very different. Although it is possible to build DWCs in which the
28 wall is not centered, if the deviation is too large hydrodynamic problems makes the DWC an
29 invalid option. This drawback can be easily solved adding a constraint that forces DWCs to
30 have similar areas in both sides of the wall (i.e. a maximum deviation around 20-30%). If we
31 force the feed and the intermediate product to be saturated liquid, the vapor flow rate in different
32 sections, but in the same side of the wall will be equal and then the areas will also be similar.
33 Including these constraints, the solution is the same in terms of states and tasks but without
34 including DWCs. The total annual costs increases to \$950,150/year. (sol 1.2)
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41 In this first case, because the dominant cost is the energy, the optimal solution is almost a fully
42 thermally coupled configuration. It is remarkable, however, the presence of a heat exchanger (a
43 condenser) in the task AB/BCD. Removing that heat exchanger and introducing a thermal link
44 instead is likely to produce some decrease in the total energy consumption. However, the
45 thermal links also produce an increase in the total vapor flow through the entire system
46 increasing the diameters of some columns.
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50 The cost correlations, the constant volatilities assumption, and some of the rules of thumb
51 introduce some uncertainty in the model. Therefore, it is of interest to obtain not only the best
52 solution but also the set of solutions inside a given tolerance (i.e. 5%). This set of solutions
53 should be evaluated with detail using rigorous models. As an example, the Figure 13 shows the
54 second best solution (sol 1.3) with a TAC of \$951,500 / year that is only 0.5% more expensive
55 than the best configuration. In this case the optimal solution includes a DWC.
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3 In both solutions the DWCs are extensively thermally coupled and integrated with the rest of the
4 system. It is also of interest to force the DWCs to be not thermally coupled with the rest of the
5 system (the DWC must have a condenser a reboiler). This can be done by adding logical
6 constraints (eq. 5). If we do that, and force the existence of at least a DWC, the optimal solution
7 is shown in Figure 14 (sol 1.4). The TAC increases to \$1,004,453/ year (6 % more expensive).
8
9

10 All previous models take between 20-30 min of CPU time to solve (using SBB under GAMS
11 version windows 7, 64 bit in a machine with a processor Intel Core2 Quad 2.40GHz and 8GB of
12 RAM). If instead of using a branch and bound search over the original model, we use the
13 heuristic algorithm proposed in previous section (maintaining the constraints to assure feasible
14 walls) we obtain a solution involving a DWC with a TAC \$952,270 / year (sol 1.5) -See Figure
15 15- Just a 0.08% larger than the best solution in only 3.7 min of CPU time.
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19 It should be noted that there are a relatively large number of alternatives with similar TAC, but
20 important structural differences, which adds an extra degree of freedom that can be used to
21 select a good alternative taking into account other considerations (controllability, environmental
22 considerations, etc.)
23
24

25 The potential of thermally coupled distillation is clear if we compare it to the optimal solution
26 using conventional columns (each column is forced to have a condenser and a reboiler) and
27 sharp separation in each column -classical column sequencing-. The optimal configuration in
28 this case is shown in Figure 16, (sol 1.6) with a TAC \$1,528,174 / year which is 61.5% more
29 expensive!
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33 Finally, in order to establish the numerical performance of the model and solution algorithms
34 Table 2 shows some statistics about the models in this and next examples.
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36

37 **Example 2. Separation of a mixture of Linear Hydrocarbons,**

38 In this example we separate a mixture of 5 linear hydrocarbons (from n-hexane to n-decane) in
39 which the relative volatilities between two consecutive components is similar, and the
40 separations are easier than in the previous example. Table 3 shows all the relevant data of this
41 problem.
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45 In this case the optimal solution has a TAC of \$632,258/year (sol 2.1) and includes the
46 maximum number of column sections ¹⁶ [N(N+1)]. Also it is almost a fully thermally coupled
47 configuration with only an internal condenser in state AB and an internal reboiler in state BCDE,
48 (see Figure 17). In this example, the flows between internal states with two contributions (BCD,
49 BC, CD) have been forced to be saturated liquid. Although from a theoretical point of view, we
50 can save some energy allowing thermal couples in this situation; this could produce important
51 control problems and column section with very different diameters. Constraints mentioned in the
52 first example about feasibility in DWCs are maintained. In this case, the optimal solution does
53 not include a DWC showing that DWCs are not always the best alternative. In some situations
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3 the DWCs are not even feasible. But one interesting conclusion is that it is likely that there are
4 solutions not involving DWCs with similar performance.
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7 If instead of solving the full model we use the two stage algorithm, the optimal solution
8 increases to a TAC of \$646,381/year (sol 2.2) that is only a 2.2% larger than the best obtained
9 solution (see Figure 18), confirming that usually thermally coupled systems have a large
10 number of solutions with similar TAC, which provides the designer with an extra degree of
11 freedom to select the best configuration taking into account any other extra considerations.
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14 Again, if we consider the sequence formed only by conventional columns, the best sequence
15 has a TAC of \$1,119,697/year (sol 2.3) that is 77% more expensive than the best solution.
16 (Figure 19)
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20 21 **Extension to multiwall column systems**

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23 Although, to our knowledge only columns with a single wall have been built and satisfactorily
24 operated, it is theoretically possible to extend the methodology to multiwall columns. It is not the
25 objective of this paper to present a comprehensive study of multiwall columns. However, a
26 general outline of how to deal with the conceptual design of these systems can be of interest.
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30 Let us first focus on systems with four components. In this case, a single column with two walls
31 should be able to separate the four components. Following the philosophy of considering only
32 basic configurations, we must study only the space of fully thermally coupled configurations (a
33 single reboiler and a single condenser in all the system). According to Agrawal¹⁶ or Caballero &
34 Grossmann¹⁷ the number of separations tasks in FTC systems varies between $(4N-6)/2$ and
35 $N(N-1)/2$ (6 separation tasks and 5 separation task respectively in the 4 components case).
36
37 The sequence of tasks and a possible arrangement of the walls for the sequence with the
38 maximum number of column sections are shown in Figure 20a, but it is not clear is how to deal
39 with the two directional flows (mixture BC in Figure 20a). The problem is produced by the two
40 contributions that form the state BC. Therefore, it would be desirable to constrain the search to
41 fully thermally coupled systems in which all the states are formed by a single contribution.
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43 Fortunately, all the sequences with $(4N-6)/2$ separation tasks fulfill this requirement. Figures
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20b to 20d show all the FTC configurations with $(4N-6)/2$ separation tasks. Among these
sequences only sequences 20c and 20d can be rearranged in a two wall column (Figure 21).
One interesting observation is that starting with a sequence of $(4N-6)/2$ tasks, the two wall
configurations can be obtained by first searching for alternatives with a single wall, then group
the states that form that DWC in a single state, and repeat the procedure, see Figure 21. This
recursive approach can be extended to sequences with more than four components to locate

