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Author: José A. Caballero Ignacio E. Grossmann

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Highlights

- A new MILP approach for generating thermally couple distillation sequences.

- The model includes from conventional to fully thermally coupled sequences

- Divided wall columns are explicitly included in the model.

- A two level superstructure is postulated to a priori optimize separation tasks.

- Logical relationships between separation tasks allow generating feasible solutions.

Optimal Synthesis of Thermally Coupled Distillation Sequences Using a Novel MILP Approach.

José A. Caballero*; Ignacio E. Grossmann**

*Department of Chemical Engineering. University of Alicante. Ap. Correos 99. 03080 Alicante. Spain

** Department of Chemical Engineering. Carnegie Mellon University. Pittsburgh, PA. USA.

Abstract

This paper introduces a novel MILP approach for the design of distillation columns sequences of zeotropic mixtures that explicitly include from conventional to fully thermally coupled sequences and divided wall columns with a single wall. The model is based on the use of two superstructure levels. In the upper level a superstructure that includes all the basic sequences of separation tasks is postulated. The lower level is an extended tree that explicitly includes different thermal states and compositions of the feed to a given separation task. In that way, it is possible to a priori optimize all the possible separation tasks involved in the superstructure. A set of logical relationships relates the feasible sequences with the optimized tasks in the extended tree resulting in a MILP to select the optimal sequence. The performance of the model in terms of robustness and computational time is illustrated with several examples.

Keywords

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

1.- Introduction

Distillation is the most widely used method in modern chemical industries to separate liquid mixtures into pure components. Distillation is also a very energy intensive method of separation, accounting for about 40% of the total energy used in the chemical and petroleum refining industries (DOE, 2005). To this end, the thermally coupled distillation (TCD), in which heat is directly transferred between columns through two streams (liquid a vapor) that substitute a condenser or a reboiler (see figure 1), has received considerable attention. Cost savings between 10 and 50% have been reported compared to the case where simple columns are employed in series to achieve the desired product purities (Agrawal & Fidkowski, 1998a; Z. T. Fidkowski & Agrawal, 2001; Halvorsen & Skogestad, 2003b, 2003c; Rudd, 1992; Wolff & Skogestad, 1995).

Although the interest in TCD is relatively recent, the first apparatus that uses TDC concepts was due to Wright in 1949 (Wright, 1949). The theoretical basis of TCD was developed in the sixties by Petlyuk and coworkers. Petlyuk et al (1965) noticed that separation sequences using

conventional columns (a single feed with two product streams, a condenser, and a reboiler) suffer from an inherent inefficiency produced by the thermodynamic irreversibility during the mixing of streams at the feed, top, and bottom of the column. This remixing is inherent to any separation that involves an intermediate boiling component and can be generalized to an *N*-component mixture. The theoretical studies developed by Petluyk and co-workers showed that this inefficiency can be improved by removing some heat exchangers and introducing thermal coupling between columns. If a heat exchanger is removed, the liquid reflux (or vapor load) is provided by a new stream that is withdrawn from another column. In this way, it is possible to reduce the energy consumption, and under some circumstances, also the capital costs. (See figure 1) A fully thermally coupled (FTC) configuration is reached when the entire vapor load is provided by a single reboiler and all the reflux by a single condenser. Halvorsen & Skogestad (2003c) proved that the minimum energy consumption for an ideal N-component mixture is always obtained for the FTC configuration.

Even though a FTC configuration has the minimum energy consumption, it cannot be concluded that FTC configurations are always superior, compared to sequences of simple columns or to partially thermally coupled configurations (PTC). Instead, the optimum configuration will be dependent on the specific mixture and feed conditions for at least the following reasons:

(1) The energy is supplied in the worst conditions: at the highest temperature in the reboiler, and removed at the lowest temperature in the condenser, preventing in most cases the use of lower cost utilities, i.e. medium or low-pressure steam in the reboiler. In the condenser this fact is especially relevant if the most volatile component must be condensed at sub-ambient temperature preventing the use of cooling water.

(2) In FTC systems the minimum vapor flow is that of the most difficult separation between adjacent key components (Halvorsen & Skogestad, 2003b, 2003c). The thermal couples transfer the vapor between columns and, therefore, some column sections could have large diameters.

(3) In FTC sequences the total number of column sections is larger than the case of sequences of simple columns -from (4N-6) to N(N-1) in FTC sequences vs. 2(N-1) in sequences of simple columns- . But, this does not imply an increase in the number of columns, but usually an increase in the total number of trays. A detailed discussion on the number of column sections needed for a given separation can be found in Agrawal (1996) and in Caballero & Grossmann (2001, 2004, 2006)

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

As a consequence an important effort has been dedicated during the last decades to develop TCD models. In the 80's and in the early 90's of the last century the main focus was on developing methods for the optimization, design and control of specific configurations, usually constrained to three component mixtures (Alatiqi & Luyben, 1986; Carlberg & Westerberg, 1989a, 1989b; Z. Fidkowski & Krolikowski, 1986, 1987; K. Glinos & Malone, 1988; K. N. Glinos et al., 1986; Nikolaides & Malone, 1987; Rudd, 1992; Terranova & Westerberg, 1989; Triantafyllou & Smith, 1992). In 1996, R. Agrawal (Agrawal, 1996) established the basis for generating TCD sequences with more than 3 components. He showed that sequences with thermal couples and non-consecutive key components do not necessarily increase the number of actual columns and established the conditions under which a given sequence can be reordered in N-1 columns (N is the number of components to be separated) the same that in

'classical column sequencing'!. These sequences, called basic sequences, form the search space for the design of any TCD system. Even though the number of final columns is not increased, the total number of column sections for a fully thermally coupled system ranges between (4N-6) and N(N-1) considerably larger than the [2(N-1)] column sections in classical column sequencing.

Even though, the structural characteristics that a TCD must obey were clearly established in the aforementioned paper, generating all the feasible basic sequences is not straightforward. Agrawal again (Agrawal, 2000a, 2003) proposed a set of rules for drawing fully and partially thermally coupled configurations that can be rearranged in N-1 distillation columns. Following a conceptual design approach, Rong and coworkers presented different alternatives for sequences with four and five components including basic and non-basic configurations (B. G. Rong & Kraslawski, 2003; B. G. Rong et al., 2000, 2001; B. G. Rong et al., 2003). Kim and coworkers (Y. H. Kim, 2001; Y. H. Kim, 2002a, 2002b, 2005a, 2005b; Y. H. Kim, 2006), Hernández and Jiménez (Salvador Hernandez & Jimenez, 1999), Hernández et al (2003), Blancarte-Palacios et al (2003), Calzon-McConville et al (2005), also presented in a set of interesting papers with the focus on the rigorous design of some specific configurations for three, four or five components mixtures. Caballero & Grossmann (2001, 2002, 2003a, 2004) , based mainly on previous work by R. Agrawal developed a set of logical rules, that can be expressed in terms of Boolean or binary variables, which ensure basic configurations, and introduced them in an optimization based environment for generating the optimal column sequence covering from conventional to fully thermally coupled distillation sequences. Later, Caballero & Grossmann (2006) performed a structural analysis of TCD showing that sequences with more than N-1 distillation columns are sub-optimal from an economic point of view. Giridhar & Agrawal (2010b) confirmed that result establishing the characteristics of a suitable search space in TCD. Giridhar & Agrawal (2010a) and Shah & Agrawal (2010b) proposed alternative methods for generating the complete space of basic alternatives.

