



Structural considerations in zeotropic distillation sequences with multiple feeds

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ABSTRACT

The separation of multiple feed streams with some common components using sequences of distillation columns produces a rich space of alternatives that must be considered. In this work, we present the main structural characteristics of sequences generated when we want to take advantage of the synergies of common components in multiple feed streams to reduce both, energy consumption and the total number of distillation columns. In general, the sequence of separation tasks of the whole system can be obtained from the sequences of separation tasks of each one of the feeds. However, the integration in actual columns is not so straightforward and we must consider aspects like the optimal location of feeds in multiple-feed columns; and the alternatives of integration of common sub-mixtures (when possible) in actual columns. Besides, the optimal sequence of separation tasks for each feed is not necessarily the same when all of them are considered simultaneously. We show that the minimum number of actual columns, without considering further intensification, depends on the number of components in each feed and on the possibilities of integration of common sub-mixtures, so we extend the concepts of regular and basic column sequences to deal with these new situations. The examples show the potential savings in energy and number of columns compared to maintain isolated each feed; mixing the feed streams or an incorrect integration.

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1. Introduction

The general separation problem was defined more than fifty years ago by Rudd and Watson (1968) as the separation of mixtures from different sources into several product mixtures. That definition is wide general and therefore is not surprising that in Westerberg (1985) claimed that the general separation problem was essentially unsolved. And, even with the impressive advances in the last decades, in all the fields of separation technologies, the general separation process is still far away to be solved. Therefore, instead of dealing directly with the general problem, the researchers have focused on specific problems or specific technologies.

In the chemical industry, over 90–95% of all the separations and purifications are based on distillation (Humphrey and Keller, 1997). In terms of energy, distillation accounts for about 3% of the total US energy consumption, equivalent to $2.87 \cdot 10^{18}$ J (2.87 million TJ) per year that is equivalent in terms of power consumption to 91

GW (Soave and Feliu, 2002). Therefore, in this work, we will focus on distillation.

While the separation based on distillation is more specific than the general separation problem it continues to be a complex problem and there is not a unified solution. Instead, it is common to classify the separations in terms of the physical characteristics of the mixture. Thus, usually, we differentiate between mixtures containing azeotropes and mixtures that do not form azeotropes. While azeotropic mixtures are considerably more difficult to separate, the set of alternatives (sequences of columns) is considerably smaller (Górak and Sørensen, 2014). Azeotropic distillation is out of the scope of this work, the interested reader can find comprehensive reviews of azeotropic and extractive distillation in Gerbaud et al. (2019), Kiva et al. (2003), Shen et al. (2016), Sun et al. (2019).

In the case of zeotropic separation, historically it has been differentiated in turn between two cases; when each distillation column performs a sharp separation between two consecutive key components, and when some components are allowed to distribute between distillate and bottoms because their volatility is in between the two key components -nonconsecutive keys- (Caballero and Grossmann, 2014a, 2014b).

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The first attempts to systematically find the best sequence of separation zeotropic mixtures using only distillation columns, studied the case of a single source mixture with sharp separation of consecutive key components using conventional columns -A conventional column can be defined as a distillation column with a single feed and two products; distillate and bottoms-. In this particular case, the problem of enumerating all the sequences is straightforward (Westerberg, 1983), but selecting the best alternative in terms of the total cost, energy consumption, or any other performance indicator is not so easy because the number of sequences increases very fast with the number of key components to be separated. Therefore, the selection of the best alternative was usually based on heuristics (Heaven, 1969; Rudd et al., 1973; Seader and Westerberg, 1977).

The earliest models using optimization techniques can be dated back to the 70 s in the last century. For example, Thompson and King (1972) used an algorithm similar to an actual branch and bound search; Hendry and Hughes (1972) used a search based on dynamic programming; while other researchers used ad hoc optimization approaches to deal with the problem (Gomez and Seader, 1976; Rodrigo and Seader, 1975; Westerberg and Stephanopoulos, 1975).

Andrecovich and Westerberg (1985) presented one of the first approaches to synthesize distillation sequences based on a superstructure and a MILP (Mixed Integer Linear Programming) optimization problem. They identified all the possible sub-mixtures (groups of components after a sharp separation) and the possible set of separations for a given sub-mixture and created a superstructure. Under the assumption of complete separation of key components Andrecovich and Westerberg showed that each possible separation can be calculated a priori, and therefore, the problem of generating the best sequence can be formulated as a linear MILP problem. Latter different researchers have used the superstructure by Andrecovich and Westerberg (1985) with models with different degree of complexity (Caballero and Grossmann, 1999; Caballero and Grossmann, 2014a, 2014b; Yeomans and Grossmann, 2000a) including rigorous tray by tray models (Bartfield et al., 2004; Yeomans and Grossmann, 2000b), or even the optimization using rigorous models in state of the art chemical process simulators (Caballero, 2015).

Novak et al. (1996) using the fact that sharp separation of N consecutive key components requires exactly $N-1$ conventional distillation columns proposed a superstructure formed by exactly $N-1$ columns. In this case, the combinatorial part is translated to the assignment of the separation tasks to each one of the columns and to the connectivity between distillation columns. Latter Yeomans and Grossmann (1999) proposed a systematization of superstructure generation, using the concepts of State; Task; and Equipment, and identified the superstructures proposed by Andrecovich and Westerberg (1985) and Novak et al. (1996) as extreme cases known as State Task Network (STN) and State Equipment Network (SEN).

Other alternatives include the representation of a distillation column as a mass and heat exchange network (Bagajewicz and Manousiouthakis, 1992). Papalexandri and Pistikopoulos (1996) used a general multipurpose heat/mass transfer module for the representation of conventional and nonconventional process units, including distillation.

There are other alternatives for systematic superstructure generation that can be extended to distillation. The interested reader can consult the review by Mencarelli et al. (2020).

When in a given separation, we assume that the key components can be non-consecutive (i.e. some of the components with volatilities between the keys are optimally distributed between distillate and bottoms) the generation of the complete space of feasible sequences is more complex. The main structural characteris-

tics of the search space were established by Agrawal (1996). However, the rigorous generation of the complete search space -all the feasible sequences of distillation columns- was developed later in parallel by different groups.

Caballero and Grossmann (2013, 2006, 2004, 2001) developed a set of logical rules that implicitly generate all the feasible sequences. Those logical rules can be transformed into algebraic equations in terms of binary variables that can be introduced in an optimization model to select the best alternative among all the set of feasible ones. Alternatively, Shah and Agrawal (2010) developed a set of rules that systematically allow generating, even at hand, all the feasible set of alternatives.

It is worth remarking that after the Agrawal work in 1996, and all the posterior contributions, the differentiation between separations considering only consecutive key components or non-consecutive is purely formal because the set of separations with consecutive key components are included in the set of all feasible zeotropic separations.

During the last decades, there have been important advances in zeotropic distillation sequences. For example, since Agrawal's seminar work (Agrawal, 1996) zeotropic distillation and Thermally Coupled Distillation (TCD) are closely related. The search space of zeotropic distillation should include also the set of partially or fully thermally coupled distillation configurations (Giridhar and Agrawal, 2010).

Other extensions to zeotropic distillation include heat integration and TCD (Caballero and Grossmann, 2006; Rong and Turunen, 2006), integration with vapor recompression cycles (Alcántara-Avila et al., 2012; Navarro-Amorós et al., 2013), multi-effect distillation (Agrawal, 2000), or heat and process integration (Skibrowski, 2020).

In process intensification there have been also important advances, like divided wall columns (Asprion and Kaibel, 2010; Kiss, 2012); sequences with a reduced number of columns by elimination of some column sections (Errico et al., 2014b, 2014a, 2009); or adding some columns to force the "liquid transfer only" that allow new divided wall columns (Madenoor Ramapriya et al., 2014) and create a good number of new alternatives. And, of course, the combination of all of them creates a new world of unexplored alternatives. A good review of recent advances in process intensification can be found in Jiang and Agrawal (2019).

The problem of designing a multiple-feed, multi-product single column has been widely studied (Adiche and Ait Aissa, 2016; Bandyopadhyay et al., 2004; Glanz and Stichlmair, 1997; Nikolaidis and Malone, 1987). However, as far as we know, the structural characteristics of the search space of the most general problem in which we have multiple streams to be separated using distillation have not been systematically addressed. The main objective of this paper is therefore to cover this gap.

In the rest of the paper, first, we introduce an overview and some basic definitions and characteristics of single feed sequences of distillation columns for separating zeotropic mixtures. Then we will show how to extend the results of single feed sequences to multiple feed sequences, together with the main considerations to take into account. As a consequence, we will have to redefine some basic concepts like the definitions of regular and basic configurations. Finally, we illustrate the methodology with some examples.

2. Sequences of single feed zeotropic separations. Some basic definitions

In this section, we do a, necessarily brief overview of some relevant characteristics of the search space of the alternatives for separating a single feed stream formed by N components that do not form azeotropes. Further details can be found in the references given and those therein.

In the rest of the discussion, we assume that a given mixture (the feed streams or any sub-mixture generated by a distillation column in the sequence) is formed by a set of components named in general A, B, C, ... sorted by decreasing relative volatilities. A given sub-mixture is identified by a subset of those components. For example, a mixture "BCD" is a stream formed by the components B, C, D. Note that in the mixture BCD could appear other minority components (e.g. traces of A).

The building block for generating all the feasible column sequences is the separation task. We can think of a separation task as a pseudo-column formed by a rectifying and a stripping section). A separation task is denoted by two subsets of components separated by a slash (i.e. ABC/CD); the components in the left are obtained by the rectifying section of the separation task and those on the right side by the stripping section. If a component appears on both sides it means that it is distributed between the distillate and bottoms of the pseudo-column.

Using the concept of sub(mixtures) -also named states by some authors- and separation tasks is straightforward to generate a feasible separation sequence. However, Caballero and Grossmann (2006) and Giridhar and Agrawal (2010) proved that, without considering further integration or intensification, the optimal sequence of separation tasks belongs to the subset of sequences that can be arranged in exactly $N-1$ columns. Note that although the total number of actual columns is $N-1$ the total number of separation tasks can range from $N-1$ in the case of consecutive key components, up to a maximum of $N(N-1)$. Fig. 1 shows some examples for the separation of a four component mixture using 3, 4, 5 and 6 separation tasks, but in all the cases exactly three distillation columns.

Around the 2000 s different methods appeared to generate feasible single feed zeotropic distillation sequences. Starting with methods to generate feasible alternatives with some interesting characteristics (Rong et al., 2003, 2000; Rong and Kraslawski, 2003; Kim, 2006, 2005, 2002, 2001). Up to the complete search space of alternatives, either based on rules (Agrawal, 2003; Caballero and Grossmann, 2014a, 2014b) or based on logic relationships (Caballero and Grossmann, 2006, 2004, 2001).

A complete description of any of the alternatives for generating the complete search space of sequences of separation tasks and/or sub-mixtures (there is a one-to-one relationship between a valid sequence of separation tasks and the involved sub-mixtures) that can be rearranged in exactly $N-1$ columns is too large to be included here. However, some basic concepts and definitions are relevant to this paper:

Since the work of R. Agrawal in 1996, zeotropic distillation and Thermally Coupled Distillation (TCD) are closely related. Agrawal showed that given a sequence of columns it is possible to remove the heat exchangers connecting two columns (heat exchangers associated with intermediate mixtures) and substitute them with thermal couples, without changing the structure of separation tasks and without modifying the number of columns or column sections of the original sequence. But with different energy consumption. Fig. 2 shows an example.