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3 alternatives with two or more walls. As an example, consider Figure 22, in which a three wall
4 column is generated from a sequence of $(4 \cdot 5 - 6) / 2 = 7$ separation tasks.
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7 Finally it is important to point out that although it is not difficult to generate all the alternatives that
8 use one, two or more walls for a given N-component mixture, the feasibility of these alternatives
9 depends on factors such as the hydrodynamics (i.e. walls give rise to different transversal areas
10 in a given sections), controllability (distribution of vapor and liquid flows in the different sides of
11 the walls) or mechanical (i.e. construction of the trays or packed distribution in each section or
12 sections with very different transversal areas). The geometrical distribution of trays could also
13 be important (i.e. Figure 22 shows at least two alternatives for the wall distribution inside a
14 column for a 5 component mixture)
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20 21 **Conclusions and final remarks**

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23 This paper has introduced a methodology for the design of distillation columns sequences of
24 zeotropic mixtures explicitly including divided wall columns. Some remarkable characteristics of
25 the proposed approach are the following:
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- 28 1. The model is very flexible, and includes from sharp conventional sequences (each
29 column has a reboiler and a condenser –classical column sequencing) to fully thermally
30 couple configurations (a single reboiler and a single condenser for all the sequence of
31 columns), going through all the intermediate possibilities, and explicitly including DWCs.
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- 33 2. Constraining the search to any of the extreme cases presented in the previous
34 paragraphs, or including any preference of the designer is very straightforward by just
35 including or removing some logical constraints in the model.
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- 38 3. The search is constrained to basic configurations. A DWC can be included if we take
39 into account that a DWC can be considered thermodynamically equivalent to a fully
40 thermally coupled subsystem formed by three separation tasks. However, the
41 particularities of the DWCs make necessary the explicit identification of these
42 substructures. Again, the model proved to be very flexible and logical relationships
43 easily control the possibility of decoupling or not (through heat exchangers) the DWC
44 from the rest of the sequence.
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- 47 4. In this work we presented a shortcut model approach based on the Underwood–Fenske
48 equations. However, the disjunctive representation of the model accommodates any
49 other aggregated or even rigorous model. In any case, the approach presented here is
50 enough for the preliminary design. It allows identifying some promising alternatives for a
51 latter detailed simulation.
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- 54 5. When we consider thermally coupled systems with DWCs, it is common that there are a
55 good number of alternatives with similar economic performance, but the best solution
56 not necessarily includes a DWC. Although these alternatives increases the difficulty of
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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 in order to avoid a large redundancy (i.e. large number of equivalent configurations with the same performance from the total annual cost point of view).

The extension to multiwall systems, if not straightforward, is not difficult. The major difficulty is in identifying structures that are able of being rearranged in a multiwall column. An outline of how to, recursively, identify these alternatives was also presented. However, in this case other considerations (hydrodynamics, controllability etc) are not yet to our knowledge, satisfactorily solved.

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 Agrawal²⁹. In this work we do not consider those alternatives but just the 'classical' divided wall columns with at most a single reboiler and a single condenser.

ACKNOWLEDGMENTS

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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.

$P_REC_s = \{\text{task } t \text{ that produces final product } s \text{ through a rectifying section.}\}$

$P_STR_s = \{\text{task } t \text{ that produces final product } s \text{ through a stripping section.}\}$

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.*

$$\bigvee_{t \in TS_t} Y_t \leq K \quad ; \quad s \in COL \quad (A1)$$

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*

$$\left. \begin{array}{l} \bigvee_{t \in RECT_s} Y_t \leq K \\ \bigvee_{t \in STRIP_s} Y_t \leq K \end{array} \right\} s \in STATES \quad (A2)$$

where K has the same meaning than in equation (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.*

$$\bigvee_{t \in (P_REC_s \cup P_STR_s)} Y_t ; s \in FP \quad (A3)$$

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.*

$$\left. \begin{array}{l} \neg \left(\bigvee_{t \in P_REC_s} Y_t \right) \Rightarrow W_s \\ \neg \left(\bigvee_{t \in P_STR_s} Y_t \right) \Rightarrow W_s \end{array} \right\} s \in FP \quad (A4)$$

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).*

$$(Y_t \wedge Y_k) \Rightarrow \neg W_s \quad \left\{ \begin{array}{l} t \in RECT_s \\ k \in STRIP_s \\ s \in STATES \end{array} \right. \quad (A5)$$

6. *Connectivity relationships between tasks in the superstructure*

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

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

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

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.

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

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.

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

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 equations (A8,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:

$$Y_t \Rightarrow Z_s; \quad t \in ST_s \quad (A10)$$

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

Equation (A10) could be read as: "if the task t , that belongs to the set of task produced by the state s , exists then the state s must exist". And equation (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 y_t or z_s , but not both. Whether y_t is declared as binary z_s can be declared as continuous between zero and one and vice-versa.

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Table 1. Data for example 1.

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)- Ethylbenzene	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	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)).

Table 2. Results and model statistics in example 1.

	Model		Sol 1.2		Sol 1.3		Sol 1.4		Sol 1.5		Sol 1.6	
	Sol 1.1											
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)	ABCD/DE	(38)	ABCD/BCDE	(7)	ABCDE/BCDE	(7)	ABCDE/BCDE	(7)	A/BCDE ^C _R (17) B/CDE ^C _R (19) CD/E ^C _R (58) D/E ^C _R (58)	
	AB/BCD ^C	(9)	AB/BCD ^C	(9)	AB/BCD ^C	(9)	A/BCD ^C	(17)	AB/BCD	(9)		
	BC/CD	(14)	BC/CD	(14)	BCD/DE	(28)	BCD/CDE _R	(12)	BCD/DE	(28)		
	A/B ^C	(17)	A/B ^C	(17)	BC/CD	(14)	B/CD ^C	(19)	B/CD	(19)		
	B/C	(19)	B/C	(19)	A/B ^C	(17)	CD/DE	(28)	A/B ^C	(17)		
	C/D	(53)	C/D	(53)	B/C	(19)	C/D ^C	(53)	C/D ^C	(53)		
	D/E _R	(58)	D/E _R	(58)	C/D	(53)	D/E _R	(58)	D/E _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	
N° equations	3028		3207		3043		3208		3043 (2933)**		1189	
N° continuous variables	1347		1347		1347		1347		1338 (1312)**		661	
Binary variables	65		65		65		65		56 (30)		20	

* 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.

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).

Table 4. Results and model statistics in example 2.