Whether a thermal couple appears in a given design, a thermodynamically equivalent configuration (TEC) can be derived. Two distillation sequences are thermodynamically equivalent if it is possible to go from one to another one by moving column sections using the two streams of the thermal couple. Figure 2 clarifies the concept of thermodynamically equivalent configurations. A comprehensive discussion on TECs and their implications in controllability can be found in papers by Agrawal (1999), Agrawal & Fidkowski (1998b), Caballero & Grossmann (2003b), Rong et al (B. G. Rong et al., 2004; B. G. Rong & Turunen, 2006b) and Alcantara-Avila et al (2008).

An especially interesting thermodynamically equivalent configuration to a fully thermally coupled three component system is the divided wall column (DWC), see figure 3. Aside from the energy savings of a FTC configuration there is reduction in investment, piping and land occupation. The development of DWCs was in parallel to TCD, and in some sense motivated the research in TCD systems. It is interesting to note that the first known TCD device, due to Wright in 1949, (Wright, 1949) was in fact a DWC. However, the first DWC was not translated to industrial practice until 1985 by BASF (Schultz et al., 2002). One of the most important considerations in TCD has been controllability. In fact, the lack of confidence in the controllability of TCD and DWC systems has been the reason that complex thermally coupled distillation sequences have not been included in industrial practice until recently. Even nowadays some plants still work with column sequences that are suboptimal compared with some thermally coupled arrangements.

However, extended studies about operation and controllability showed that TCD with or without DWCs can be satisfactorily operated (Gómez-Castro et al., 2008; Segovia-Hernández et al., 2007; J. G. Segovia-Hernandez et al., 2002; Juan Gabriel Segovia-Hernandez et al., 2005; Juan Gabriel Segovia-Hernandez et al., 2004; Serra et al., 1999; Serra et al., 2000, 2001; Wolff & Skogestad, 1995; Zavala-Guzmán et al., 2012).

Other relevant aspects in TCD have also been studied. Some of them include: modification of the number and characteristics of vapor and liquid transfer between columns (Agrawal, 2000c; B. G. Rong & Kraslawski, 2002); Simultaneous design of thermally coupled and heat integrated systems (Agrawal, 2000b; Caballero & Grossmann, 2006; B. G. Rong & Turunen, 2006a, 2006c), thermodynamic analysis (Agrawal & Fidkowski, 1998a, 1999; Halvorsen & Skogestad, 2003a, 2003b, 2003c; V. H. Shah & Agrawal, 2010a), generation and analysis of sequences with reduced number of column sections (Errico & Rong, 2012; J. K. Kim & Wankat, 2004; B. G. Rong & Errico, 2012; Shenvi et al., 2012), alternatives for columns with one or multiple walls (Agrawal, 2001; Caballero & Grossmann, 2012).

The design of TCD sequences is much more complex than conventional distillation (each column with a condenser and a reboiler) by at least two reasons. First, the number of alternatives is much larger, and second when we introduce a thermal couple we are introducing also two thermodynamically equivalent configurations (TEC) (Agrawal & Fidkowski, 1998b; Caballero & Grossmann, 2003b). Therefore, the number of alternatives rapidly increases (i.e. in a five component mixture there are 203 basic configurations, more than 5000 if we consider internal heat exchangers and around $2 \cdot 10^5$ if we take into account TEC). In order to avoid the degeneracy created by TEC, it is convenient to use a task based approach instead of a column based approach (Caballero & Grossmann, 2001, 2004, 2006). –All TEC shares the same sequence of separation tasks-. But even using a task based approach and shortcut methods, the resulting models are large non convex MINLP (Caballero & Grossmann, 2001, 2002, 2003a, 2004, 2006; Caballero & Grossmann, 2011, 2012) models that are difficult to solve and in general we cannot ensure the global optimum solution.

The goal of this paper is to present an MILP approach for synthesizing TCD sequences, maintaining the rigorous of existing MINLP models. The rest of the paper is organized as follows. First, the problem is defined, including its limitations and strengths. Then a comprehensive model description is presented. Finally, some examples illustrate the model and its capabilities.

2. Problem statement.

The problem can be stated as follows: Given is a mixture of M components that do not form azeotropes. The objective is to obtain the optimal (or minimum cost) sequence of distillation columns, including conventional, non-conventional, and divided wall columns to completely separate N (N ≤ M) components. These N components are separated with high recoveries (i.e. sharp separations). The rest are allowed either to distribute in all the final streams to perform the separation with the minimum energy consumption, or if the components are classified by groups (i.e. C4s, C5s,…) the separation is performed in such a way that all the components of a group exit from the system all together. Note that 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.

Agrawal (2003) classifies the TCD in sequences with exactly N-1 columns, more than N-1 columns and less than N-1 columns (N is the number of key components to be separated). Configurations with exactly N-1 columns are called basic configurations and should form the basic search space for any TCD systems (a detailed discussion about this topic can be found in the work by Giridhar & Agrawal (2010b)). Configurations with more than N-1 columns, called non-basic- have higher operating cost than the best basic configuration, and tend to have also higher capital cost due to the additional distillation columns. Non-basic configurations can be removed from the search space. Configurations with reduced number of columns also have higher operating costs, especially for obtaining high purity products. However, the reduced number of columns could compensate the extra energy consumption. In the literature some of this cases can be found, for example those due to Brugma (1942), Kaibel (1987), Kim & Wankat (2004), or Errico & Rong (2012). However, in this paper we will focus only on basic configurations.

DWCs deserve special consideration. Strictly speaking a DWC uses less than N-1 columns. However, a DWC is thermodynamically equivalent to a sequence of three fully thermally coupled separation tasks that can always be arranged in two columns (in fact there are 4 thermodynamic equivalent alternatives for rearrange the three separation tasks in two columns (Agrawal, 1999; Caballero & Grossmann, 2003b)). In that sense we can consider a DWC as "two columns in a single shell", and therefore DWCs are included in the set of basic alternatives. (See figure 3)

2.1 MILP model in thermally coupled distillation sequences

As discussed above, the model of thermally coupled distillation systems lead to complex nonlinear and non-convex MINLP models. Notwithstanding, as noted by Andrecovich & Westerberg (1985), when we consider only the sharp separation of consecutive key components (assume that the components are sorted by decreasing volatilities) using conventional columns (a column with a single feed, two products, reboiler and condenser), it is possible to a priori, optimize each possible column in the sequence, and then use a MILP approach to extract the optimal sequence. Consider for example the superstructure presented in figure 4, originally presented by Andrecovich & Westerberg (1985) for the separation of a four component mixture. If we assume a high recovery in each separation, it is possible to assume with negligible error that the flow of a given component entering the system is the same in all the sub-mixtures along the superstructure. For example if there are 80 kmol/h of component B in the feed we can assume that if a given submixture containing B exists (ABC, BCD, AB, or BC) there will be exactly 80 kmol/h of B in that mixture. In other words, we know a priori the composition, the total flow and the thermal state of the mixture entering to each column and therefore we can design that column a priori using from shortcut to rigorous models and then a simple MILP to select the correct sequence.

Following this approach to deal with thermal couples, Shah and Kokossis (2001, 2002) introduce the concept of "supertask". A supertask groups some known complex structures like side-columns, Petlyuk arrangements, DWCs, and side-streams. In that way it is possible to a

priori calculate all the possible individual tasks or supertasks, and determine the optimal configuration through an MILP model. Therefore, it is possible to generate complex arrangements, where each task or supertask can be optimized a priori using shortcut (used in the original paper) or rigorous models. The major drawback is that there are a large number of basic configurations that are not taken into account (i.e. all those that include thermal couples between more than two consecutive columns).