Giridhar and Agrawal (2010) proved that the search space of alternatives must include also all the configurations containing thermal couples. To that end, Shah and Agrawal (2010) introduced the concept of «regular configuration» that is a configuration with exactly $N-1$ columns independently of the internal structure of heat exchangers and thermal couples.

Shah and Agrawal (2010) also introduced the concept of «basic configuration» as a regular configuration with each column having one reboiler and one condenser. A basic configuration is important because the sequence of separation tasks is unique for each basic sequence. The set of all basic sequences allows generating the

complete space of regular sequences just by sequentially removing heat exchangers associated with internal sub-mixtures and substitute them with thermal couples. In consequence to generate all the set of regular configurations we only need to generate the set of basic configurations. As an example, Fig. 2b is a basic configuration, and the rest 2c to 2i are the rest of regular configurations generated from the basic one.

Even though, if we are interested in obtaining the best separation sequence in some performance index (e.g. energy, cost, etc.) we must consider the space of regular configurations; the structural considerations for generating valid column sequences depend only on the sequence of separation tasks that generate all the products and are rearrangeable in $N-1$ actual columns. In other words, we need only to study the space of basic configurations.

Note that instead of generating the 'basic configurations' we could generate sequences of separation tasks rearrangeable in $N-1$ columns, which is a more general concept than basic configuration because it does not assume any particular distribution of separation tasks in actual columns or any internal structure of heat exchangers (condensers and reboilers). However, the concept of basic configurations has been widely accepted, and therefore we will use it in the rest of the paper.

While generating all basic configurations is no straightforward checking if a sequence of separation task can be rearranged to form a basic configuration is easy and fast just by checking the following rules:

1. All the final products must be reachable.
2. If an intermediate sub-mixture appears (an intermediate sub-mixture is any group of compounds reachable by distillation, except the feed and the final products), it must be generated by one or two contributions. If it is generated by two contributions then one must come from the rectifying section of a separation task and the other from a stripping section of another separation task, and there is not heat exchanger associated with this sub-mixture (See Fig. 3a and b).
3. A final product can be generated by one or two separations tasks.
 - 3.1. If it is generated just by one separation task then there is a heat exchanger associated with that product (condenser if it comes from a rectifying section, or reboiler if it is generated by a stripping section).
 - 3.2. If it is generated by two separation tasks then one must come from the rectifying section of a separation task and the other from a stripping section of another separation task, and there is not heat exchanger associated with this product See Fig. 3c.

3. Structural considerations in zeotropic separations with multiple feed streams

In this section, we extend the characteristics of the search space of a single feed to deal with multiple feeds. While most of the considerations in previous sections continue to be valid we need to take into account the following considerations:

- Although two or more feeds share some components, usually the optimal solution is not to introduce those streams in the same column.
- The best separation sequence of each feedstream considered isolated from the rest is not necessarily the best one when they are considered simultaneously.
- The common components (or some sub-mixtures with some common components) allow integrating separation tasks coming from different feeds and reduce the number of actual columns and consequently reduce the total energy consumption.

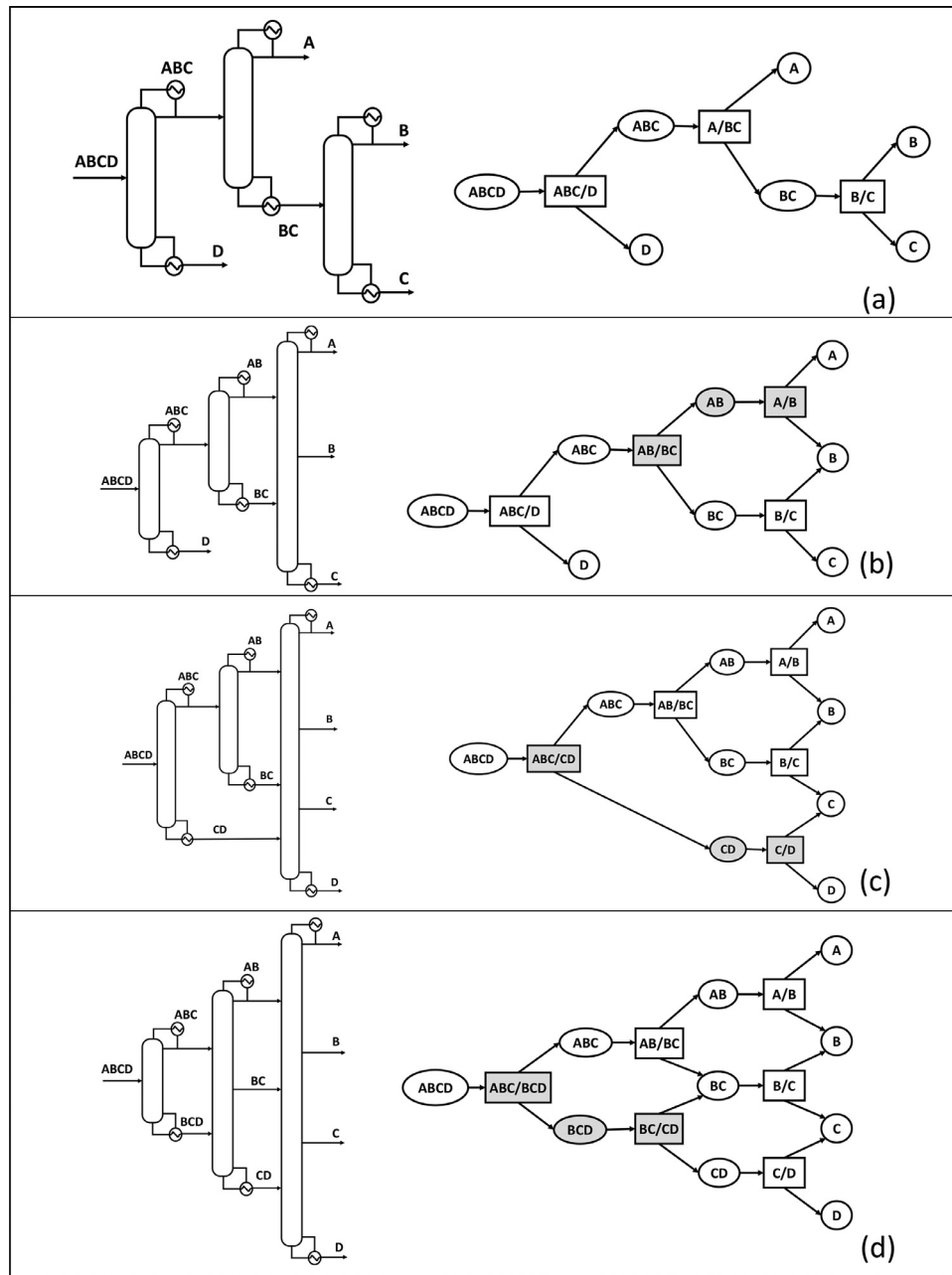


Fig. 1. Examples of sequences of separation of 4 component mixture with different number of separation tasks that can be rearranged in three distillation columns. (a) three separation tasks (ABC/D, A/BC and B/C). (b) 4 separation tasks (ABC/D, AB/BC, A/B, B/C) the component B is distributed between distillate and bottoms in the separation AB/BC. (c) 5 separation tasks (ABC/CD, AB/BC, A/B, B/C and C/D). The components B and C are distributed between distillate and bottoms in separations AB/BC and ABC/CD respectively. (d) 6 separation tasks (ABC/BCD, AB/BC, BC/CD, A/B, B/C and C/D) in this case the key components in each separation tasks are those components with extreme volatilities.

tion and eventually also the capital cost. The result is a new space of alternatives no previously presented.

- As a consequence of the previous point, the concepts of 'Basic configuration' and 'Regular configuration' must be re-defined. A regular configuration cannot be defined anymore as a sequence formed by exactly $N-1$ columns (N is the total number of components to be separated) because the common components could eventually reduce the total number of actual columns.

When we have more than a single feed, the concept of basic configuration is not valid in its actual definition (as we will show later), so at the moment let us use to introduce the concept of Basic Structural Configuration. Two separation sequences have

the same Basic Structural Configuration if they share the same sequence of separation tasks (or the same sequence of sub-mixtures).

The following considerations allow us to systematically generate all the feasible Basic Structural Configurations from which we can generate the new space of basic sequences and therefore the set of all regular configurations. Remember that the structural considerations that characterize a valid sequence with a single feed continue to be valid and form the basis over which we build the extension to multiple feed streams:

As a general rule, «it is possible to generate all the basic structural configurations of a system with multiple feeds, from the combination of common separation tasks (or common sub-mixtures) of each one of the single-feed basic structural configurations.» Remember

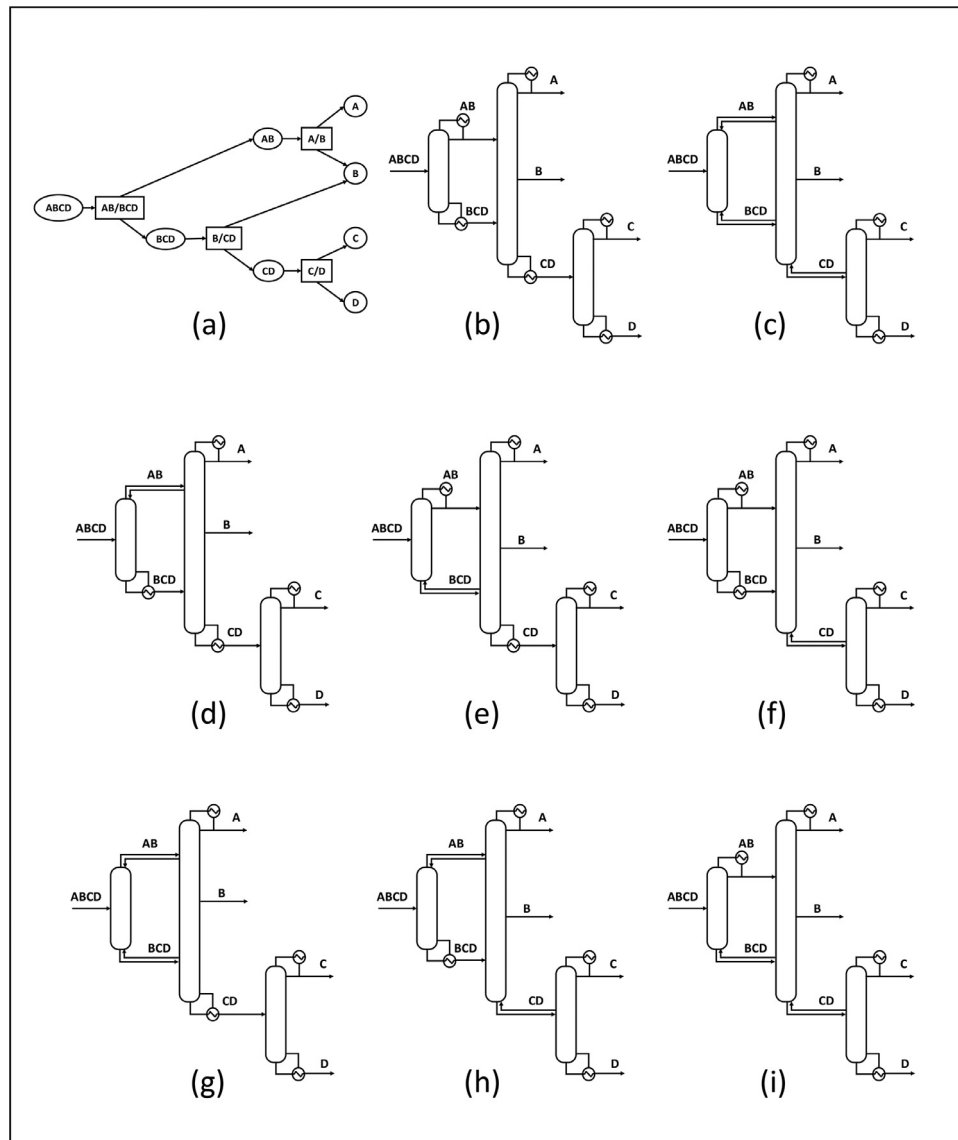


Fig. 2. Example of regular columns sequences for separating 4 components, all of them with the same sequence of separation tasks. (a) Sequence of separation tasks. (b) Basic sequence: each column with a reboiler and a condenser. (c) Fully thermally coupled sequence. (d–f) sequences with a thermal couple. (g–i) sequences with two thermal couples.

that a single-feed basic structural configuration is any sequence of separation tasks that can be rearranged exactly in $N-1$ distillation columns.