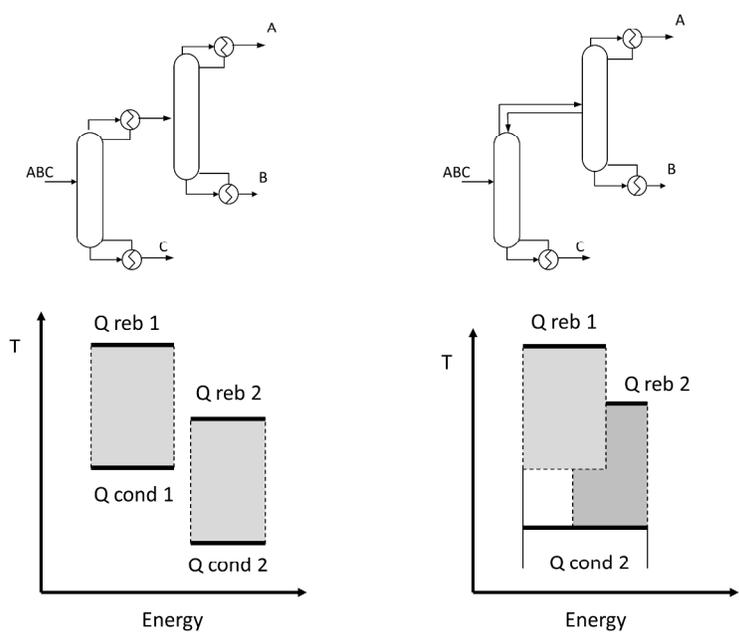
	Model		
	Sol 2.1	Sol 2.2	Sol 2.3
Total vessels cost (k\$)	413.994	468.127	361.006
Total tray cost (k\$)	123.810	135.268	96.383
Total reboilers cost (k\$)	244.198	192.704	477.674
Total condensers Cost (k\$)	215.735	266.341	438.680
Total steam cost (k\$/year)	439.376	442.061	844.981
Total cooling water 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)	BCD/CDE (8)	
	AB/BC ^C (11)	A/BC ^C (22)	AB/CDE ^C _R (22)
	BC/CD (11)	BC/CD (11)	C/DE ^C _R (22)
	CD/DE (12)	CD/DE (12)	A/B ^C _R (22)
	A/B ^C (22)	B/C ^C (22)	D/E ^C _R (23)
	B/C (22)	C/D (22)	
	C/D (22)	D/E _R (23)	
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

* 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.

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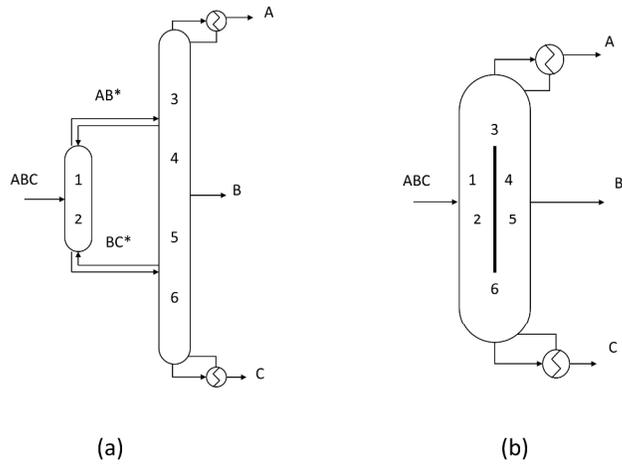


Sequence of conventional columns (left) and thermal couple (right) by removing the condenser in the first column.

254x190mm (300 x 300 DPI)

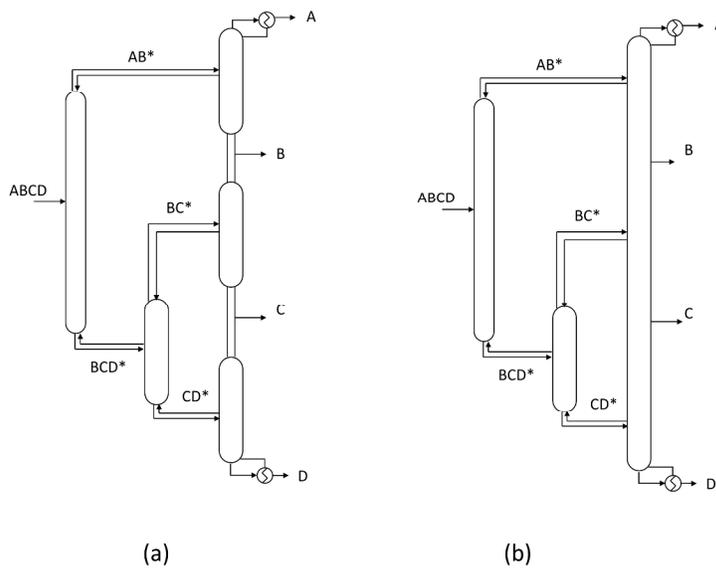
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(a) Petlyuk configuration. (b) Divided Wall Column. Both are thermodynamically equivalent.
254x190mm (300 x 300 DPI)

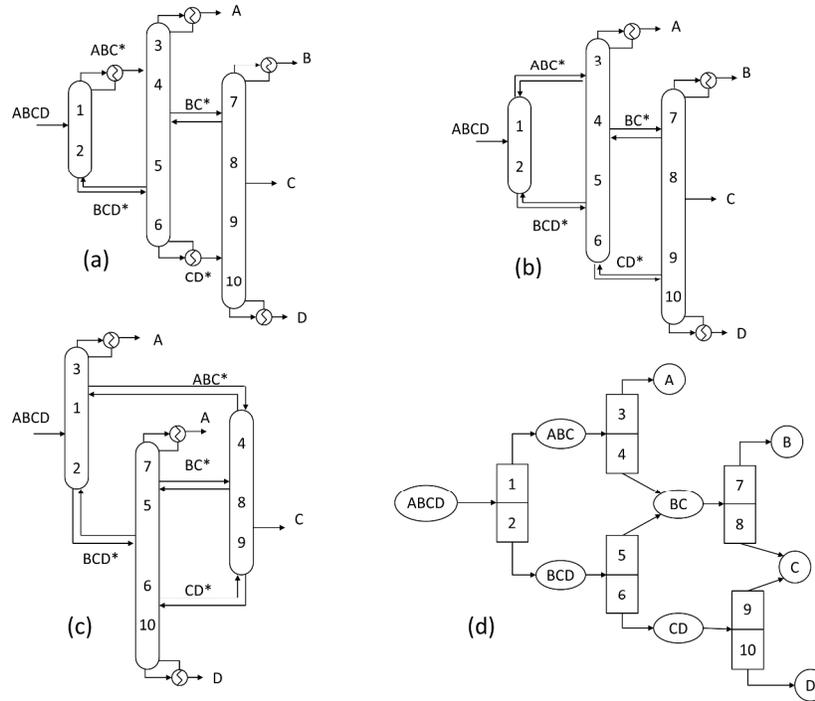
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(a) Separation sequence using 5 columns and (b) one out of the 16 possibilities rearrangement using three distillation columns.