The rest of this section presents an extension of the Andrecovich & Westerbeg ideas to thermally coupled systems. In that way it would be possible to develop a MILP model maintaining the rigorous of existing MINLP models –same result should be obtained with both approaches- with the advantage of the numerical performance of MILP models and the guarantee of global optimality

When we deal with TCD the direct application of Andrecovich & Westerberg ideas is not possible for the following reasons:

1. Recycle of information in the thermal couples. A major problem in the rigorous simulation, and therefore in optimization of thermally coupled distillation systems, is related with the «two side streams» that form a thermal couple because they introduce recycle of information in the systems (see figure 5). The numerical solution is usually sensitive to the initial values of those streams. It is not possible a priori to know the flows and compositions of those streams.

2. Vapor and liquid flow transfers between columns. Consider for example figure 6. In that case it is possible to optimize columns C2 and C3 independently and obtain the optimal operating parameters: number of trays, feed tray position(s) and internal flows. However, it is clear that the column with largest flows will be the dominant, and it will be necessary to modify the internal flows of the other column which, at the same time, increases the column diameters and the utilities. Again, in complex arrangements it is not possible to know a priori what will be the dominant column.

3. The performance of a column depends on the feed composition and thermal quality. TCD involves separation tasks with sharp separation of non-consecutive key components. Components with volatilities between the key components are allowed to distribute between the distillate and bottoms and, in general, we do not know a priori what the optimal distributions of the non-key components are. Therefore, for a given sub-mixture, we do not know a priory the composition because it depends on the previous separations. Figure 7 clarifies this last point.

The first step to develop a MILP approach for complex TCD systems consists of trying to overcome all these difficulties. In the next paragraphs we show how to deal with these problems:

1. Recycle of information in thermal couples. Carlberg & Westerberg (1989a, 1989b), in the context of near ideal systems, showed that the thermal couple between the rectifying section of a separation task and another column (see figure 5a) is equivalent to a single stream whose net flow is the difference of flows between columns ($V_1 - L_1$ referred to figure 5a) that is superheated vapor. They also showed that the thermal state (degree of superheating) can be calculated as

$$q = -\frac{V_1}{D} = -\frac{V_1}{V_1 - L_1} = -R \quad (q < 0) \tag{1}$$

where q is the liquid fraction (q<0 means superheated vapor). V_1 is the vapor flowing from the first to the second column. L_1 is the liquid entering in the top of the first column and R is the reflux ratio in the first column.

The two streams connecting the stripping section of a task (figure 5b) with another column are equivalent to a single stream whose flow is the net flow (L_2-V_2 referred to figure 5b) that is sub-cooled liquid. The thermal state (liquid fraction) can be calculated as follows:

$$q = \frac{V_2}{B} + 1 = \frac{L_2}{B} = \frac{L_2}{L_2 - V_2} \quad (q > 1) \tag{2}$$

Navarro et al (2011) extended the methodology to be applied in chemical process simulators. They showed that the degree of superheating or sub-cooling can be so large that the direct application in a process simulator is not always possible. Instead they showed that a superheated (sub-cooled) stream is equivalent to saturated stream plus (minus) an energy stream. The application of this approach in complex TCD sequences showed that the error in heat loads and internal flows was around 2% (even in very non ideal systems), and rarely is over 5%.

2. Vapor and liquid flow transfer between columns. A way of overcoming that problem consists of Introducing a heat exchanger in the connection point (see figure 6b-c) -a reboiler if the dominant column is the upper column, and a condenser if the dominant column is the lower column. In that way, all the column sections are operated at their optimal conditions. An energy balance shows that the duty of the new heat exchanger is similar to the extra duty in the original thermally coupled configuration (equal if we assume constant enthalpies). There is a benefit side effect; the temperature at which the heat must be supplied (removed) is between the temperature in the condenser of the upper column and the temperature in the reboiler of the lower column. Therefore, in some situations we can use a cheaper utility (i.e. if we have to heat we will do it at lower temperature than in the reboiler; if we have to cold we will do it at higher temperature than in the condenser). Of course, we have to pay the price of the new heat exchanger. An economic analysis is necessary to determine which the best option is. It is worth noting that in general, there should be not too much difference in total cost between both configurations, so a posterior analysis will allow «optimizing the details». In summary, we assume a heat exchanger in each unbalanced connecting point which allows operating each separation in its optimal conditions and then a posterior analysis will show what heat exchangers can be removed.

3. The performance of a column depends on the feed composition and thermal quality. As discussed above, due to the optimal distribution of non-key components, it is possible generate mixtures –streams connecting two columns- with the same components but different compositions (at difference to sharp separations and consecutive keys where the composition of a given mixture can be calculated a priori). If we use the approach described in point 1, we also generate mixtures with the same composition but different

feed quality (i.e. saturated, superheated vapor and sub-cooled liquid). In this paper we propose explicitly to take into account each one of these alternatives. In that way it is possible to generate a superstructure in which it is possible a priori to calculate each one of the separation tasks.

With all the previous information in mind, the first step consists of generating a superstructure. Before introducing the superstructure it is necessary to consider the following points:

- It is convenient that the superstructure be based on separation tasks. A given sequence of separation tasks can be rearranged in a large number of thermodynamically equivalent configurations. All the thermodynamically equivalent configurations have the same temperatures, flows compositions… and perform the same separations. Differences appear in the controllability and in some pressures depending on the arrangement of the actual columns. However, from a preliminary optimization point of view, those differences are negligible and considerably complicate the problem. Therefore a column based approach should be avoided in the first stages of design (Caballero & Grossmann, 2003b, 2004, 2006).
- A separation task can be considered like a pseudo-column formed by two sections (rectifying and stripping sections, by similarity with a conventional columns. As a consequence a separation task can be optimized using any of the models available for conventional columns.
- The model of the separation task can be separated from the heat exchange. In other words, a column needs a liquid stream entering at the top to provide the reflux, and a vapor stream entering at the bottoms to provide the vapor load to the column. However, it is not important if those streams come from a reboiler, a condenser or from another column.
- A state can be defined as any stream in a sequence of columns. Usually a state is qualitatively identified with a minimum set of properties. The components that form that stream are usually enough to define it. For example, the state BCD means that the stream is formed by a mixture of B, C and D inside some specifications (although other minor components could be also present).
- Identify the separation tasks that a given state can give rise is straightforward. For example, consider the state ABCD, sorted by decreasing volatilities, the possible separation task involving two key components are A/BCD; AB/BCD (separate A from C and let B to be optimal distributed between distillate and bottoms); AB/CD; ABC/BCD; ABC/CD; ABC/D.

With all the previous information, generating a superstructure based on the State Task Network formulism (Yeomans & Grossmann, 1999) is straightforward. We only have to identify the states, the separation tasks (including heat exchange) and join the related states and tasks. Figure 7a shows this superstructure. For generating a MILP model this superstructure must be extended to explicitly take into account that states with the same components but different composition or thermal quality are different states and generates different separation tasks figure 7b. However, it is convenient to use this superstructure to establish the basic relationships between states, tasks, condensers and reboilers that ensure that a given sequence of tasks and states can be rearranged in N-1 distillation columns.