However, when we combine separation tasks generated from different feeds we must take into account the following considerations:

1. When two (or more) sub-mixtures formed by the same components, but different compositions (i.e. each sub-mixture comes from a different feed) are merged in a single column, then we must consider a two (or multi) feed column instead of mixing the feed streams. In another case, we generate a point of inefficiency due to the irreversible mixture of streams with different compositions. In other words, there is an extra degree of freedom to determine the relative positions of feeds in the new column.
2. According to the previous point, two (or more) streams with the same components but different compositions generated from different external feeds must be separated in the same column. However, the optimal relative position of these feeds influences the number of column sections and the possibility

that some zones of 'retro mixing' (inherent thermodynamic inefficiency) could appear. The following example will clarify all previous statement:

Consider a mixture ABC that is separated by a direct sequence (A/BC; B/C), and another feed BCD separated using a pre-fractionator (BC/CD; B/C, C/D). Remember that following the general rule, we can generate a valid basic structural configuration, simply merging these two separation sequences. Fig. 4a. Both sequences share the sub-mixture BC. Then the separation B/C must be carried out in the same column either with a two feed column or previously mixing both BC streams.

If we decide to use a two feed column, we need to determine the optimal location of each one of the feeds. And again different situations can appear:

- 2.a. If the optimal location of sub-mixture BC coming from a rectifying section of a previous separation is above the sub-mixture BC coming from a stripping section, then from the point of view of energy consumption we should not merge those two BC streams in the same column and we need to

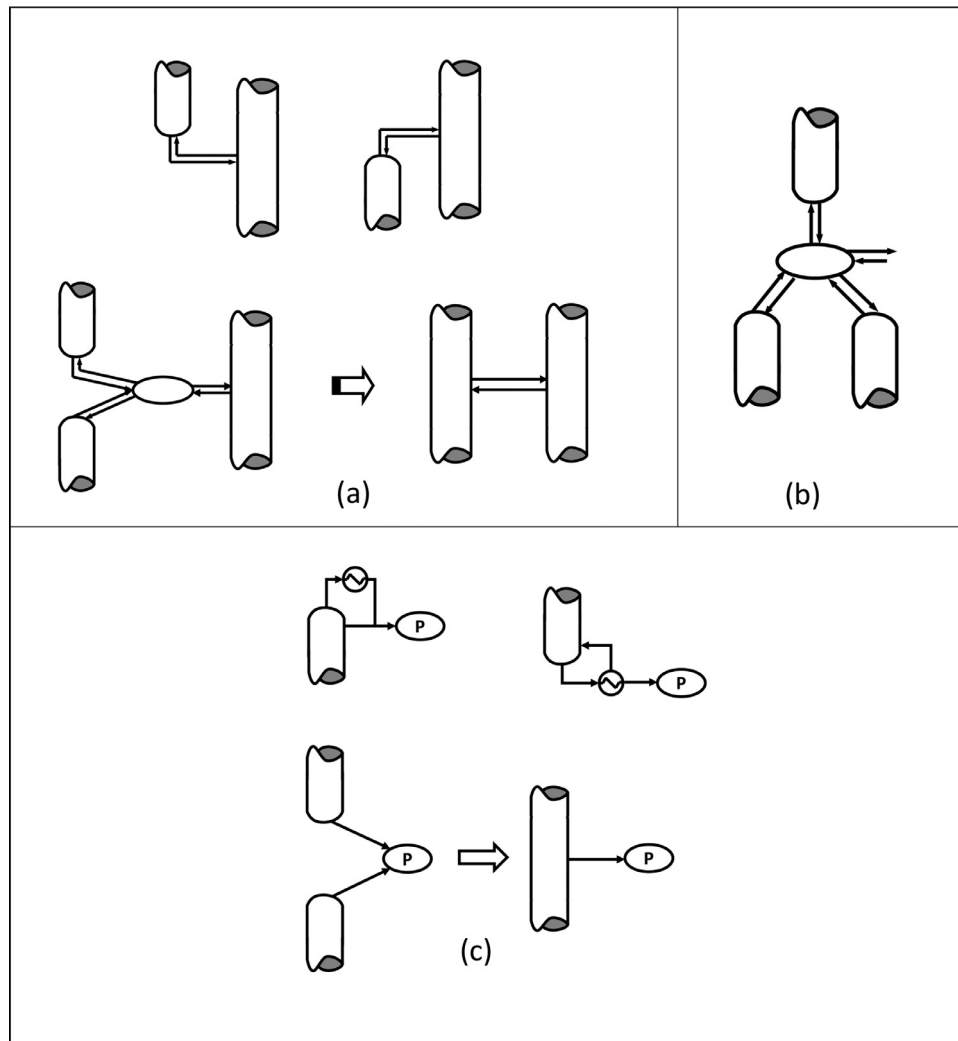


Fig. 3. Alternatives for sub-mixtures to form actual columns. (a) The submixture is reached by one or two contributions. If the sub-mixture is formed by two contributions, one comes from a rectifying section and another from a stripping section. (b) A sub-mixture is formed by two contributions coming from rectifying sections. In this case we must add an extra column. (c) Alternatives for products: if product *P* is formed by a single contribution it must have a heat exchanger; if it is formed by two contributions the heat exchanger can be removed.

add one more column (Fig. 4b).

The important extra cost of adding a new column suggests that despite the inherent thermodynamic inefficiency of some mixing, that is a better option than adding a new column. There are two possibilities: 1. Mixing the two streams like in Fig. 4c. 2. Merge both sections in a single column by adding an extra column section (Fig. 4d), but again the inherent inefficiency created by the retro-mixing in this new section is likely that does not compensate for the benefit of the correct placement of the two BC streams in the second column. But the best alternative is case-dependent and we should take all of them into account.

2.b If the optimal feed location of the sub-mixture BC coming from a stripping section is above the sub-mixture BC coming from a rectifying section then a two feed column must be implemented, Fig. 4e. In this last case, the extra column section between both BC streams does not introduce important inefficiencies compared to the benefit of the correct placement of the two feeds.

3. Given *m* feeds each one with n_m components, for a total of *N* different components, in which a given feed shares at least one component with another feed. If we sort the components by volatility, and in each one of the feeds there is not any

component missing between the lightest and heaviest in that feed, it is possible to generate basic structural configurations that can be arranged in column sequences that can range from

$$\max_{i=1 \dots m} \{n_i - 1\} \text{ to } \sum_{i=1}^m (n_i - 1) - (m - 1).$$

The minimum number of columns can be obtained in two situations:

3.1 There is a feed stream that contains the *N* key components to be separated ($\max\{n_m\} = N$) and the rest of the feeds are formed by sub-mixtures that are reachable from that stream. Under those conditions, there must exist a configuration of *N*-1 columns in which the feeds with less than *N* components can be integrated through multi-feed column sections.

Consider as an example the case in which we have three feeds: ABCD, BC, ABC. The first feed (ABCD) contains all the *N* key components, and sub-mixtures BC and ABC are reachable from ABCD using adequate separation tasks. Fig. 5 illustrates two configurations of 3 columns that integrate the three feeds. In Fig. 5a the external feed ABC is added together with the sub-mixture ABC generated from the external feed ABC. In Fig. 5b the external feed ABC is added as

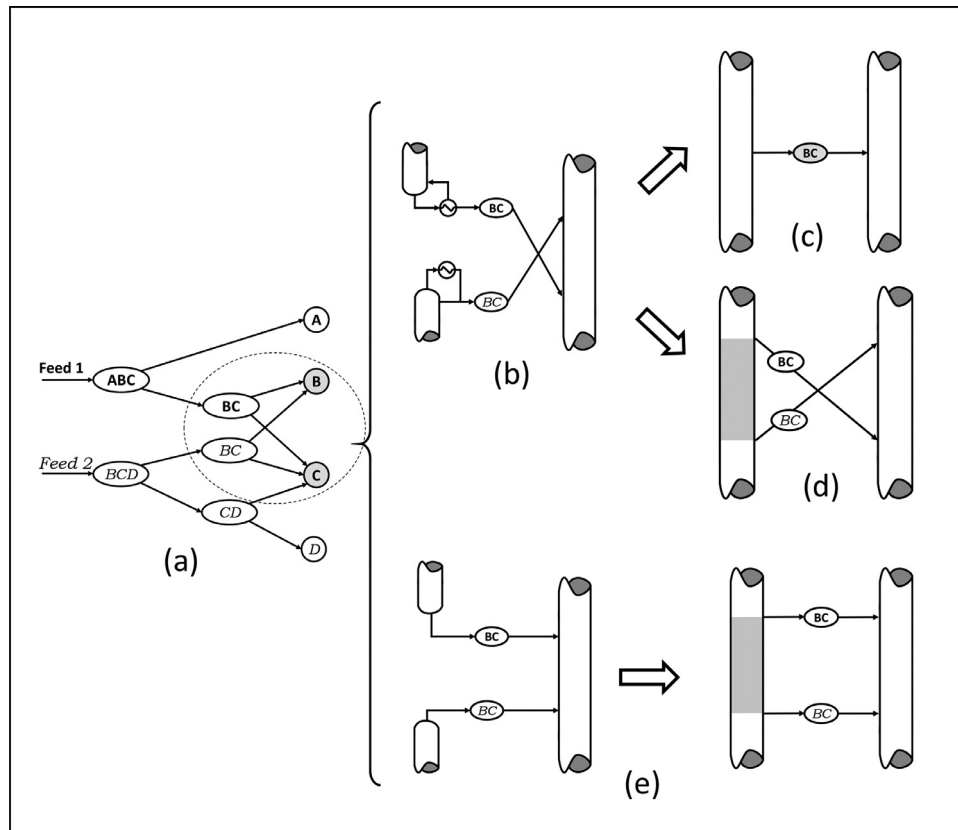


Fig. 4. Alternatives for distribute two sub-mixtures generated by different feed streams. (a) Sub-mixtures generated by each feed -The sequence of separation tasks is implicit in the sequence of sub-mixtures-. (b) Maintaining the feed identity when the optimal location in separation B/C requires to cross the feeds. (c) Mixing BC coming from each feed. (d) Add a column section (gray) and maintain optimal feed location when separation B/C requires to cross the feeds. (e) Optimal configuration when the optimal location in B/C does not require crossing the feeds. An extra column section is needed.