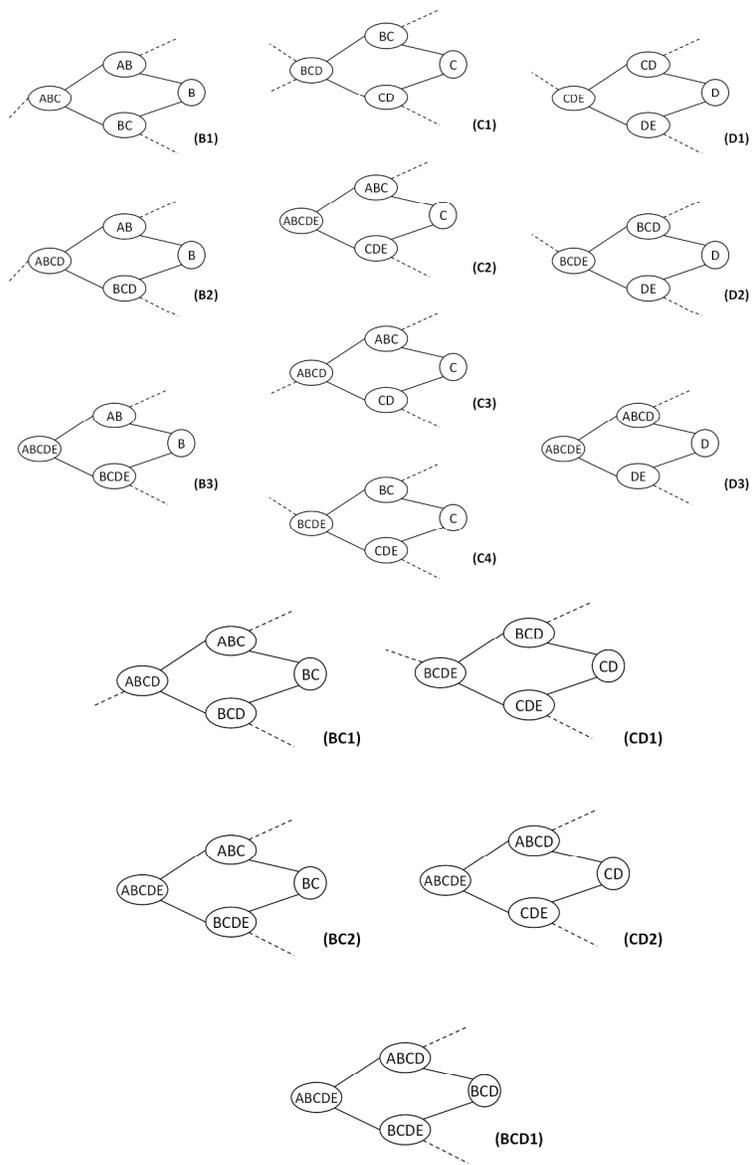
254x190mm (300 x 300 DPI)

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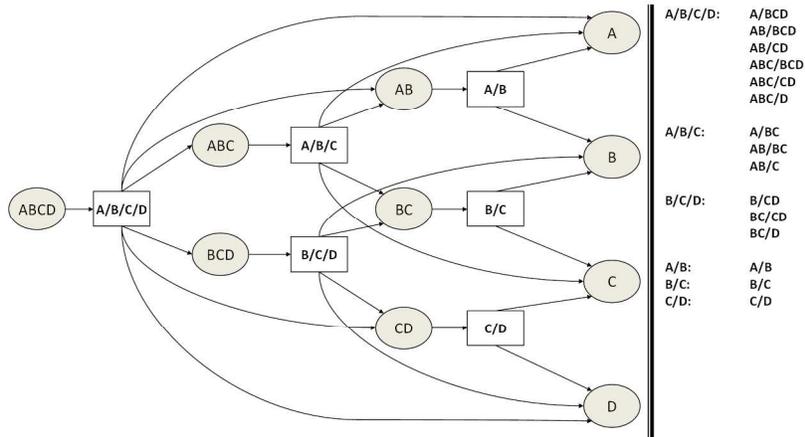
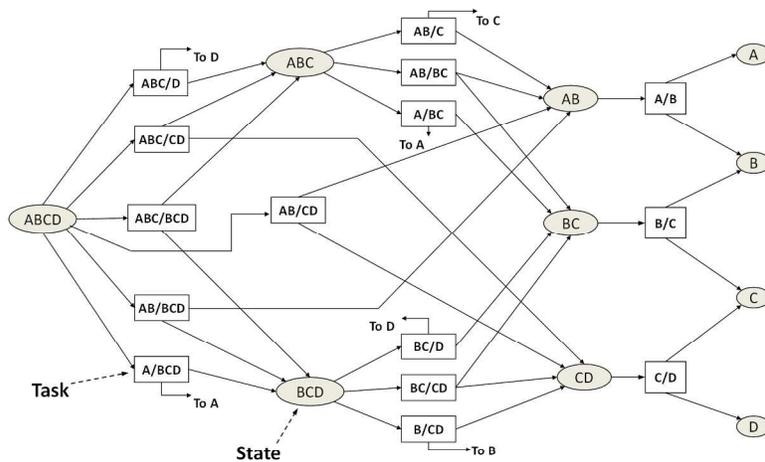
Three sequences of columns with the same basic sequence. (a) and (b) differ in the internal heat exchangers and they are not equivalent. Figures (b) and (c) are thermodynamically equivalents. (d) Sequence of separation tasks common to the three column arrangements
 254x190mm (300 x 300 DPI)

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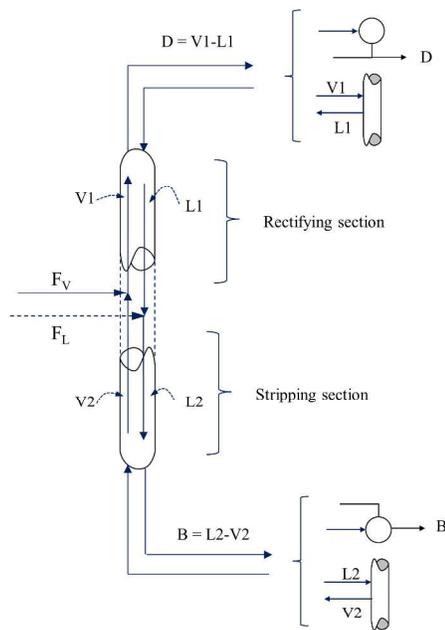


Sequences of states that can produce a DWC in a 5 component mixture.
190x254mm (300 x 300 DPI)

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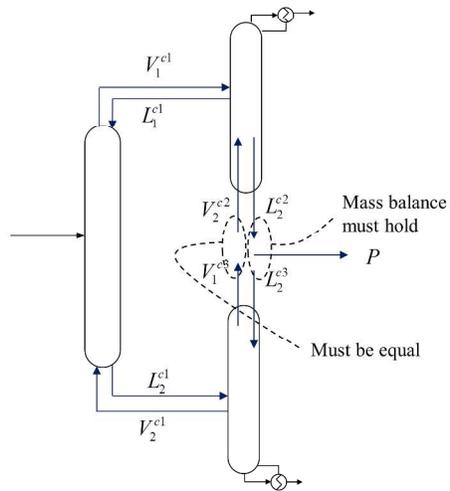
Two equivalent superstructures for a 4 component separation.
190x254mm (300 x 300 DPI)



Equivalence of a separation task with a pseudo-column. Some relevant nomenclature is included for clarity.
 254x190mm (300 x 300 DPI)