Let us define the following index sets

STATES = [s | s is a state]

TASK = [t | t is a separation task]

DWC = [m | m is a divided wall column}

And the following Boolean variables

$$
\begin{aligned}
Y_t &= \quad \textit{True if task } t \textit{ is selected}; \quad \textit{False otherwise} \\
Z_s &= \quad \textit{True if state } s \textit{ is selected}; \quad \textit{False otherwise} \\
H_s^{COND} &= \quad \textit{True if state } s \textit{ has a condenser}; \quad \textit{False otherwise} \\
H_s^{REB} &= \quad \textit{True if state } s \textit{ has a reboiler}; \quad \textit{False otherwise} \\
ZM_m &= \quad \textit{True if the divided wall column } m \textit{ is selected}; \textit{False otherwise}
\end{aligned}
$$

In general the logical relationships can be written as follows:

$$
f(Y_t, Z_s, H_s^{COND}, H_s^{REB}, ZM_m) = TRUE \tag{3}
$$

The detailed description of the logical relationships is too large to be included here. But, in the appendix B, a brief description of those equations is presented. A comprehensive description can be found in previous works by Caballero & Grossmann (2001, 2004, 2006; Caballero & Grossmann, 2012). The explicit inclusion of DWC can be found in the work by Caballero & Grossmann (2012)

From this point we extend the superstructure taking into account that states with different compositions or thermal qualities produce quantitatively different separation tasks. The final result is a tree that contains all the relevant information of each separation task including the heat exchangers (reboilers and condensers). The procedure to generate that tree is as follows:

- The first stage consist of optimizing each one of the initial separation tasks (i.e. in a four component mixture we optimize the following separation tasks A/BCD_1; AB_1/BCD_2; AB_2/CD_1; ABC_1/BCD_3; ABC_2/CD_2; ABC_3/D. Note that we consider that two states are different if they have different compositions.
- For each one of the states involving more than one component ($BCD_{1,2,3}$, $AB_{1,2}$; $CD_{1,2}$; $ABC_{1,2,3}$). We generate two new states that differ in thermal quality, one corresponding to a saturated stream, indicating that there is a heat exchanger (reboiler or condenser) and another whose thermal quality is either superheated or subcooled depending on whether it comes from a rectifying or a stripping section and indicating that there is a thermal couple.
- Each one of the states in the previous point generates a new separation task that can be optimized. Then we continue with that procedure until all the separation tasks have been optimized.

In this paper we use the shortcut method by Underwood (1948), Fenske (1932) , Gilliland (1940) with the explicit equation by Molokanov (1972) and Krikbride (1944) for feed tray location (FUG), implemented in Matlab^{TM} (MATLAB., 2006.) and connected to Aspen-Hysys^{TM} through the activeX capabilities in order to obtain accurate physical properties for calculating the

volatilities and rigorous enthalpies to determine, if necessary the heat loads in reboilers and condensers.

It is obvious that the number of separation tasks rapidly increases, although it is considerably lower than the number of column sequences. If the number of key components to be separated is too large, the time for generating the complete tree can be prohibitive. However, for a 5 component mixture using constant volatilities and constant enthalpies Matlab^{TM} needed around 5 seconds of real time to complete the generation of the tree. This time includes the complete calculation of each tasks: number of trays, internal flows, reboiler and condenser heat loads, fixed and operating capital costs, etc. (the computer uses Intel(R) Core(TM)2Quad CPU 2.4GHz 2.39 GHz. RAM 8 GB under Windows 7). This time increases to around 60 seconds if the properties for each separation task and state are rigorously calculated using Aspen-Hysys. For a 6 component mixture, assuming constant volatilities the entire tree was generated in 60 seconds (around 10 minutes using Hysys for rigorously calculating the physical properties). Therefore, the procedure is feasible for much of the separations that are of industrial interest.

The next step consists of extracting the optimal sequence formed by the individual tasks in the extended tree. It is worth remarking that a feasible sequence of separation tasks and heat exchangers (reboilers and condensers) in the basic superstructure shown in figure 7a corresponds exactly to a unique sequence of separation tasks in the extended tree. Therefore, it is necessary to introduce a set of logical equations to relate the original STN with the extended tree.

To that end let us first define the following index sets, data and Boolean variables:

Index Sets:

ST: [st | st is a extended task in the extended superstructure]

TaskRep (t,st): [Set of extended tasks st that share the same basic task t.] For example, all separations A/B that differs in composition or feed thermal quality.

TaskParent (st, st') [The task st is generated from task st']. The task st' is the parent of task st in the extended tree.

TaskParentR (st, st') [The task st is generated from task st' by a rectifying section]

TaskParentS (st, st') [The task st is generated from task st' by a stripping section]

TaskWithChildrenR (st) [Tasks st that is able to generate other tasks by the rectifying section]

TaskWithChildrenS (st) [Tasks st that is able to generate other tasks by the stripping section]

FRecHE (s)   [States s with a condenser]. If they have a condenser they must be generated by a rectifying section.

FstrHE (s)   [States s with a reboiler]. If they have a reboiler they must be generated by a stripping section.

SrecHE (s,st)   [task st that generates the state s by a rectifying section. The state s has a condenser.

SstrHE (s,st)   [task st that generates the state s by a stripping section. The state s has a reboiler.

Data: As mentioned before, it is possible optimize a priori each one of the separation tasks in the extended tree. For each separation task we obtain the minimum and actual number of trays, the number of trays in each section (feed tray location), the actual vapor and liquid flows in both the rectifying and stripping sections, the relative volatilities, the diameter of each column section, the heat load in condenser and reboiler (if necessary), the equivalent thermal state of distillate and bottoms if a thermal couple appears (equations (1) and (2)), the area of the reboilers and condensers, the investment cost of columns and heat exchangers and the operating costs. While the tree is generated all the relations between tasks are explicitly used to dynamically create the index sets needed for the model.

Boolean and binary variables. We use upper case letters for Boolean variables and the corresponding lower case letter for binary variables.

$$W_{st}: \quad True\ if\ the\ extended\ separation\ task\ st\ is\ selected;\ False\ otherwise$$

The following logical relationships relate the variables of the STN original approach with those in the extended tree. For the sake of clarity we write both, the logical relationships in terms of boolean variables, and the equivalent linear algebraic equation(s) in terms of binary variables.

1.a. If the task t is selected one of the equivalent separation tasks in the extended tree must be selected.

$$\left.\begin{array}{l} Y_t \Rightarrow \bigvee_{st \in TaskRep} W_{st} \qquad \forall t \in TASK \\ 1 - y_t + \sum_{st \in TaskRep} w_{st} \geq 1 \ \forall t \in TASK \end{array}\right\} \qquad (4)$$

1.b. If the task t is not selected then we must not select any of the equivalent separation tasks in the extended tree.

$$\left.\begin{array}{l} \neg Y_t \ \Rightarrow \ \neg W_{st} \qquad (t,st) \in TaskRep_{t,st} \\ y_t + \ 1 - w_{st} \geq 1 \qquad (t,st) \in TaskRep_{t,st} \end{array}\right\} \qquad (5)$$

Note that logical equation (5) is equivalent to stating that if an extended separation task is selected, then the equivalent separation t must be selected.