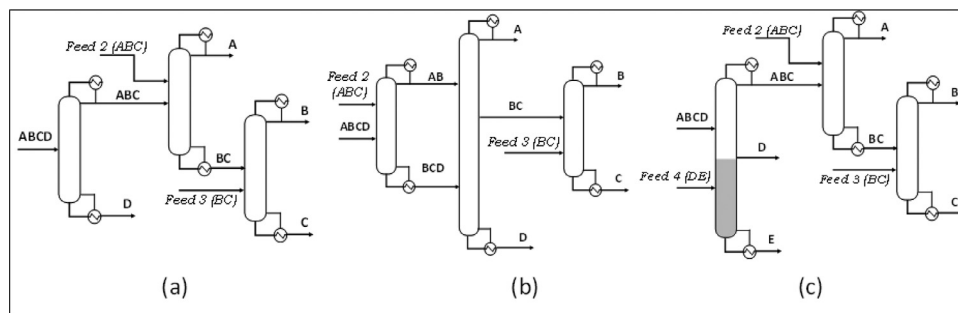


Fig. 5. Example optimal feed location of feeds in a separation. (a) Feed 2 and feed 3 are formed by sub-mixtures reachable from feed1 (ABCD). (b) Sub-mixture ABC does not appear in the sequence, therefore feed 2 -ABC- is introduced in the first column as a second feed (c) Integration of a new feed (feed 4) that only shares the component D with the feed 1 using the same sequence than in case (a).

a second feed to the first column (together with the external feed ABCD). In this case, the sub-mixture ABC does not appear in the sequence, and of course the sequence of separation tasks is different.

3.2 We have a sub-set of feeds that comply with the conditions of case i, and the rest are two-component feeds that share one component with at least any other feed.

For example, we have four feeds: ABCD, BC, ABC (same that in case i), and DE. This last feed shares component D with the first feed (ABCD). The new separation task D/E can be integrated through component D with the rest of the separation without increasing the number of columns (Fig. 5c).

The maximum number of sections is produced for feeds that share exactly one component with another feed. For example, the

feeds ABC, CDE, EFG. Each feed needs exactly two columns, however taking advantage of the common component, we can integrate the two columns with that common feed, and reduce by one the number of columns per each common component. Thus we finish with a configuration formed by 4 columns. Fig. 6 clarifies this case. Therefore, the maximum number of columns is equal to the sum of columns needed for the separation of the component in each feed without considering the rest of the feeds minus the number of integrations through common components:

$$NC^{\max} = \sum_{i=1}^m (n_i - 1) - (m - 1) \quad (1)$$

Note that the previous expression cannot be generalized to fix the number of columns when some feeds have more than one common component. In this case, we have to take into account

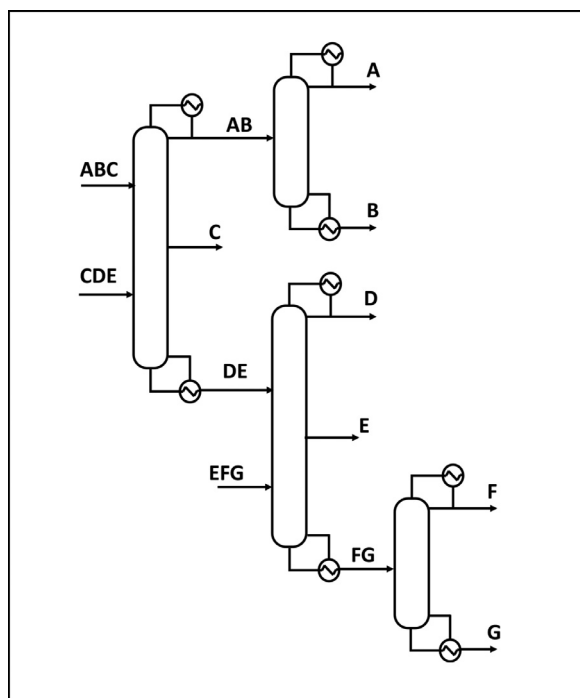


Fig. 6. Example of Integration of three feeds, each one formed by three components, in which each feed shares exactly one component with another feed.

also how many common sub-mixtures coming from different feeds are generated, and if they were generated by a stripping or a rectifying section of a separation task. Remember that we can integrate two common sub-mixtures in a single column when one of them comes from a rectifying section of a separation task and another from a stripping section, in other cases, we have to increase by one the number of columns. If a common sub-mixture is produced by three contributions, at most we can integrate two of them.

The concept of regular/basic configurations continues to be useful because our final objective is to synthesize a sequence of actual columns. We can generalize Agrawal's concept of *Regular Columns* as all the sequences of columns that can be obtained from *Basic Structural Configuration*. A *Basic column* is a regular column sequence in which each column has a reboiler and a condenser.

4. If in some of the feeds there are missing components between the lightest and the heaviest one, then we must explicitly consider the separations of sub-mixtures not reachable from any of the feeds without missing components.

Let us illustrate this case with an example. Assume we have two feeds, the first one include four components: ABCD, and the second one only three: ACD -Note that in this second feed component B is missing-. In this case, the sub-mixture AC is not reachable from the feed ABCD, but it is from ACD. Therefore, we must explicitly take into account the two following alternatives:

- 4.1. Explicitly consider the A/C and AC/CD separation tasks.
- 4.2. Add the feed (or sub-mixture) ACD as a second feed together with the sub-mixture ABC.

While the first case will yield lower energy consumption, it also includes one more distillation column. Therefore, both situations must be considered. Fig. 7 shows an scheme that involves all the possible alternatives and some feasible basic configurations in actual columns.

3.1. Examples

The objective of the examples is to illustrate how to systematically generate all the basic structural configurations for the separation of multiple feed streams that share some components using distillation. To obtain a sequence of actual columns instead of only a representation in terms of mixtures and/or separation tasks, we show the corresponding basic column sequence. Note that it is possible to generate all the set of regular configurations just by successively changing the heat exchangers that connect to columns by a thermal couple, but these new configurations do not introduce any structural difference compared with the basic one. Therefore, without losing generality we constraint to only basic sequences.

As the number of feed streams or total components increases the number of basic structural configurations (or basic column configurations) increases exponentially and it is not practical to explicitly generate all the possible alternatives, for that reason we will show examples involving two feed streams and up to four components. But it is worth pointing out that the following examples include all the possible casuistry that we could find in larger systems.

The objective is not to get the best alternative in terms of a given performance index but to show the structural considerations that must be taken into account to systematically generate the complete search space of alternatives. However, to quantitatively appreciate the effect of the correct location of the feed streams and the effects of different alternatives for merging tasks in a column we have optimized each one of the basic configurations using the Underwood equations. The objective was to minimize the total vapor flows in the reboilers of the columns. Vapor flow in the reboilers of the columns is considered a good performance index to compare configurations because the larger this flow the larger the column diameter, a larger vapor flow also indicates a more difficult separation and therefore a column with more trays. Finally, the vapor flow generated in the reboilers is directly proportional to the utility's consumption. In the appendix, we have included a comprehensive description of the model.

3.2. Two feed streams of hydrocarbons

The objective of this first example is twofold, first show how it is possible to systematically generate all the Basic Sequences taking into account the considerations of the previous section, and quantitative and qualitative show the advantages of the correct placement of different feeds and sub-mixtures generated from them.

In this example, we have two feed streams, the first one formed by a mixture of three components ABC and the other also formed by three components BCD. (A = Benzene; B = Toluene; C = Ethylbenzene; D = 1,3,5-trimethylbenzene). For the sake of simplicity, especially in the notation, we continue using A, B, C, and D to name the components. Table 1 gives all the relevant data to the example.

Table 1
Data for example 1.

Component	Relative volatility	Feed 1 (kmol/h)	Feed 2 (kmol/h)
A: Benzene	7	50	—
B: Toluene	4	30	20
C: Ethylbenzene	2.5	20	40
D: 1,3,5-trimethylbenzene	1	—	20

Relative volatilities estimated at 150 kPa.
Minimum recovery of each key component in a separation task = 95%.
Minimum global recovery of each component = 99.9%.

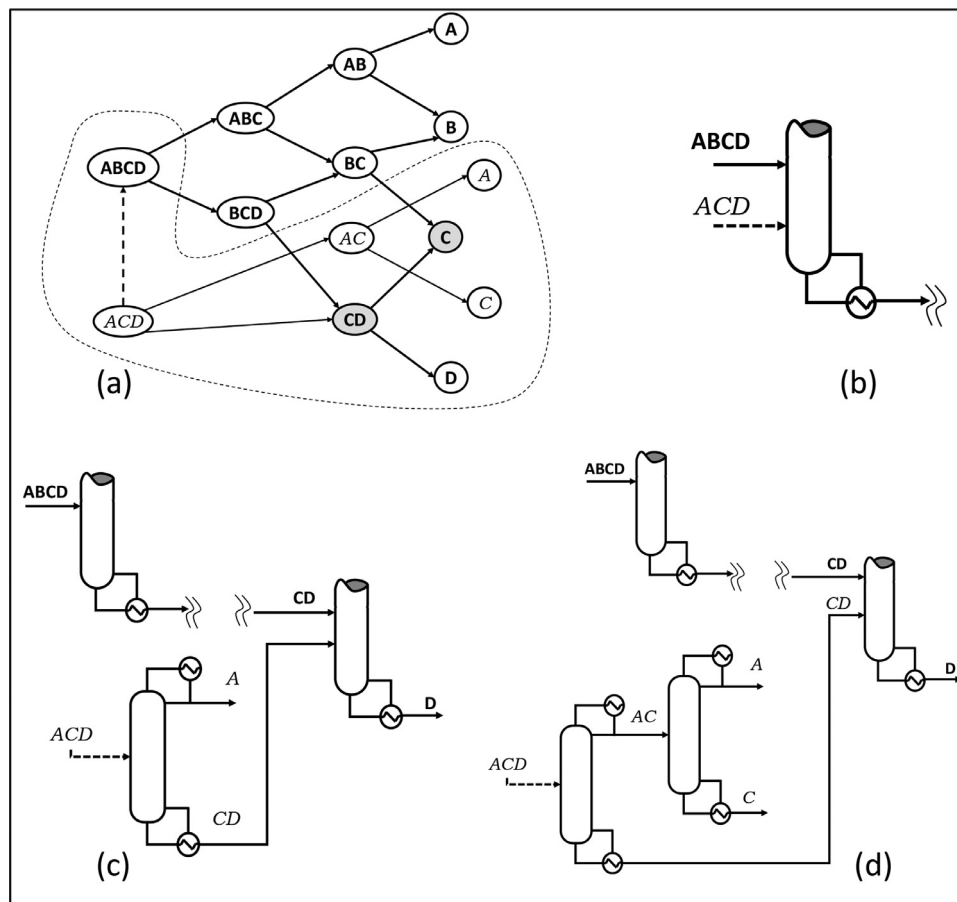


Fig. 7. Alternatives for integrating two feeds. (a) Scheme of all possible alternatives for integration. Note that in the feed ACD the component B does not appear. Shaded in gray are the mixes achievable by both feeds. The dashed line indicates that feed ABC can be added as a second feed together with the ABCD feed. (b) The ACD feed is integrated in the first column with ABCD, and the set of alternatives are the same than with only the ABCD feed. (c) The ACD first undergoes the A/CD separation and then CD is integrated with the CD mixture coming from the ABCD feed. (d) Same than (c) but now ACD feed first separates AC/CD and a column is needed for separating A from C.