View only

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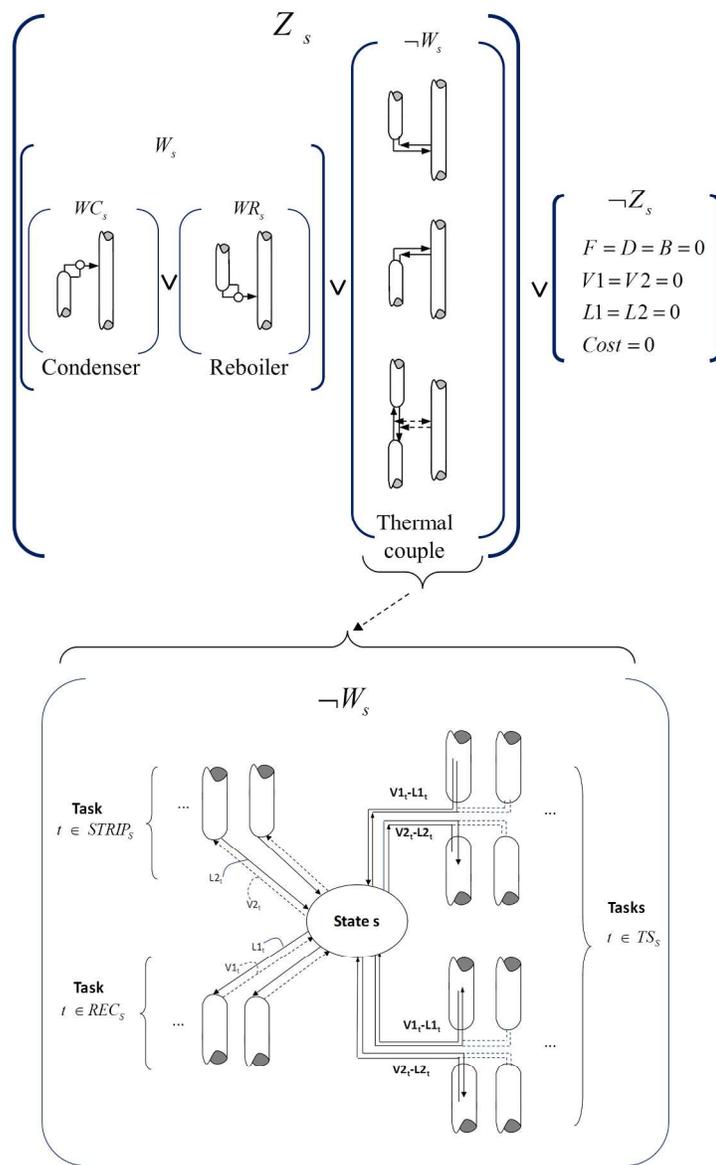


Flows in column 2 or/and column 3 must be adjusted to assure that:

$$V_2^{e2} = V_1^{e3} ; L_2^{e2} = L_2^{e3} + P$$

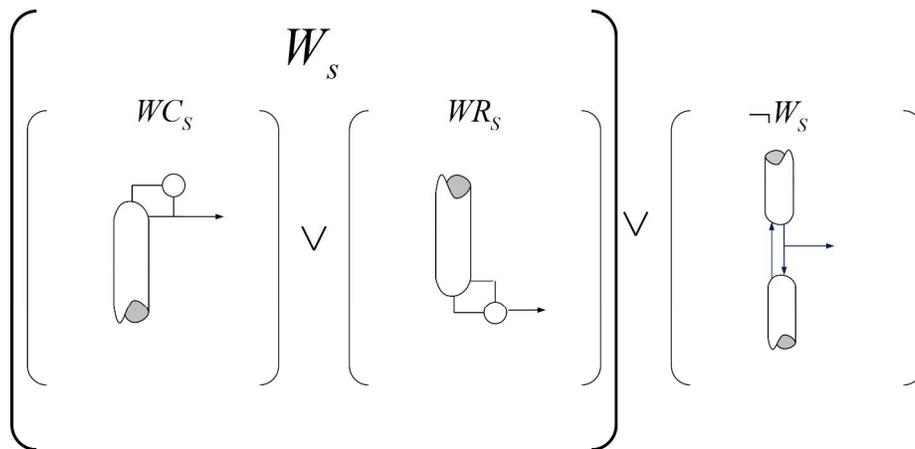
Example of how the flows in some sections must be modified to satisfied the mass balances.
254x190mm (300 x 300 DPI)

new only



Conceptual graphical description of disjunction D-2 (see text).
 190x254mm (300 x 300 DPI)

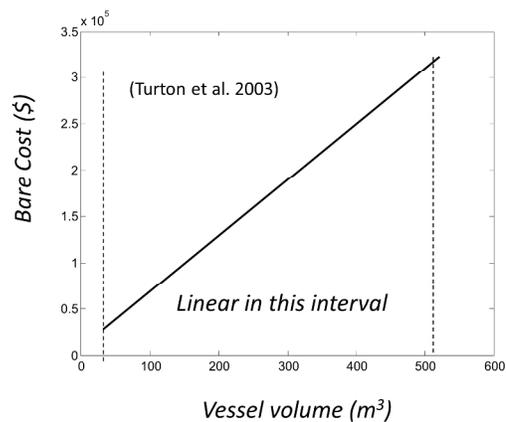
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Conceptual graphical representation of disjunction D-3 (see text).
254x190mm (300 x 300 DPI)