2. Connectivity relations between extended tasks.

2.a. If the task st is selected then the parent task st' that generated it must also be selected.

$$\left. \begin{array}{ll} W_{st} \Rightarrow W_{st'} & \forall (st, st') \in TaskParent_{st, st'} \\ 1 - w_{st} + w_{st'} \geq 1 & \forall (st, st') \in TaskParent_{st, st'} \end{array} \right\} \tag{6}$$

2.b. A given task st must generate two 'children', one by the rectifying section and the other by the stripping section, except if it is a final product.

$$\left. \begin{array}{ll} W_{st} \Rightarrow \underset{st' \in TaskParentR}{\vee} W_{st'} & \forall st \in TaskWithChildrenR_{st} \\ 1 - w_{st} + \underset{st' \in TaskParentR}{\sum} w_{st'} \geq 1 & \forall st \in TaskWithChildrenR_{st} \end{array} \right\} \tag{7}$$

$$\left. \begin{array}{ll} W_{st} \Rightarrow \underset{st' \in TaskParentS}{\vee} W_{st'} & \forall st \in TaskWithChildrenS_{st} \\ 1 - w_{st} + \underset{st' \in TaskParentS}{\sum} w_{st'} \geq 1 & \forall st \in TaskWithChildrenS_{st} \end{array} \right\} \tag{8}$$

2.c. A given task must generate at most one separation task by the rectifying section and at most one by the stripping section.

$$\left. \begin{array}{ll} at\ most\ one: W_{st} & \forall st' \in TaskWithChildren_{st'} \\ {}_{st \in TaskParentR_{st, st'}} & \\ \underset{st \in TaskParentR_{st, st'}}{\sum} w_{st} \leq 1 & \forall st' \in TaskWithChildren_{st'} \end{array} \right\} \tag{9}$$

$$\left. \begin{array}{ll} at\ most\ one: W_{st} & \forall st' \in TaskWithChildrenR_{st'} \\ {}_{st \in TaskParentS_{st, st'}} & \\ \underset{st \in TaskParentS_{st, st'}}{\sum} w_{st} \leq 1 & \forall st' \in TaskWithChildrenS_{st'} \end{array} \right\} \tag{10}$$

3. Relates the states s and the associated heat exchangers with the tasks in the extended tree that can generate those states.

3.a. If there is a condenser in the state s generated by a rectifying section, then a task st, among all the tasks that can generate that state, must be selected. If there is no condenser associated to the state s, none of those tasks can be selected.

$$\left. \begin{array}{ll} H_s^{COND} \Rightarrow \underset{st \in SRecHE_{s, st}}{\vee} W_{st} & \forall s \in FRecHE \\ 1 - h_s^{COND} + \underset{st \in SRecHE_{s, st}}{\sum} w_{st} \geq 1 & \forall s \in FRecHE \end{array} \right\} \tag{11}$$

$$\left. \begin{array}{ll} \neg H_s^{COND} \Rightarrow \neg W_{st} & \forall (s, st) \in SRecHE_{s, st} \\ h_s^{COND} + 1 - w_{st} \geq 1 & \forall (s, st) \in SRecHE_{s, st} \end{array} \right\} \tag{12}$$

3.b. If there is a reboiler in the state s generated by a stripping section, then a task st, among all the tasks that can generate that state, must be selected. If there is no reboiler associated to the state s, none of those tasks can be selected.

$$
\left. \begin{array}{l}
H_s^{REB} \Rightarrow \underset{st \in SStrHE_{s,st}}{\vee} W_{st} \qquad \forall s \in FStrHE \\
1 - h_s^{REB} + \sum_{st \in SStrHE_{s,st}} w_{st} \geq 1 \quad \forall s \in FStrHE
\end{array} \right\} \tag{13}
$$

$$
\left. \begin{array}{l}
\neg H_s^{REB} \Rightarrow \neg W_{st} \quad \forall (s, st) \in SStrHE_{s,st} \\
h_s^{REB} + 1 - w_{st} \geq 1 \quad \forall (s, st) \in SStrHE_{s,st}
\end{array} \right\} \tag{14}
$$

With all those previous logical relationships it is possible to generate all the feasible sequences. However, is still necessary to explicitly taken into account the data associated to a given task if that task is selected. This is done by the following disjunction:

$$
\begin{bmatrix}
W_{st} \\
Cost\ Column_{st} = CostVessel_{st}^{Data} + Cost\ Internals_{st}^{Data} \\
\begin{bmatrix}
H_{st}^{COND} \\
Cost\ Condenser_{st} = Cost\ Cond_{st}^{Data} \\
QCond_{st} = QCond_{st}^{Data} \\
Cost\ Cold\ Utility_{st} = C_{cold}\ QCond_{st}^{Data}
\end{bmatrix} \vee \begin{bmatrix}
\neg H_{st}^{COND} \\
Cost\ Condenser_{st} = 0 \\
QCond_{st} = 0 \\
Cost\ Cold\ Utility_{st} = 0
\end{bmatrix} \\
\begin{bmatrix}
H_{st}^{REB} \\
Cost\ Reboiler_{st} = Cost\ Reb_{st}^{Data} \\
QReb_{st} = QReb_{st}^{Data} \\
Cost\ Hot\ Utility_{st} = C_{cold}\ QReb_{st}^{Data}
\end{bmatrix} \vee \begin{bmatrix}
\neg H_{st}^{REB} \\
Cost\ Reboiler_{st} = 0 \\
QReb_{st} = 0 \\
Cost\ Hot\ Utility_{st} = 0
\end{bmatrix}
\end{bmatrix} \vee \begin{bmatrix}
\neg W_{st} \\
Cost\ Column_{st} = 0
\end{bmatrix} \tag{15}
$$

In disjunction (15) the superscript '*Data*' makes reference to data in the separation task calculated before determining the optimal sequence. Figure 8 shows a graphical representation of what the disjunction means.

Finally, it is also necessary to calculate the investment and operating conditions of the extra heat exchangers introduced in the connection points to correct the imbalance in vapor and liquid flows of different column section (figure 6). For that end we first define a new index set.

CP (p)   [p | p is a connection point]

RCP (p, t, t')   [The connection point p involves stripping section of task t and the rectifying section of task t']

Two new Boolean variables are necessary to decide if we have to introduce a reboiler or a condenser:

$$HR_p : \{ True \ if \ in \ the \ connection \ point \ p \ a \ reboiler \ is \ needed; \ False \ otherwise \}$$
$$HC_p : \{ True \ if \ in \ the \ connection \ point \ p \ a \ condenser \ is \ needed; \ False \ otherwise \}$$

The following disjunction deals with the heat exchangers in the connection points:

$$
\begin{bmatrix}
HR_p \\
V_2^t \geq V_1^{t'} + eps \\
QREB_p = \Delta Hvap(V_2^t - V_1^{t'}) \\
Cost \ Heat \ Exchanger = f_{Reb}(Area_p)
\end{bmatrix}
\vee
\begin{bmatrix}
HC_p \\
V_1^{t'} \geq V_2^t + eps \\
QCOND_p = \Delta Hvap(V_1^{t'} - V_2^t) \\
Cost \ HeatExchanger = f_{Cond}(Area_p)
\end{bmatrix}
\vee
\begin{bmatrix}
\neg (HR_p \vee HC_p) \\
-eps \leq V_1^{t'} - V_2^t \leq eps \\
Cost \ HeatExchanger = 0
\end{bmatrix}
$$
$$p \in CP; \ (p,t,t') \in RCP_{p,t,t'} \tag{16}$$

In disjunction (16) V_2 makes reference to the vapor flow in the stripping section and V_1 to the vapor flow in the rectifying section (see figure 6). The heat load of condenser or reboiler can be calculated from data generated with each of the tasks involved. In order to preserve the linearity of the model, the reboiler and condenser costs are calculated using a linear relationship. If that approximation cannot be considered accurate enough, it is possible to use a stepwise linear approximation.

The model is completely defined by the set of equations (3), logical relationships equations 4 to 14, and disjunctions (15), (16). Disjunctions (15) and (16) can be transformed to linear equations with binary variables using the convex hull reformulation (Grossmann, 2002; Raman & Grossmann, 1994).