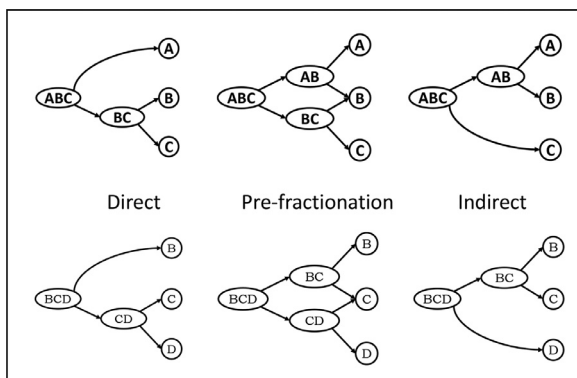


Fig. 8. Basic structural alternatives for separating both three-component mixtures. Separations tasks are not explicitly shown, but they are implicit by the sub-mixtures.

The two feeds share components B and C, and there are no missing components of intermediate volatility in any of the feeds. Following the general rule, we can generate all the possible basic configurations by combining the sequence of separation tasks (or sub-mixtures) of each one of the possible basic structurally different configurations generated by each feed.

For a three-component single feed, there are three basic structurally different configurations: Direct split; Pre-fractionation; and Indirect split (See Fig. 8). So, the combination of the three alterna-

tives for feed ABC and the three for BCD generate 9 possible combinations.

1. Starting with the direct (ABC)- direct (BCD) combination (Fig. 9), we can see that product B is generated by the rectifying section of separation B/C (feed ABC) and the rectifying section of separation B/CD (feed BCD). Component B is generated by two rectifying sections and consequently, we cannot merge them in a single column, and product B must be recovered from two different locations in the sequence.

However, component C is obtained from the stripping section of separation B/C (feed ABC) and from the rectifying section of separation C/D (feed BCD). Therefore, we can merge both column sections, by removing the heat exchangers associated with C and get C as a side stream (Fig. 9).

2. In the Direct (ABC) – Prefractionation (BCD) combination (Fig. 10) two BC sub-mixtures generated each one for a given feed appear. Depending on the compositions of these two BC mixtures, and consequently, on which would be the optimal placement of these two feeds, we can generate the three alternatives shown in Fig. 10.

Product C is generated from a rectifying section of the separation B/C (that is shared by the two feeds) and the stripping section of separation C/D from feed BCD. Then, like in the previous case, the two separation tasks that form the component C can be merged in a single column (Fig. 10.)

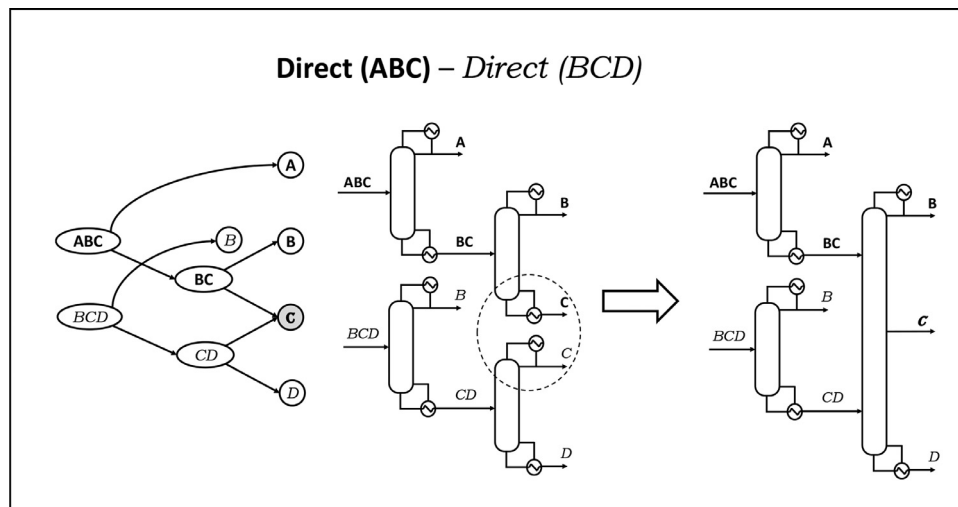


Fig. 9. Basic column configurations from the integration of the Direct (ABC)- Direct (BCD) separation sequences. The shadow mixture -C- is obtained from separation B/C that comes from feed ABC and from separation C/D that comes from feed BCD. We can use this common product to merge two columns and extract C as a side stream.

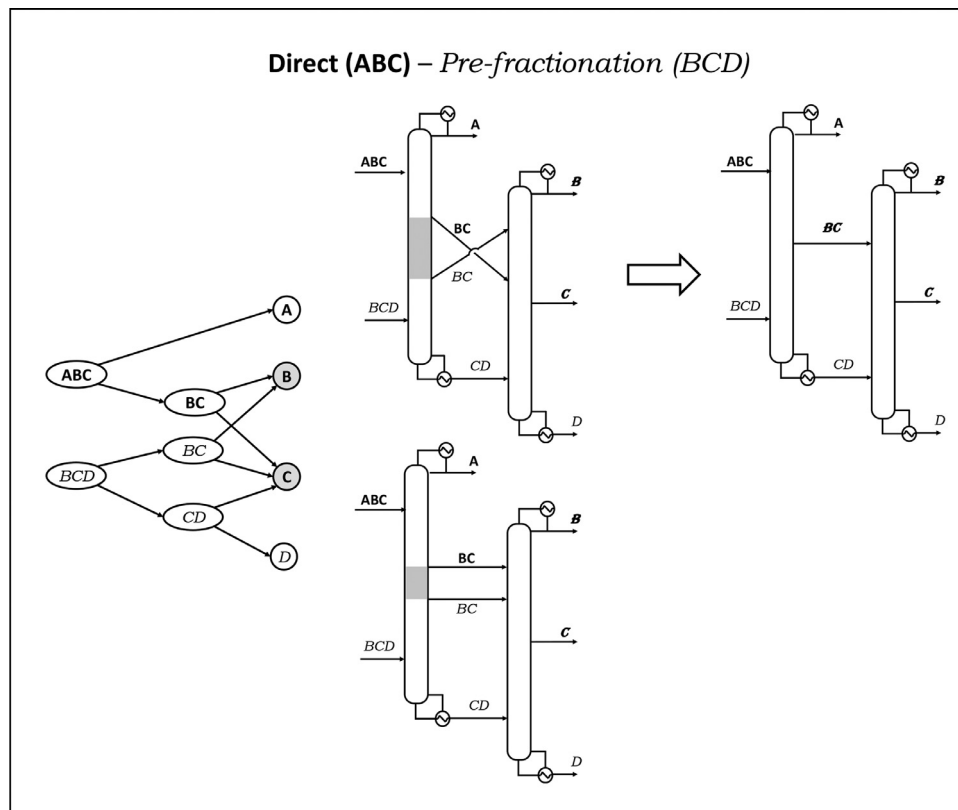


Fig. 10. Basic column configurations from the integration of the Direct (ABC)- Pre-fractionation (BCD) separation sequences.

3. Especial discussion deserves the combination of Pre-fractionation (ABC) – Direct split (BCD).- [Fig. 11](#)- Component C is generated by separations B/C from the feed ABC, and C/D from the feed BCD. So, like in previous cases, the two separation tasks that form the sub-mixture C can be merged in a single column.

However, component B is generated by three contributions: by separation A/B and B/C from the feed ABC, and by the separation of B/CD from the feed BCD. To merge two separation tasks in a single column, one of the contributions must come from a rectifying section, and the other for a stripping section. In this

case, product B is produced by two rectifying sections (B/C and B/CD) and one stripping section (A/B). In consequence, we have two options: merging in a single column A/B and B/C or merging A/B and B/CD -See [Fig. 11](#). In both cases, we have a three-column configuration, and in both the product B must be recovered from two different locations.

The rest of the combinations (4 to 9) do not introduce any novelty and can be systematically obtained with the same considerations as in the previous ones. [Fig. 12](#) shows all the remaining basic configurations.

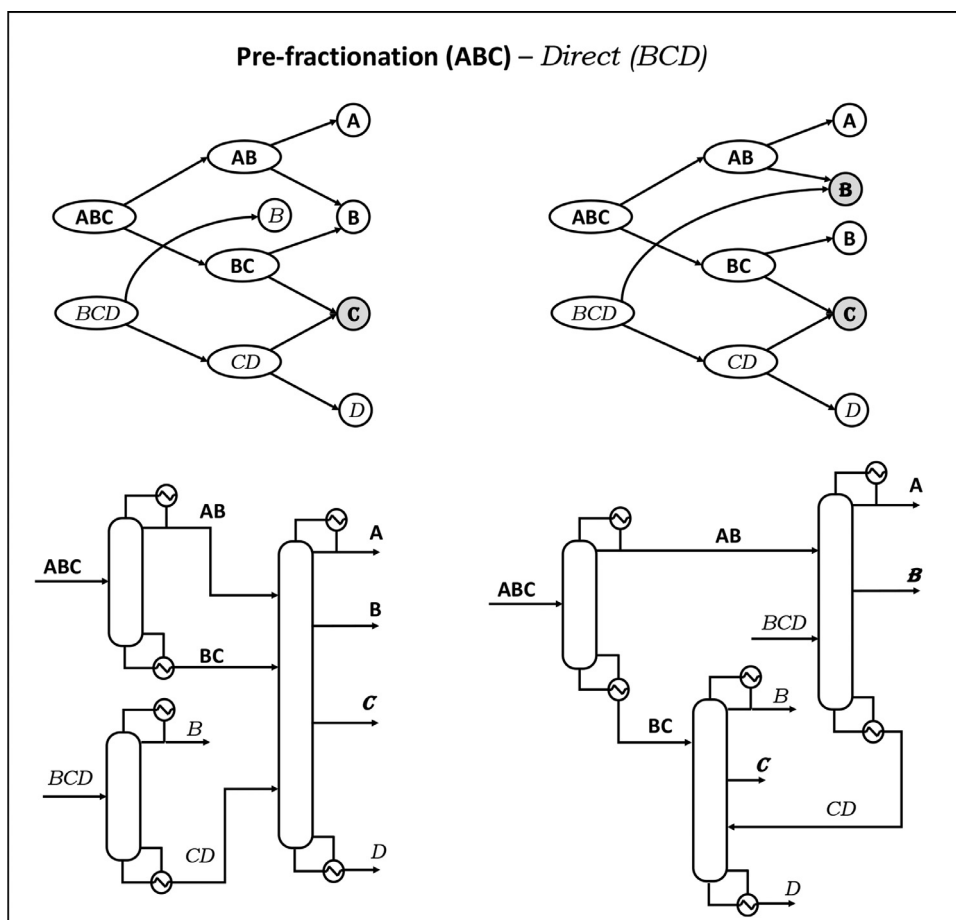


Fig. 11. Basic column configurations from the integration of the Pre-fractionation (ABC)- Direct (BCD) separation sequences.