Review only

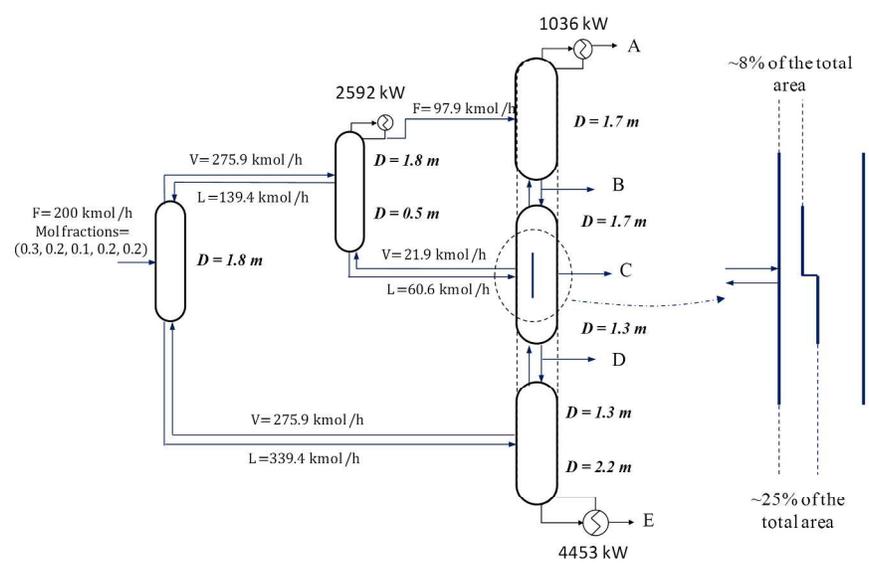
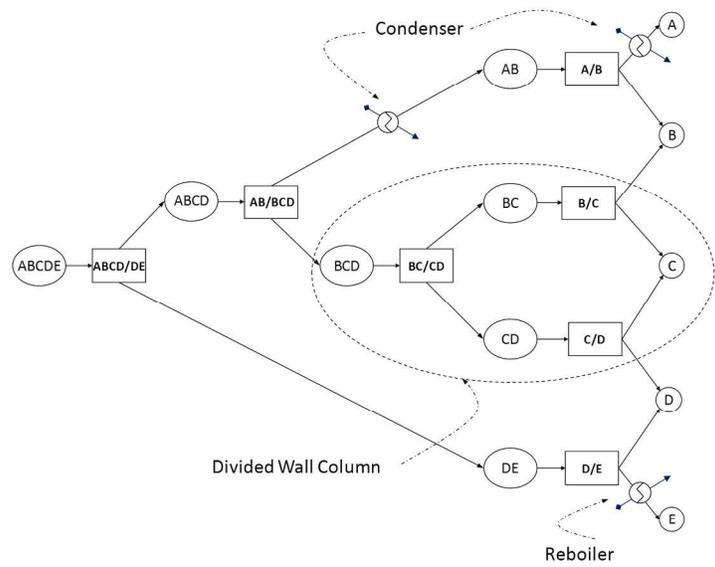
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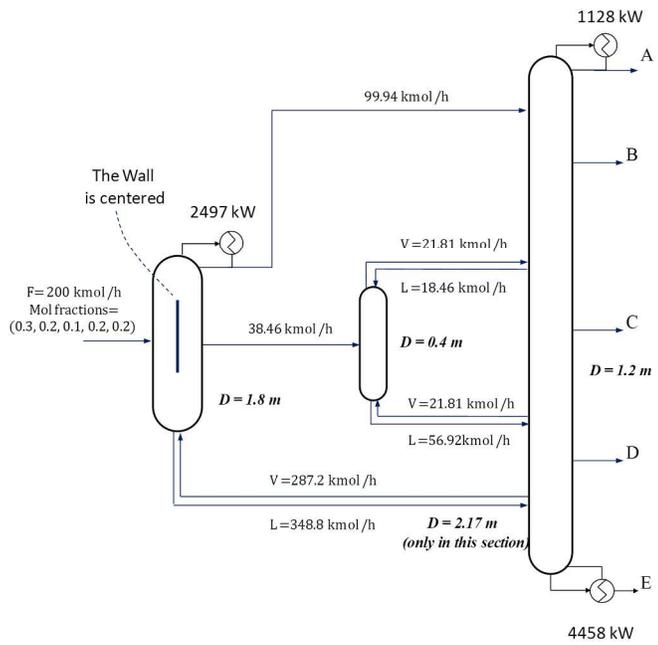
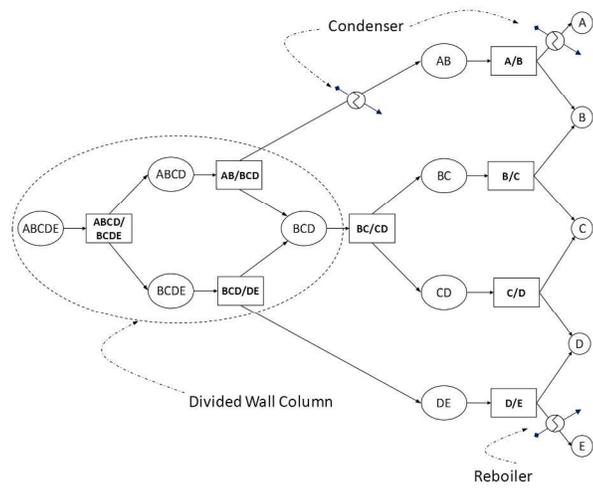
Bare cost module of the vertical vessel as a function of its volume
254x190mm (300 x 300 DPI)

iew only

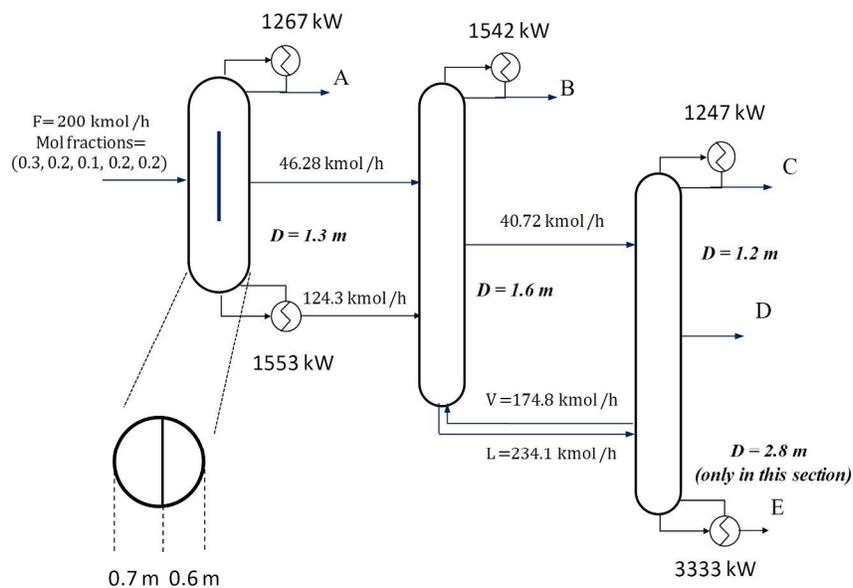
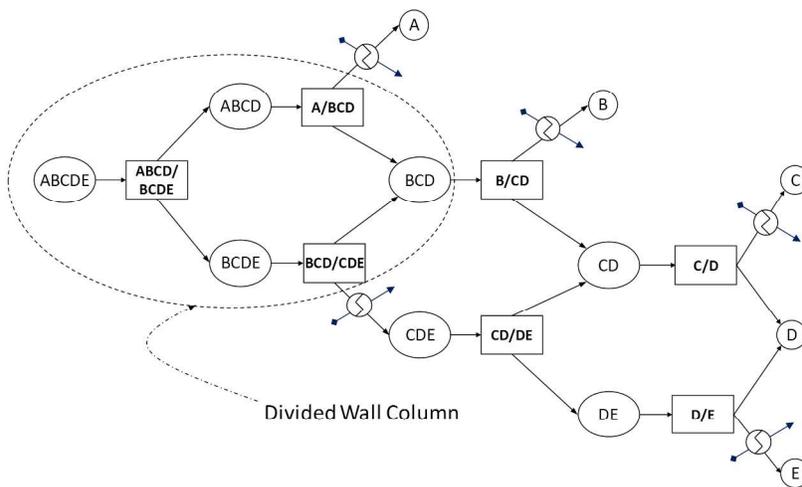
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Best solution for example1 (sol 1.1). Sequence of tasks and states and one out of the four thermodynamically equivalent possible arrangements in actual columns 190x254mm (300 x 300 DPI)



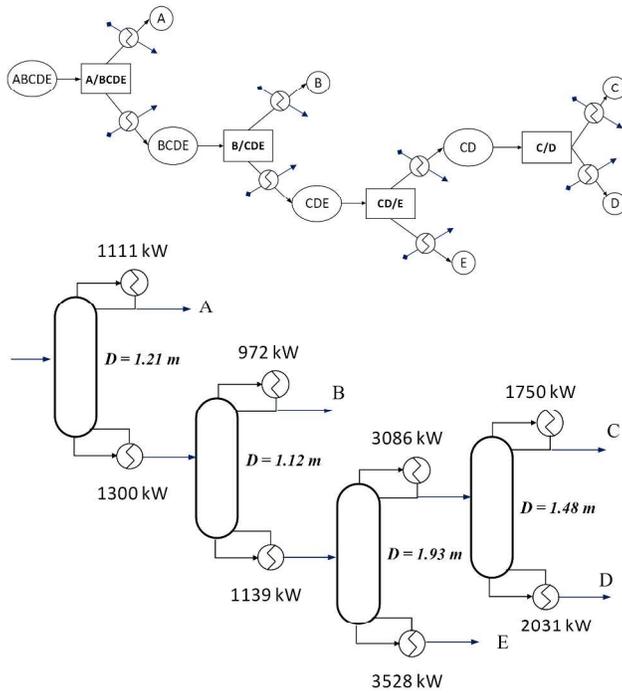
Second best solution for example 1. (sol 1.3).
190x254mm (300 x 300 DPI)