3.- Examples

3.1- Example 1. Separation of a mixture of alcohols

This example illustrates some of the capabilities of the proposed model. Here we present the separation of a five component mixture (Ethanol, 2-Propanol, 1-Propanol, i-Butanol, 1-Butanol). All the relevant data for the problem is presented in table 1. According to the previous comments in the paper, we constraint the search to basic configurations: the sequence of tasks and states can be rearranged in N-1 actual distillation columns. Each DWC reduces by one the number of actual columns.

To estimate the investment costs (in this example and in the next one) we used the correlation proposed by Turton et al. (2003), that takes into account the direct and indirect costs (purchased costs, materials required for installation, labor to install equipment, taxes insurances, contingency fee, etc). The cost of each vessel is calculated independently for each column section. Fortunately, according to the correlation given by Turton et al (2003), the bare cost depends linearly with the vessel volume in a large interval of volumes. In that way it is possible to calculate the costs of the vessels by adding the cost of each section. When a DWC

column appears a fixed value is subtracted to take into account the reduced number of vessels (Caballero & Grossmann, 2012).

In order to obtain accurate results, both the volatilities and the energy balances are calculated for each possible separation tasks using Aspen-Hysys. The errors are only due to the accuracy of the FUG model but not in the assumption of constant volatilities in all the system or in the energy balances.

The optimal solution obtained from the MILP model is shown in figure 9, with a total annual cost of $1059065/year. The first separation task consists of separating A from E (ethanol from 1-butanol) allowing the rest of the components to distribute between the distillate and bottoms. Both bottoms and distillate are thermally coupled. The distillate is then separated by the task AB/BCD (basically ethanol from i-butanol, and the rest of products -2-propanol and 1-propanol distributed along the column). The separation from the bottoms of the first column is BCD/DE (2-propanol from 1-butanol). The distillate of this last task and the bottoms of the previous one share the state BCD, that correspond with a fully thermally sub-sequence. This subsystem can be rearranged in a DWC that the model identifies. The intermediate product of this DWC (state BCD) is separated again following the sequence BC/CD – B/C – C/D that can be rearranged again in a second DWC. The other two binary separations A/B and D/E can be coupled with the rest of binary separations (see figure 9). In all the connecting points a reboiler in needed to compensate the flow differences between both sections. The validation of the model has been done simulating the obtained design using Aspen-Hysys. The comparison of heat duties and internal flows shows a very good agreement as shown in table 2.

The next step consists of rearranging the sequence of separation task in actual columns. The presence of two divided wall columns suggests that the complete separation can be performed using only two distillation columns, instead of the four columns. The figure 10 shows the most obvious alternative. However, there are some practical aspects to take into account:

1. The total number of trays in the second column is quite large, especially due to the difficult separation between ethanol and 2-propanol, but also due having to fit the four separation tasks in a single shell.

2. There are important differences in the diameters of some sections. For example the upper side of the second column should have a diameter of 1.2 m; while the lower part of the column have a diameter around 1.8 m (difference around 50% respect to the one with smallest diameter).

Fortunately, for this example a feasible and practical alternative can be developed. First, the separation A/B (ethanol from 2-propanol) can be performed in a separate shell, although the thermal couple is maintained. A small pressure gradient must be introduced to control the vapor flow with a valve. The lower section of the column can be transferred to the first column taking advantage of the thermal couple. The resulting configuration is shown in figure 11. Simulation in Aspen-Hysys shows that it is possible to build each column with a single diameter. In this example the internal walls result to be centered, and no further action is necessary. Although, it is possible to build columns with different areas in each side of the internal wall, if the difference is too large the practical operation (and building) of these columns could be very difficult (if not impossible).

Another possible modification consists of removing some of the final heat exchangers (reboilers in this example) that were introduced in the connecting points to correct the differences in internal flows, especially those with low heat duty. In this example, for reboilers in states B and C the differences in total cost were quite small (around 1%) and are within the error of the correlations used to calculate investment costs. A more detailed model would be needed. However, removing the reboiler in state D, has an important impact in the investment cost, because the diameter of the separation task (D/E) –lower part of the column is considerably increased-.

It is worth noting that it is possible to find a relatively large number of solutions with very similar TAC. For example, in this example there are 10 solutions within a difference of 5% in TAC, showed in table 3. All of them include the binary separations (A/B; B/C; C/D; D/E) and also the state BCD. Eight out of the ten first sequences share the same sequence of states with the best solution; the difference is in the distribution of heat exchangers. Also, in the first five solutions the feed to the separation A/B is saturated liquid. This is consistent with the fact that a thermal coupled would increases the vapor flow, and then in a very large column an important increase in the vessel cost would be expected.

Thermal coupling reduces the energy consumption. Therefore, in difficult separations, like in this example, the trend is to obtain systems with a large degree of thermal coupling and to include non-sharp split intermediate separations, and consequently to increase the total number of column sections. Solutions between 6 and 10 include the maximum number of column sections.

Finally, the best solution using conventional columns and sharp separation was obtained. The optimal solution (the direct sequence A/BCDE – B/CDE – C/DE – D/E) was $2093338/year, almost twice as expensive.

In relation to the resulting MILP model, as expected the number of variables and equations is relatively large (12064 equations, 3142 variables -2563 binaries-). However, the problem was solved in just 13.2 seconds of CPU time (see table 2 for further details).

3.2.- Example 2. Mixture linear hydrocarbons.

This example consists of the separation of a mixture of 5 hydrocarbons (n-pentane; n-hexane, n-heptano, n-octane, n-nonane). Table 4 shows all the relevant data to this problem.

In this case the optimal solution has a TAC of $795856 /year. (see figure 12). As expected, most of the connectivity between columns is through thermal coupling. The total number of column section is 16, while the minimum is 8 column sections (i.e. sharp separation in conventional columns), and for a fully thermally coupled system with 5 components, the number of column sections ranged from 14 (4N-6) to 20 N(N-1). This is a good example that shows that the optimal separation sequence usually is an intermediate situation between FTC and conventional sequences. Table 5

The optimal configuration has sixteen thermodynamically equivalent configurations $\left(2^{Number\ of\ thermal\ couples}\right)$ (Caballero & Grossmann, 2003b), which provides an extra degree of freedom to the designer. The final arrangement in actual columns should take into account other considerations like controllability, optimal distribution of trays in columns, a feasible

distribution of section diameters or build complex columns with different diameters, etc. Figure 13 shows a possible arrangement in actual columns in which the first and third columns have a single diameter; the second column has two different diameters. In this configuration it is possible to establish a pressure gradient in such a way that the vapor flows always from high to lower pressure.

As mentioned above, it is worth noting that there are a large number of alternative solutions with similar TAC. In this example there are 17 solutions within a 5% difference with the best solution. However, in contrast to the first example, the optimal sequence of separation tasks is only repeated in solution number 7, which gives the designer the flexibility to select another alternative sequence based on other criteria (i.e. operability, safety, etc.).

Again, the optimal configuration using conventional columns and sharp separations was obtained. The TAC is $1456800/year, which is 83% higher (AB/CDE – A/B – C/DE-D/E).

It is important to compare the results obtained in all the examples using this novel MILP approach, with existing MINLP models (Caballero & Grossmann, 2001, 2004, 2006; Caballero & Grossmann, 2012). In particular we have adapted the model presented in our previous work (Caballero & Grossmann, 2012) that includes also DWCs. For a fixed configuration, as expected the solution is exactly the same with only small differences due to the 100% sharp separation assumption. However, the MINLP approach although in general produce good solutions, due to its non-convex nature not always obtained the global optimal solution. The performance of the MINLP model is dependent both on the initial values and on the solver used. The interested reader is referred the original work for further details.