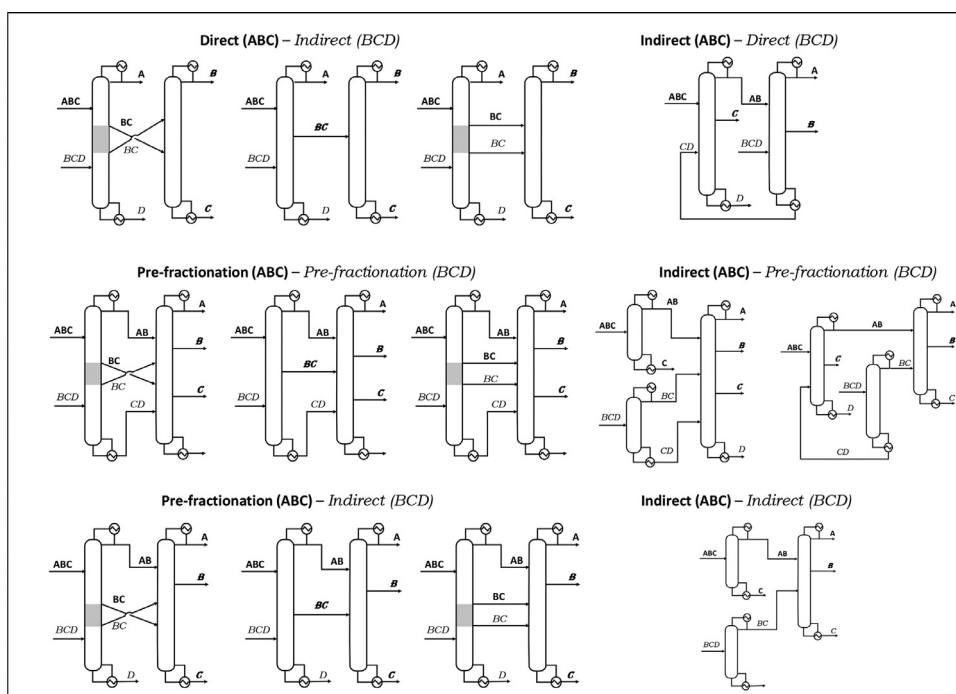


Fig. 12. Basic configurations from the integration of feeds ABC and BCD are not presented in Figs. 9–11.

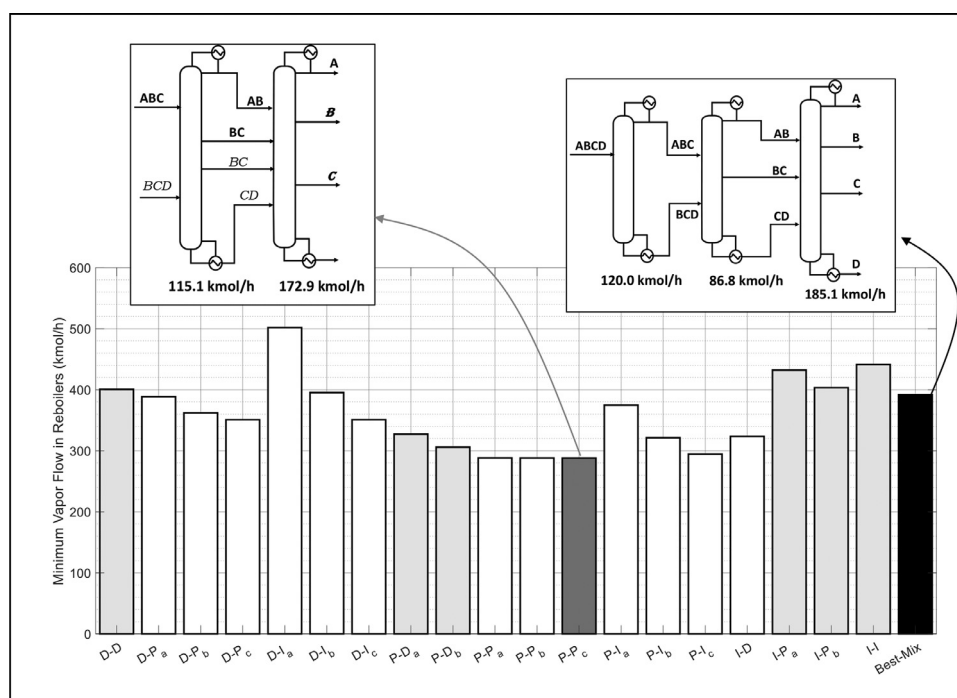


Fig. 13. Comparison of minimum vapor flows in reboilers of the basic sequences for the separation of mixtures ABC and BCD of example 1. Shaded in gray are configurations formed by three columns. The last bar corresponds to the best basic sequence when both feeds are mixed before entering the separation sequence. D: Direct; P: Prefractionation; I: Indirect. Subscripts a, b, c indicate the different basic alternatives in the same order as presented in Figs. 8–11.

For modeling the multiple-feed columns we adapted the model proposed by Nikolaides and Malone (1987). In each separation, we specify a recovery of at least 95% of key components with a global recovery of final products of at least 99.9%. The models were implemented in GAMS (Rosenthal, 2012) and solved to global optimality using BARON (Sahinidis, 1996). In the worse case, the CPU time was of some seconds, but usually, it was around one or two seconds and therefore it will be not reported with the rest of the results.

The best configuration among all the basic ones corresponds to the case in which both feeds are performing a prefractionation sequence. This sequence can be arranged in two columns. For this particular case, the best configuration corresponds to the case in which sub-mixture BC is introduced in two different locations, but there is only a marginal difference with the case in which the BC contributions coming from each one of the feeds are mixed (lower than 0.1%). So, from a practical point of view merging both BC contributions in a single stream is the best option.

The third best sequence (Prefractionation - Direct), is only 6.2% worse than the best one, and it is formed by three columns. Even though this extra column could suppose a penalty, for example, if we calculate the total cost, the energy benefits could eventually compensate it. Therefore, sequences that cannot be rearranged in a minimum number of columns must be also considered if we are interested in the best sequence in any performance index.

To quantitative compare the benefits of the correct placement of feeds, we have solved the case in which both feeds are mixed before entering the column sequence. The optimal basic sequence includes the separations ABC/BCD; AB/BC; BC/CD; A/B, B/C; C/D, and is formed by three columns. The total vapor flow is 36% larger than the best sequence in which the feeds are not mixed. See Fig. 13.

Table 2 shows a summary of the main results for each one of the basic sequences. Fig. 13, shows a comparison of all the configurations.

3.3. Example 2

In this example, we consider the case in which, in some of the mixtures there are missing components. We have two feeds, one formed by a mixture ABCD and another by a mixture ACD (component B is missing). The different alternatives in terms of separation tasks to be considered where graphically presented in Fig. 7. Table 3 shows all the relevant data for this example.

If we determine the best basic sequence for each one of the feeds (two independent column sequences) we get for the feed ABCD that the best sequence is ABC/BCD – AB/BC – BC/CD – A/B – B/C – C/D with a total molar flow in reboilers of 160.65 kmol/h and three columns. For the feed ACD, the best basic sequence is AC/CD – A/C – C/D with a total vapor flow in reboilers of 120.87 kmol/h and two columns. Globally we would get a total molar flow in reboilers of 281.5 kmol/h and 5 distillation columns.

If we integrate the best independent sequences, we can use the common sub-mixture CD and implement a two-feed column (Fig. 14a). The minimum vapor flow in reboilers of this sequence is 272.35 kmol/h. (around a 3.26% lower than without integration). It is worth noting that the correct placement of the two feeds in the separation C/D has an important effect on the separation performance. The CD sub-mixture coming from the stripping section of separation AC/CD must be placed above the CD sub-mixture coming from the stripping section of separation BC/CD. In another case, the total feed flow in reboilers increases up to 339.93 kmol/h, 24.81% higher! These numbers reflect the importance of the correct placement of feeds in multiple-feed distillation sequences. This configuration requires 5 distillation columns.

However, the best separation sequence of an isolated mixture is not necessarily the same when it is integrated with different feeds. In this case, if the second feed (ACD), separates first A/CD and then CD is integrated using a two-feed column, the total vapor flow in reboilers is reduced to 264.94 kmol/h. Around 6% lower than when sequences are considered independent and it requires only four distillation columns (Fig. 14b). Again, the correct place-

Table 2
Main results of example 1.

Sequence	# actual columns	Minimum vapor flow rate in reboilers		Total minimum vapor flow rate
		Task	kmol/h	
Direct-Direct	3	A/BC B/CD C/D	162.3 124.9 112.9	400.6
Direct-Prefrac. ^(a)	2	BC/CD C/D	162.3 226.2	388.5
Direct-Prefrac. ^(b)	2	BC/CD C/D	162.3 199.6	361.9
Direct-Prefrac. ^(c)	2	BC/CD C/D	162.3 188.5	350.8
Direct – Indirect ^(a)	2	BC/D B/C	162.5 339.3	501.8
Direct – Indirect ^(b)	2	BC/D B/C	162.3 233.0	395.3
Direct – Indirect ^(c)	2	BC/D B/C	162.3 188.5	350.8
Prefrac. – Direct ^(d)	3	AB/BC B/CD C/D	104.0 112.8 110.4	327.2
Prefrac. – Direct ^(e)	3	AB/BC B/CD C/D	104.0 148.0 53.9	305.9
Prefrac. – Prefract. ^(a)	2	BC/CD C/D	115.21 172.9	288.1
Prefrac. – Prefract. ^(b)	2	BC/CD C/D	115.1 172.9	288.0
Prefrac. – Prefract. ^(c)	2	BC/CD C/D	115.1 172.8	287.9
Prefrac.-Indirect ^(a)	2	BC/D B/C	115.2 259.5	374.7
Prefrac.-Indirect ^(b)	2	BC/D B/C	115.1 206.2	321.3
Prefrac.-Indirect ^(b)	2	BC/D B/C	115.1 179.5	294.6
Indirect- Direct	2	B/CD C/D	128.2 175.5	323.7
Indirec-Prefrac. ^(f)	3	AB/C BC/CD C/D	180.4 66.6 136.3	432.3
Indirec-Prefrac. ^(g)	3	B/C BC/CD C/D	156.3 66.6 180.4	403.3
Indirect-Indirect	3	AB/C BC/D B/C	180.4 104.8 156.3	441.5

In the sequence, the first separation refers to sequence of separation tasks of feed ABC and the second to the feed BCD.

^(a) The two feeds to the two-feed separation task 'cross' each other.

^(b) The two feeds are mixed before entering as feed to the new separation task.

^(c) The two feeds to the two-feed separation task do not cross each other.

^(d) Separations A/B and B/C are in the same column.

^(e) Separations A/B and B/CD are in the same column.

^(f) Separations B/C and C/D are in the same column.

^(g) Separations AB/C and C/D are in the same column.

Table 3
Data for example 2.

Component	Relative volatility	Feed 1 (kmol/h)	Feed 2(kmol/h)
A: n-butane	10	20	10
B: n-pentane	5	30	—
C: n-hexane	2	20	30
D: n-heptane	1	45	45

Relative volatilities estimated at 350 kPa.
Minimum recovery of each key component in a separation task = 95%.
Minimum global recovery of each component = 99.9%.

ment of the feeds in separation C/D is very important. The total vapor flow in reboilers increases up to 345.87 (30.5%) if the feeds are not correctly placed.