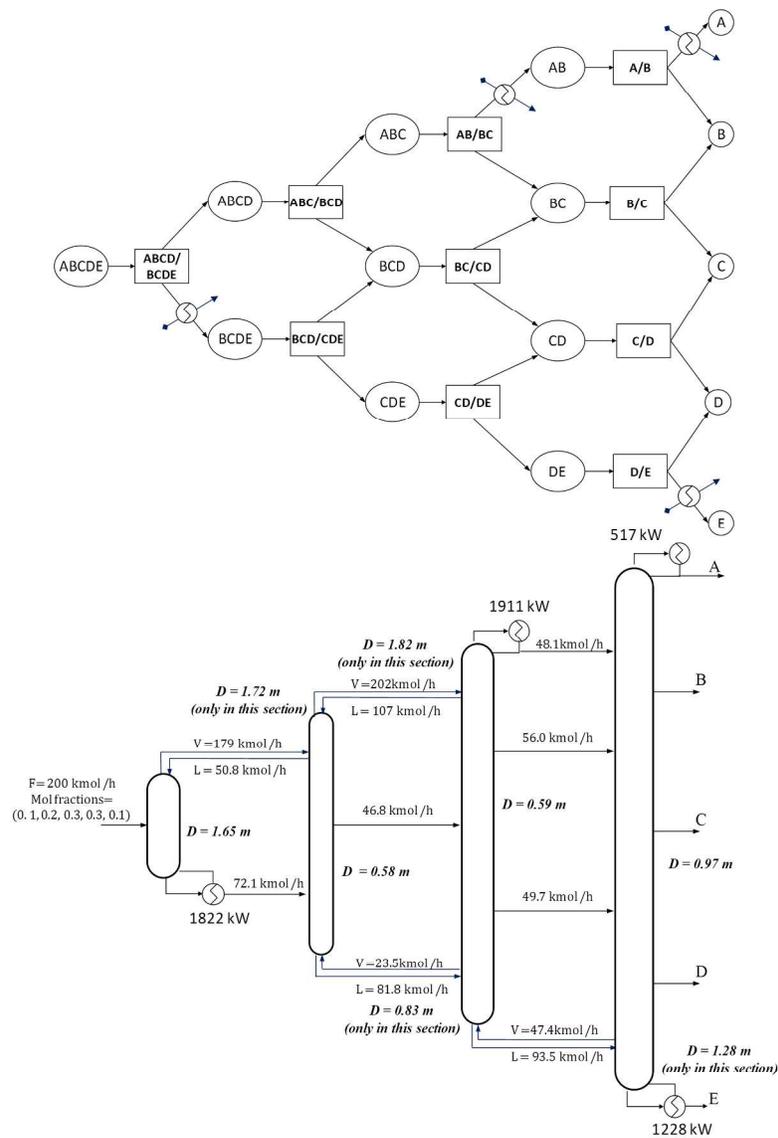
Best solution for example 1 including a DWC that is not thermally coupled with the rest of the system (sol 1.4).

190x254mm (300 x 300 DPI)

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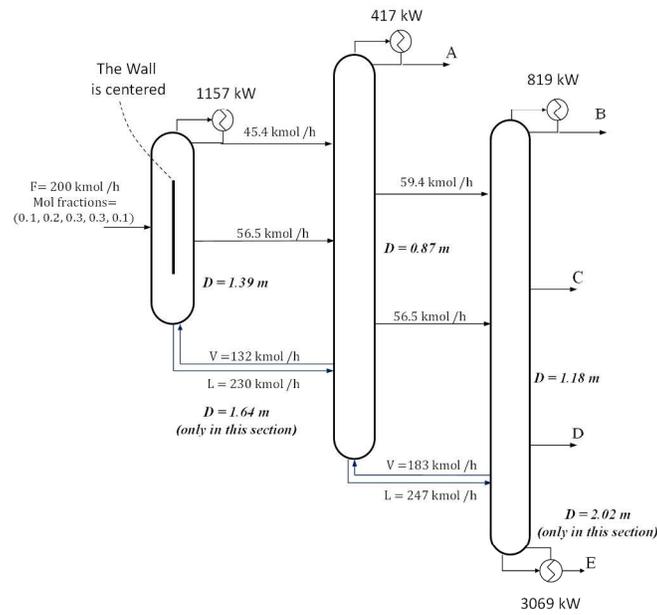
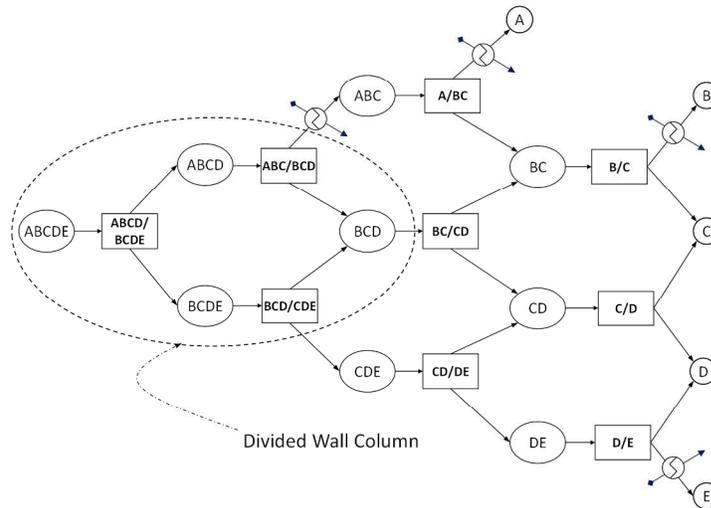
Best solution for example 1, using only conventional columns, "classical column sequencing". (Sol 1.6)
254x190mm (300 x 300 DPI)