4.- Conclusions

This paper has introduced a novel MILP approach for the design of distillation columns sequences of zeotropic mixtures explicitly including from conventional to fully thermally coupled sequences and divided wall columns with a single wall.

The model is based on the use of two superstructure levels. In the upper level a superstructure is postulated that includes all the basic sequences of separation tasks and all the possibilities of heat exchange (condensers and reboilers). In the lower level an extended tree that explicitly includes all the alternatives for a given separation task (different thermal states and compositions of the feed to a given separation task). In that way, it is possible to a priori optimize all the possible separation tasks involved in the superstructure. A set of logical relationships relates the feasible sequences (upper level) with the optimized tasks in the extended tree resulting in a MILP to select the optimal sequence.

Some remarkable characteristics of the proposed approach are the following:

1. The model is very flexible, and includes from sharp conventional sequences (each column has a reboiler and a condenser –classical column sequencing) in this case the

model is equivalent to those proposed by Andrecovich and Westerberg (1985), to fully thermally couple configurations (a single reboiler and a single condenser for all the sequence of columns), going through all the intermediate possibilities, and explicitly including DWCs.

2. The search is constrained to basic configurations. Although it is known that some configurations with reduced number of columns can be optimal under some circumstances, these are 'special cases' and were not taken into account in this work. A DWC can be included if we take into account that a DWC can be considered thermodynamically equivalent to a fully thermally coupled subsystem formed by three separation tasks.

3. In this work the a priori optimization of each separation task follows a hybrid approach. The internal flows, number of trays, and feed position are based on the Underwood–Fenske-Gilliland equations, but the relative volatilities in each separation task and energy balances were rigorously done using a process simulator. However, the disjunctive representation of the model accommodates any other aggregated or even rigorous model. In any case, the approach presented here is enough for the preliminary design. It allows identifying some promising alternatives for a subsequent detailed simulation.

4. It is well known that some sections in thermally coupled systems operate in suboptimal conditions due to the imbalance of internal flows as a consequence of the thermal couples. To avoid this problem, we introduce heat exchangers (reboilers or condensers) in the connection points to provide (remove) extra flow and in this way maintain all the section operating in the optimal conditions. In a post analysis it is possible to decide if those heat exchangers can be removed. However, in general, there is not too much difference in the TAC between both alternatives and rigorous models and other considerations (i.e. operability) should be taken into account.

5. When we consider thermally coupled systems, it is common that there are a significant number of alternatives with similar economic performance. Although these alternatives increase the difficulty of the search, 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 task 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 numerical performance of the MILP model is very good. Even though the number of tasks to be optimized is large (but considerably smaller than the number of sequences), the preliminary optimization for a 5 component mixture is done in just a couple of minutes, and the

MILP model in less than 15 s. (See tables 2 and 5). The computational time rapidly increases with the number of components, but it can be used for most of the zeotropic mixtures with industrial interest.

Acknowledgements

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.

TASK = t | t is a given task

STATES = s | s is a state

IM_S = s | s is an intermediate state. All but initial and final products

TS_S = tasks t that the state s is able to produce

ST_S = tasks t that are able to produce state s

RECTs = task t that produces state s by a rectifying section

STRIPs = task t that produces state s by a stripping section

FPs = s | s is a final state (pure products)

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

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

DWC = w | w is a DWC;

$DWY_{w,s}$ = 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. *A given state s can give rise to at most one task.*

$$\bigvee_{t \in \underline{TS}_t} Y_t \ \underline{\vee} \ K \quad ; \quad s \in COL \tag{A1}$$

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*

$$\left. \begin{array}{l} \bigvee_{t \in \underline{RECT}_S} Y_t \ \underline{\vee} \ K \\ \bigvee_{t \in \underline{STRIP}_S} Y_t \ \underline{\vee} \ K \end{array} \right\} \quad s \in STATES \tag{A2}$$

where K has the same meaning than in equation (A1). 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.*

$$\bigvee_{t \in \left(P\_REC_s \cup P\_STR_s\right)} Y_t \ ; \quad s \in FP \tag{A3}$$

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.*

$$\left. \begin{array}{l} \neg \left(\bigvee_{t \in P\_REC_s} Y_t \right) \Rightarrow HE_s \\ \neg \left(\bigvee_{t \in P\_STR_s} Y_t \right) \Rightarrow HE_s \end{array} \right\} \quad s \in FP \tag{A4}$$

Where *HE* indicates the presence of a heat exchanger.

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).*

$$Y_t \wedge Y_k \ \Rightarrow \neg HE_s \quad \begin{cases} t \in RECT_s \\ k \in STRIP_s \\ s \in STATES \end{cases} \tag{A5}$$

6. *Connectivity relationships between tasks in the superstructure*

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

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

$$HE_s \Rightarrow \bigvee_{ST_s} Y_t ; \quad s \in STATES \tag{A7}$$

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

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.*

$$\begin{aligned} Y_t \wedge HE_s &\Rightarrow HEC_s & t \in RECT_s \\ Y_t \wedge HE_s &\Rightarrow HER_s & t \in STRIP_s \end{aligned} \tag{A8}$$

It is convenient to complete the pervious rule adding that:

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

$$\neg HE_s \Rightarrow \neg HEC_s \wedge \neg HER_s \quad s \in STATES \tag{A9}$$

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:

$$Y_t \Rightarrow Z_s ; \quad t \in ST_S \tag{A10}$$

$$Z_s \Rightarrow \bigvee_{t \in TS_s} Y_t \tag{A11}$$

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

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

$$\begin{aligned} CW_w &\Rightarrow Z_s & \forall w, s \in DWY_{w,s} \\ CW_w &\Rightarrow \neg Z_s & \forall w, s \in DWN_{w,s} \end{aligned} \tag{A12}$$

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

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

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

(A13)

13. Any heat exchanger associated to an internal state in a DWC must not be selected

$$CW_w \Rightarrow \bigwedge_{s \in DWCINT_{s,w}} \neg HE_s$$

(A14)

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Table captions

Figure captions.

Figure 1. Example of thermal couple. The Liquid and vapor streams substitute the condenser in the first column.

Figure 2. Example of Thermodynamically Equivalent configurations.

Figure 3. Thermodynamically equivalent configurations for a three component mixture. (a) to (d) using two columns. (e) Divided Wall Column.

Figure 4. Superstructure by Andrecovich and Westerberg for separating a 4 component mixture assuming sharp separations and conventional columns.

Figure 5. A thermal couple is equivalent to a superheated / subcooled stream or to a saturated stream plus/minus and energy stream.

Figure 6. Scheme of internal flows in the connection points and the effect of an intermediate heat exchanger.

Figure 7. Postulated superstructure for the separation of a four component mixture (upper side) and a detail of the extended tree.

Figure 8. Schematic representation of disjunction 15 (see text).

Figure 9. Optimal solution for example 1. Each box represents a separation task. Numbers inside the box are the number of actual trays in each section.

Figure 10. A possible rearrangement in actual columns for the optimal solution of example 1.

Figure 11. A feasible rearrangement in actual columns for the optimal solution of example 1.