If instead of connecting the separation of those two feeds in the separation C/D, we introduce the feed ACD into the first col-

umn (separation ABC/BCD) -Fig. 14c- the total molar flows in reboilers increases up to 290.18 kmol/h, that is a 9.5% greater than the best one. However, the sequence needs only three distillation columns and a detailed economic evaluation is needed to decide which one of the sequences should be eventually implemented. In

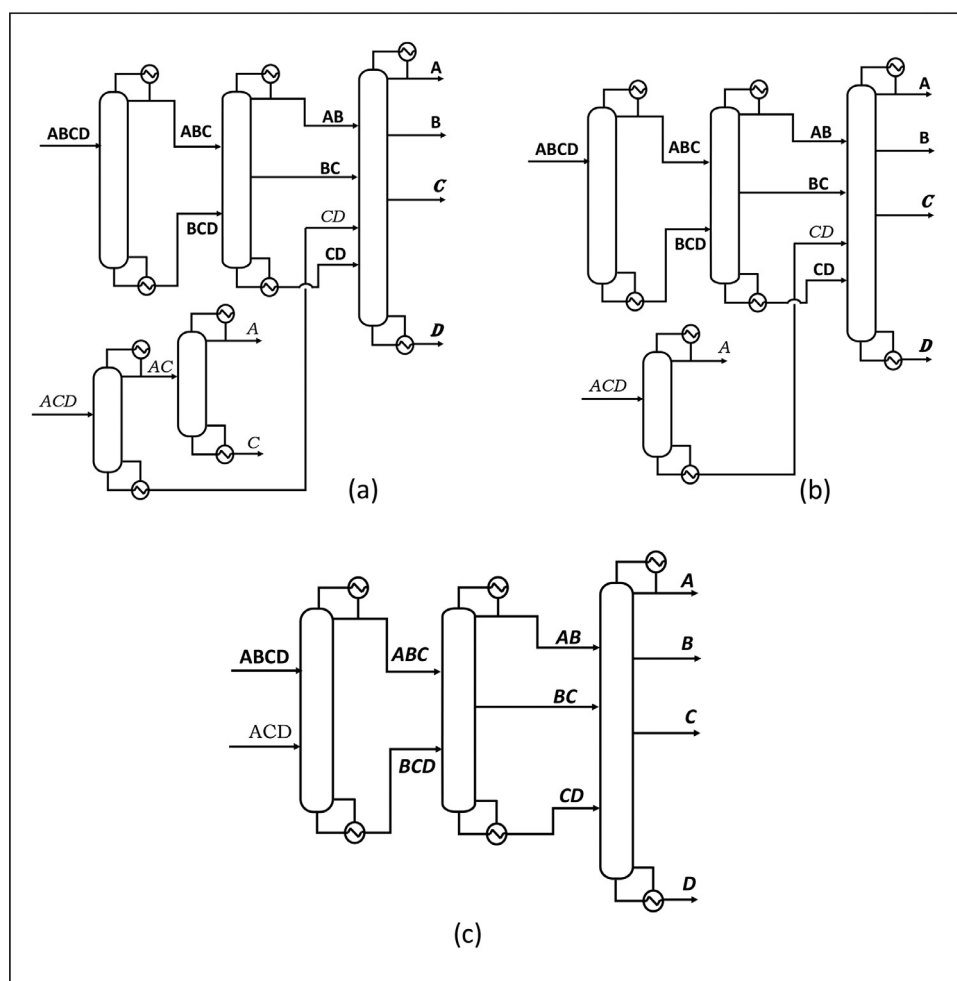


Fig. 14. Alternatives for the integration of the two feeds in example 2. (a) Basic five-column sequence from the integration of best sequences of isolated feeds. (b) Best column sequence when both feeds are simultaneously optimized -it requires only 4 columns-. (c) Best basic sequence when the feed ACD is added to the first column -three-column sequence-.

this case, the four-component feed (ABCD) must be added above the three-component feed (ACD). In another case, the total molar flow in reboilers increases up to 322.14 kmol/h.

4. Conclusion

The main structural considerations for the separation of multiple zeotropic feed streams using distillation columns have been presented. While the main structural characteristics of a single feed sequence that ensure the generation of the complete space of alternatives are maintained, the presence of multiple feeds can produce different sub-mixtures for each feed. Some of these sub-mixtures can only be reachable by some of the feeds, and therefore, the total number of separation tasks increases, although not necessarily the total number of distillation columns.

In general, it is possible to generate a basic sequence involving multiple feeds, by merging the sequences of separation tasks generated by each one of the feeds. We have shown that integration is possible in those common separation tasks by implementing a multiple-feed column, where the correct location of the feeds is critical to the system performance. However, the best-integrated sequence does not necessarily have the same sequence of separation tasks as the best individual sequences when feeds are not integrated. In general, increasing the integration degree tends to reduce the energy consumption of the whole system, but this depends also on the relative flow of each feed; on the relative

volatility of the separation; and on the synergic effect of common sub-mixtures due to the possibilities for integrating common sub-mixtures coming from different feeds in the same distillation column.

We have redefined the concept of basic sequence, and consequently the concept of regular configuration. With multiple feeds, a basic sequence is not necessarily formed by exactly $N-1$ columns. The total number of actual columns depends on the components shared by the feeds, and on the number of sub-mixtures (including final products) that can be integrated into a single column. Consequently, we have introduced the more general concept of Basic Structural Configuration. Then we redefined the concept of Regular column sequences as all the sequences of columns that can be obtained from Basic Structural Configuration. A Basic column sequence is a regular column configuration in which each column has a reboiler and a condenser.

When in some of the feeds there are missing components (e.g. components with intermediate volatility that do not appear in at least one of the feeds). We must consider the alternative of integrating that feed in a multiple feed column with the more similar sub-mixture without missing components and also, we must consider the possibility of explicitly including separation tasks of those sub-mixtures that are not reachable by any sub-mixture without missing components.

Even though it is out of the scope of this paper, it is worth noting that most (maybe all) of the alternatives available for inten-

sification and or process integration in a single feed sequence are also valid for the case of multiple feeds. Those include, among others, divided wall columns: classical divided wall columns or vertical partitions with or without external liquid transfer; removing some column sections (transfer blocks); changing thermal couples by liquid only transfer, together with multi-effect integration, simultaneous heat and mass integration, etc.

The focus of this paper was on establishing the main structural characteristics of zeotropic separations with multiple feeds and on showing how it is possible to systematically generate all the Basic Structural Configurations, and from them, the search space of actual columns (regular configurations). As the number of alternatives grows up very fast with the number of components and the number of feeds, the complete enumeration of all the alternatives is not, at least, a practical option -Note that even for the relatively small examples discussed in previous sections we have focused only on the basic sequences-. A superstructure optimization (based on deterministic or metaheuristic algorithms) is necessary for larger problems. Even though superstructure optimization is out of the scope of this paper we have presented the basis that any optimization approach must take into account to solve this multiple-feed streams separation problem using only distillation columns.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

José A. Caballero: Conceptualization, Visualization, Formal analysis, Writing – review & editing. **Juan Javaloyes-Anton:** Visualization, Formal analysis. **Juan A. Labarta:** Conceptualization, Formal analysis, Visualization.

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Appendix

Mathematical model for evaluating the basic sequences with multiple feeds.

Let us define the following index sets:

C	{ i i is a component}
T	{ t t is a separation task}
P	{ p p is a final product}
S	{ s s is an individual separation task for multiple feed task}
FS	{ f f is a feed stream}
R	{ r r is an element of all possible Underwood roots}

When we talk about a multiple feed separation task, we refer to a separation task defined only by the key components (e.g. separate A from C) of two or more feeds with different compositions. Note also that the multiple feed separation task can perform the separation of multiple feeds involving the same components with different compositions or a different separation task for each feed but with the same key components. For example, it can separate two feed streams formed both by components A, B, and C with key components A and C -separation AB/BC- or a feed formed by A, B, and C and other only for A and C. In this last case, the first separation is AB/BC, and the second one A/C.

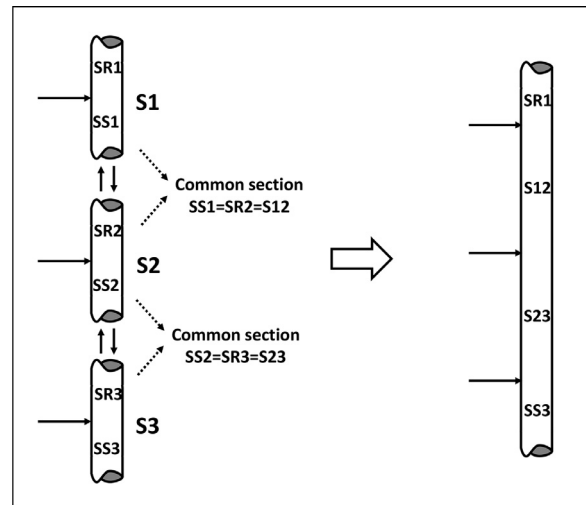


Fig. A1. Individual task in a multiple-feed separation task (left) and distribution in an actual column. Note that the liquid and vapor flows in the common sections are forced to be equal through constraints in the model.

The set S is an ordered set. Here we follow the criterion that the first element corresponds to the separation task placed in the upper section of the separation task (first feed counting up to down) then the second feed, etc. Fig. A1 clarified this point.

We also define the following sub-sets and mappings between sets.

SF_T	Single feed separation tasks
MF_T	Multiple feed separation task
$MFST_{s,T}$	The individual separation task t entering to multiple feed task is assigned to sub-task s
$RUA_{T,R}$	Active underwood roots in task t
$MRUA_{S,R,T}$	Active Underwood roots in subtask s
LK_T	Light key component in separation task t
HK_T	Heavy key component in separation task t
$PI_{p,i}$	Relation between component i and final product p
$FT_{f,t}$	Assignment of external feed streams f to a given separation task t
$MFTD_{s,t,t'}$	The Distillate of separation task t is the feed of separation s in the multiple feed separation task t'
$MFTB_{s,t,t'}$	The Bottoms of separation task t is the feed of separation s in the multiple feed separation task t'
$FTD_{t,t'}$	The Distillate of separation task t is the feed of separation t'
$FTB_{t,t'}$	The Bottoms of separation task t is the feed of separation t'
$CSR_{t,t'}$	The stripping section of the separation task t is connected with the rectifying section of column task t'
$TPD_{t,p}$	The separation task t produces product P as distillate
$TPB_{t,p}$	The separation task t produces product P as bottoms

We know the following DATA:

$Feed_{f,i}$	Molar flow of component i (kmol/h) in feed stream f
α_i	Relative volatility of component i . Referred always to the heaviest one.
$recL_{t,i}$	Minimum recovery of light key in distillate
$recH_{t,i}$	Minimum recovery of heavy key in bottoms
$recG_i$	Minimum global recovery of component i

We can consider a single feed separation task as a pseudo-column formed by two sections, a rectifying section, and a stripping section. However, the different separation task of a sequence can be arranged in actual columns in different ways, as commented in the paper, therefore when we talk about distillate/bottoms we refer to the distillate/bottoms streams of separation tasks that could or not coincide with the distillate/bottoms streams of actual columns.