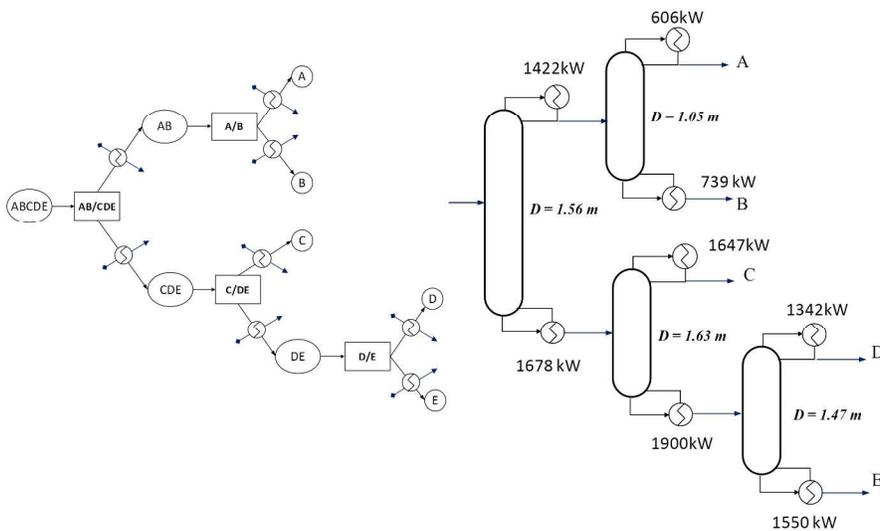
Optimal solution in example 2. (Sol 2.1)
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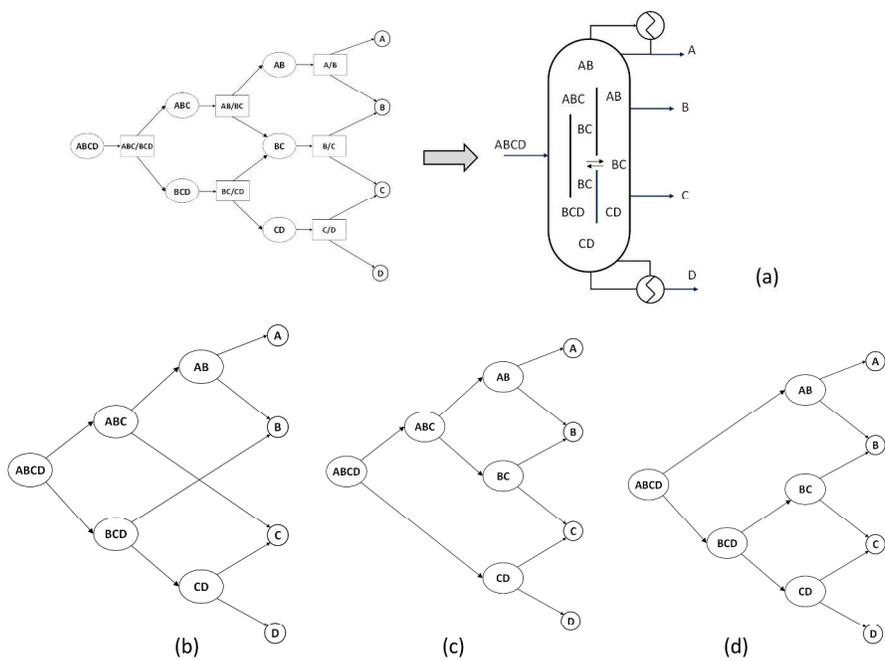


Best solution for example 2 using the heuristic algorithm. (Sol 2.2)
190x254mm (300 x 300 DPI)

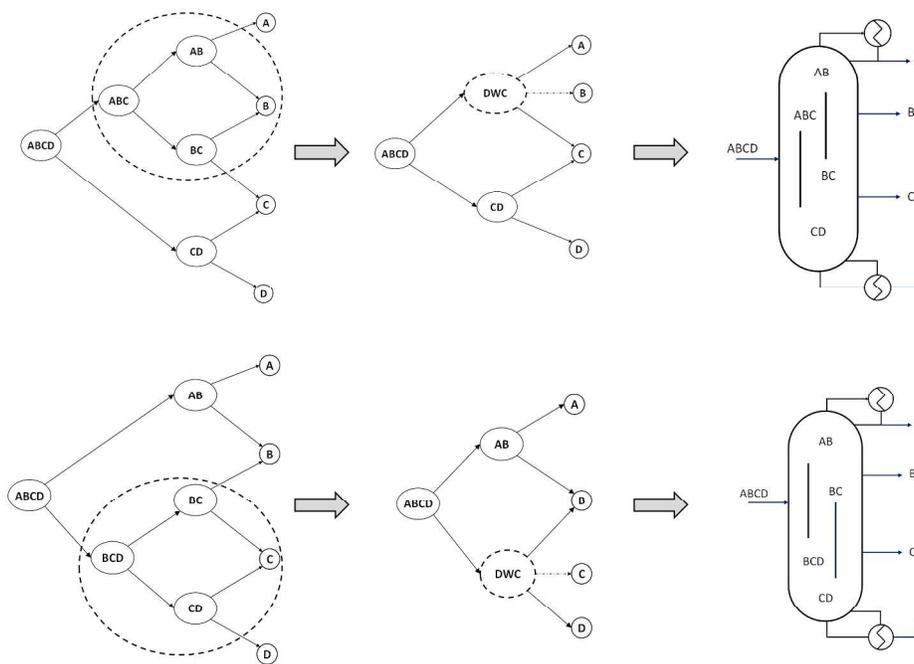


Best solution for example 2, using only conventional columns, "classical column sequencing". (Sol 2.3).
254x190mm (300 x 300 DPI)

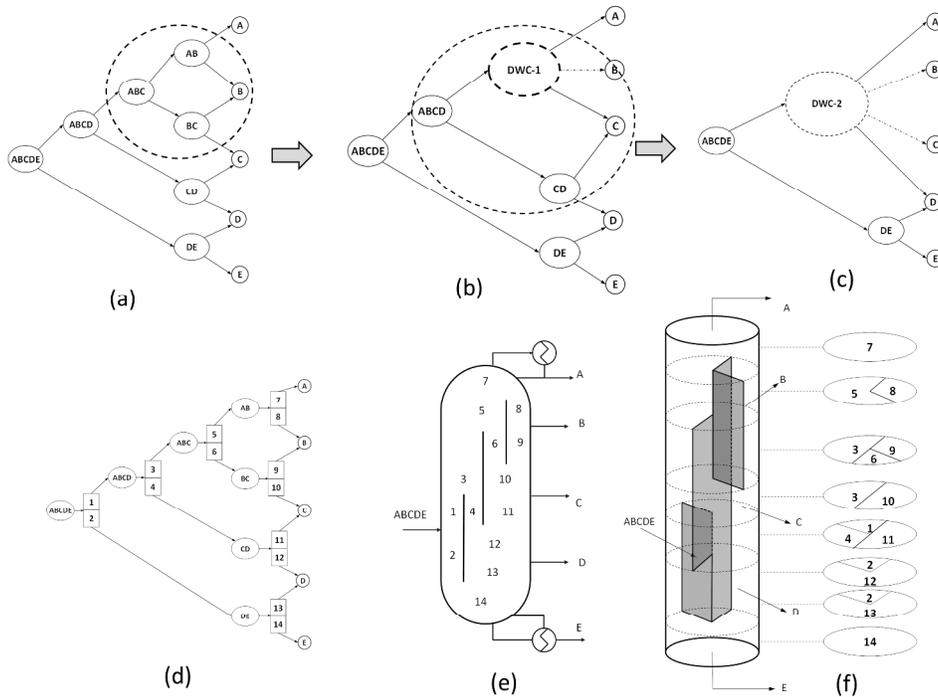
Preview only



Fully thermally coupled sequences of task for the separation of a 4 component mixture. (a) maximum number of separation tasks $(N(N-1)/2 = 6)$ and an arrangement using two internal walls. (b, c, d) Sequences using the minimum number of separation tasks $((4N-6)/2 = 5)$.
254x190mm (300 x 300 DPI)



The two feasible arrangements using two internal walls for 4 component mixtures with the minimum number of separation tasks
 254x190mm (300 x 300 DPI)



Recursive approach for generating an arrangement of multiple internal walls for a 5 component separation sequence (a-c). (d) sequence of states and tasks, (e) and (f) two possible arrangements of the internal wall in an actual column.

254x190mm (300 x 300 DPI)