In a multi-feed separation task, we consider also that each separation task is formed by two sections, but one of the intermediate sections is shared by the different separation tasks (See Fig. A1).

The variables of the problem are:

F_t	Total molar flow entering the task t (kmo/h)
$Fl_{t,i}$	Molar flow of component i in the feed of task t (kmol/h)
D_t	Total molar flow in the distillate of separation task t (kmol/h)
$DI_{t,i}$	Component molar flow i in the distillate of separation task t (kmol/h)
B_t	Total molar flow in bottoms of separation task t (kmol/h)
$BI_{t,i}$	Component molar flow i in bottoms of separation task t (kmol/h)
$FF_{s,t}$	Total molar flow for the feed entering in the separation task s of a multi-feed separation task t (kmol/h)
$FFI_{s,i,t}$	Total molar flow i for the feed entering in the separation task s of a multi-feed separation task t (kmol/h)
$V1_t$	Vapor Molar flow in rectifying section of separation task t (kmol/h)
$V2_t$	Vapor Molar flow in stripping section of separation task t (kmol/h)
$L1_t$	Liquid Molar flow in rectifying section of separation task t (kmol/h)
$L2_t$	Liquid Molar flow in stripping section of separation task t (kmol/h)
$VU1_t$	Auxiliary variable. Calculates the minimum vapor flow in a rectifying section of a single feed separation task t when it is isolated from the rest of the system.
$VU2_t$	Auxiliary variable. Calculates the minimum vapor flow in a stripping section of a single feed separation task t when it is isolated from the rest of the system.
$VV1_{s,t}$	Vapor flow in rectifying section of task s in multiple feed separation task t (kmol/h)
$VV2_{s,t}$	Vapor flow in stripping section of task s in multiple feed separation task t (kmol/h)
$LL1_{s,t}$	Liquid flow in rectifying section of task s in multiple feed separation task t (kmol/h)
$LL2_{s,t}$	Liquid flow in Stripping section of task s in multiple feed separation task t (kmol/h)
$\phi_{t,r}$	Underwood root r in separation task t
$\phi_{s,t,r}^M$	Underwood root r in separation task s in a multi-feed separation task t
$Pfinal_{p,i}$	Molar flow of component i in final product p

We can divide the model into equations of the single feed separation tasks, equations for the multiple feed separation tasks, and connectivity between separation tasks.

For the single feed separation task, the model is as follows:

Relation between individual and total feed flows:

$$D_t = \sum_{i \in C} DI_{t,i} \quad \forall t \in SF_t \quad (A.1)$$

$$B_t = \sum_{i \in C} BI_{t,i} \quad \forall t \in SF_t \quad (A.2)$$

$$F_t = \sum_{i \in C} FI_{t,i} \quad \forall t \in SF_t \quad (A.3)$$

Global Mass balances in each separation task.

$$F_t = D_t + B_t \quad \forall t \in SF_t \quad (A.4)$$

$$FI_{t,i} = DI_{t,i} + BI_{t,i} \quad \forall t \in SF_t ; i \in C \quad (A.5)$$

Mass balances in the feed to each column (In this paper we focus only on basis sequences, thus the feed to each separation tasks, is always saturated liquid).

$$F_t = L2_t - L1_t \quad \forall t \in SF_t \quad (A.6)$$

$$V1_t = V2_t \quad \forall t \in SF_t \quad (A.7)$$

Mass balance in the upper side of a separation task (if there is a condenser is equivalent to a mass balance in the condenser).

$$V1_t = L1_t + D_t \quad \forall t \in SF_t \quad (A.8)$$

Mass balance in the lower part of the separation task (if there is a reboiler is equivalent to a mass balance in the reboiler).

$$L2_t = V2_t + B_t \quad \forall t \in SF_t \quad (A.9)$$

Underwood equations.

$$\sum_{i \in C} \frac{\alpha_i FI_{t,i}}{\alpha_i - \phi_{t,r}} = VU1_t - VU2_t \quad \forall t \in SF_t ; r \in RUA_{t,r} \quad (A.10)$$

$$\sum_{i \in C} \frac{\alpha_i FI_{t,i}}{\alpha_i - \phi_{t,r}} = VU1_t \quad \forall t \in SF_t ; r \in RUA_{t,r} \quad (A.11)$$

$$\sum_{i \in C} \frac{\alpha_i FI_{t,i}}{\alpha_i - \phi_{t,r}} = -VU2_t \quad \forall t \in SF_t ; r \in RUA_{t,r} \quad (A.12)$$

We are assuming liquid saturated in all the feeds, so:

$$VU1_t = VU2_t \quad \forall t \in SF_t \quad (A.13)$$

The actual internal vapor flows at minimum reflux must be greater than minimum vapor flows when we consider the separation task isolated from the rest of the system:

$$V1_t \geq VU1_t \quad \forall t \in SF_t \quad (A.14)$$

$$V2_t \geq VU2_t \quad \forall t \in SF_t \quad (A.15)$$

The individual recoveries in each separation task:

$$DI_{t,i} = FI_{t,i} \quad \forall t \in SF_t ; i \in C / i < LK_t \quad (A.16)$$

$$DI_{t,i} = recL_t FI_{t,i} \quad \forall t \in SF_t ; i \in LK_t \quad (A.17)$$

$$BI_{t,i} = BI_{t,i} \quad \forall t \in SF_t ; i \in C / i > HK_t \quad (A.18)$$

$$BI_{t,i} = recH_t FI_{t,i} \quad \forall t \in SF_t ; i \in HK_t \quad (A.19)$$

For the multiple feed separation task, the model is as follows:

Relation between individual and total feed flows:

$$D_t = \sum_{i \in C} DI_{t,i} \quad \forall t \in MF_t \quad (A.20)$$

$$B_t = \sum_{i \in C} BI_{t,i} \quad \forall t \in MF_t \quad (A.21)$$

$$FF_{s,t} = \sum_{i \in C} FI_{s,i,t} \quad \forall (s, t) \in MFST_{s,t} \quad (A.22)$$

Mass balances in the feed to each column. Remember that the feeds are saturated liquid.

$$FF_{s,t} + LL1_{s,t} = LL2_{s,t} \quad \forall (s, t) \in MFST_{s,t} \quad (A.23)$$

Relation between internal flow and distillate and internal flows and bottoms:

$$VV1_{s,t} = D_t + LL2_{s,t} \quad \forall (s, t) \in MFST_{s,t} \quad s = 1 \quad (A.24)$$

$$LL2_{s,t} = B_t + VV2_{s,t} \quad \forall (s, t) \in MFST_{s,t} \quad s = |S| \quad (A.25)$$

In previous equations $s = 1$ refers to the first element in the ordered set S . $s = |S|$ refers to the last element in the set s (position equal to the cardinality of the set).

Global mass balance in the complete multiple-feed separation task:

$$\sum_{s \in MFST_{s,t}} FFI_{s,i,t} = DI_{t,i} + BI_{t,i} \quad \forall t \in MF_t, \quad \forall i \in C \quad (A.26)$$

Underwood equations

$$\sum_{i \in C} \frac{\alpha_i FFI_{s,i,t}}{\alpha_i - \phi_{s,t,r}^M} = VVU1_{s,t} - VVU2_{s,t} \quad \forall (s, r, t) \in MRUA_{s,r,t} \quad (A.27)$$

$$\sum_{i \in C} \frac{\alpha_i \left(D_{t,i} - \sum_{s' < s} FFI_{s',i,c} \right)}{\alpha_i - \phi_{s,t,r}^M} = VVU1_{s,t} \quad \forall (s, r, t) \in MRUA_{s,r,t} \quad (A.28)$$

$$\sum_{i \in C} \frac{\alpha_i \left(B_{t,i} - \sum_{s' > s} FFI_{s',i,c} \right)}{\alpha_i - \phi_{s,t,r}^M} = -VVU2_{s,t} \quad \forall (s, r, t) \in MRUA_{s,r,t} \quad (A.29)$$

We are assuming liquid saturated in all the feeds, so:

$$VVU1_{s,t} = VVU2_{s,t} \quad \forall (s, t) \in MFST_{s,t} \quad (A.30)$$

The actual internal vapor flows at minimum reflux must be greater than minimum vapor flows when we consider the separation task isolated from the rest of the system:

$$VV1_{s,t} \geq VVU1_{t,t} \quad \forall (s, t) \in MFST_{s,t} \quad (A.31)$$

$$VV2_{s,t} \geq VVU2_{t,t} \quad \forall (s, t) \in MFST_{s,t} \quad (A.32)$$

Minimum recovery of components in each separation task

$$D_{t,i} = \sum_{s' \in S} FFI_{s',i,t} \quad \forall (s, t) \in MFST_{s,t}, i \in C/i < LK_t \quad (A.33)$$

$$D_{t,i} = recL_t \sum_{s' \in S} FFI_{s',i,t} \quad \forall (s, t) \in MFST_{s,t}, i \in LK_t \quad (A.34)$$

$$B_{t,i} = \sum_{s' \in S} FFI_{s',i,t} \quad \forall (s, t) \in MFST_{s,t}, i \in C/i > HK_t \quad (A.35)$$

$$B_{t,i} = rech_t \sum_{s' \in S} FFI_{s',i,t} \quad \forall (s, t) \in MFST_{s,t}, i \in HK_t \quad (A.36)$$

Global recovery

$$P_{final,p,i} \geq recG_i \sum_{f \in FS} Feed_{f,i} \quad \forall (p, i) \in PI_{p,i} \quad (A.37)$$

The last part consists of establishing the *connectivity among all the separation tasks*.

Assignment of external feeds to separation tasks:

$$Feed_{f,i} = F_{t,i} \quad \forall (f, t) \in FT_{f,t}, \forall i \in C \quad (A.38)$$

Assignment of feeds to multiple feed separation tasks.

$$\sum_{t \in MFTD_{s,t,t'}} D_{t,i} + \sum_{t \in MFTB_{s,t,t'}} D_{t,i} = FFI_{s,i,t'} \quad \forall (s, t, t') \in MFTD_{s,t,t'} \cup MFTB_{s,t,t'}, \forall i \in C \quad (A.39)$$

Connectivity between distillate, bottoms and feeds of the rest of separation task.

$$\sum_{t \in FTD_{t,t'}} D_{t,i} + \sum_{t \in FTB_{t,t'}} D_{t,i} = F_{i,t'} \quad \forall (t, t') \in FTD_{t,t'} \cup FTB_{t,t'}, \forall i \in C \quad (A.40)$$

Connectivity between separation tasks that form part of same column:

$$V2_t + VV2_{s,t \setminus s=|S|} = V1_{t'} + VV2_{s,t' \setminus s=1} \quad (t, t') \in CSCR_{t,t'} \quad (A.41)$$

$$L2_t + LL2_{s,t \setminus s=|S|} = L1_{t'} + LL1_{s,t' \setminus s=1} + B_t + D_{t'} \quad (t, t') \in CSCR_{t,t'} \quad (A.42)$$

Final products.

$$\sum_{t \in TPD_{t,p}} D_{t,i} + \sum_{t \in TPB_{t,p}} B_{t,i} = P_{final,p,i} \quad \forall p \in P, \forall i \in C \quad (A.43)$$

Finally, the objective function is the minimization of the sum of vapor flow rates in reboilers:

$$\min : \sum_{t \in TR_t} (V2_t + VV2_{s,t \setminus s=|S|}) \quad (A.44)$$

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