Figure 12. Optimal solution for example 2. Each box represents a separation task. Numbers inside the box are the number of actual trays in each section

Figure 13. A feasible rearrangement in actual columns for the optimal solution of example 2.
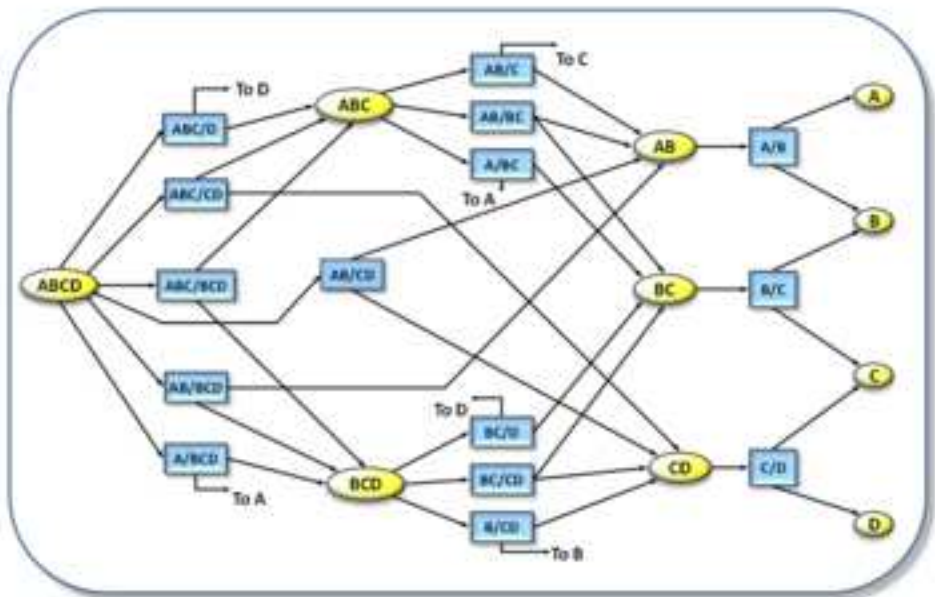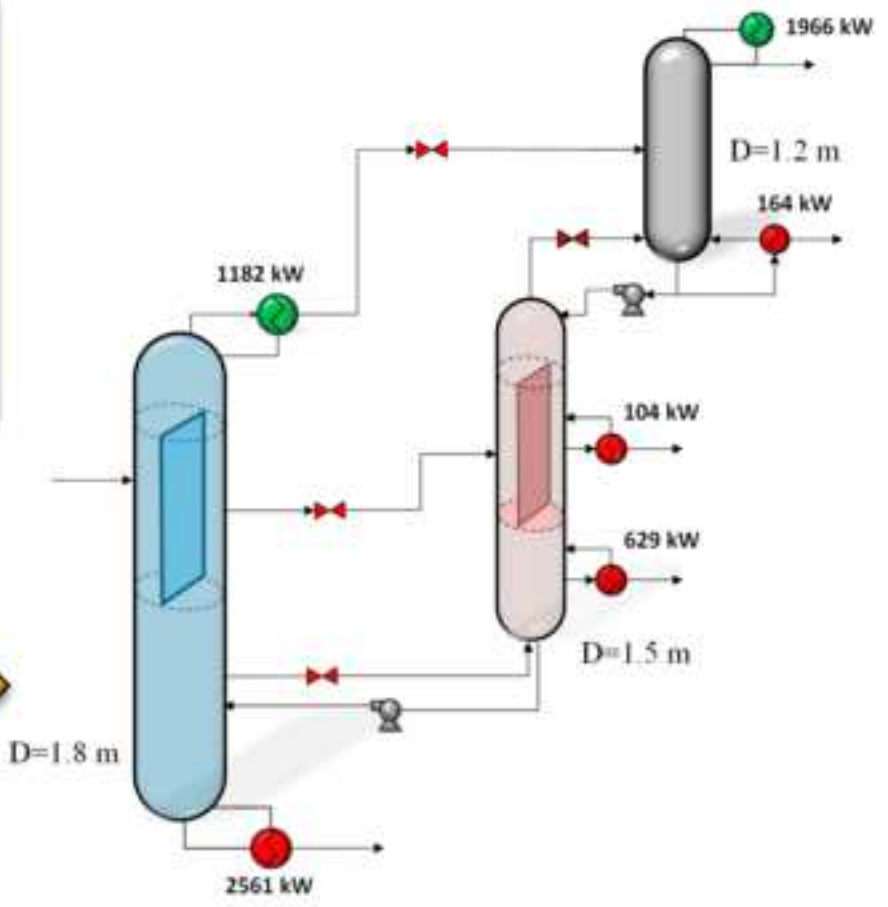
Table 1. Data for example 1.

Component	Feed composition (mol fraction)		
(A)- Ethanol	0.06	Feed Total Flow	100 kmol/h
(B)- 2-Propanol	0.27	Pressure	1 atm
(C)- 1-Propanol	0.3	Feed Liquid Fraction	1
(D)- i-Butanol	0.27		
(E)- 1-Butanol	0.1		
Steam cost	220.8 $/(kW year) (8000 h/year of operation)		
Cold water cost	9.216 $/ (kW year)		
Charging factor for annualizing investment costs.	0.18 (8% interest for 10 years)		
Recovery	0.99 of light and heavy key in each separation		
Thermodynamics	NRTL default Hysys parameters: estimation of relative volatilities and energy balances in condensers and reboilers		

Table 2. Results and model statistics for example 1.

Separation Task	Number of actual trays		Condenser	Reboiler
	NR	NS	(kW)	(kW)
ABCD/BCDE	6	7	---	---
AB/BCD	12	12	1182 (*1183*)[++]	---
BCD/DE	13	12	---	---
BC/CD	10	13	---	---
A/B	42	65	1966 (*1960*)[++]	164* (*222*)[++]
B/C	19	19	---	104* (*42*)[++]
C/D	25	2	---	629* (*647*)[++]
D/E	28	22	---	2561 (*2681*)[++]

DWC1: ABCD/BCDE – AB/BCD – BCD/DE
DWC2: BC/CD – B/C – C/D

Economic results
   Total Vessels cost (k$) 593.9
   Total tray cost (k$) 267.9
   Total reboilers cost (k$) 378.3
   Total condensers cost (k$) 241.1
   Total investment (k$) 1481.2
   Total steam cost (k$/year) 763.4
   Total cooling water cost (k$/year) 29.0
   TAC (charging factor = 0.18) (k$/year) **1059**

Model statistics.
   CPU time (s)** 13.1
   Nº equations 12064
   Nº Variables (total) 3142
   Nº binary variables 2563

NR = Number of trays in the rectifying section; NS = Number of trays in the stripping section.
*. Heat exchangers in the connecting points (see text)
++ Numbers in parenthesis are the values obtained in the Hysys simulation of the optimal solution
[++] Using Cplex 12.5, no parallel processing, under GAMS in Windows 7; Processor Intel(R) Core(TM)2Q Quad CPU 2.40GHz 2.39 GHz; RAM 8.00GB.

Table 3. Solutions inside a 5% of TAC for example 1 (optimal solution excluded)

	Sol 1.2	Sol 1.3	Sol 1.4	Sol 1.5	Sol 1.6	Sol 1.7	Sol 1.8	Sol 1.9	Sol 1.10
Sequence	ABCD/BCDE AB/BCD BCD/DE A/B B/C C/D D/E	ABC/BCDE BCD/CDE AB/BC BC/CD CD/DE A/B B/C C/D D/E	ABCD/BCDE AB/BCD BCD/DE A/B B/C C/D D/E	ABCD/BCDE AB/BCD BCD/DE A/B B/C C/D D/E	ABC/BCDE BCD/CDE AB/BC BC/CD CD/DE A/B B/C C/D D/E	ABCD/BCDE AB/BCD BCD/DE A/B B/C C/D D/E	ABCD/BCDE AB/BCD BCD/DE A/B B/C C/D D/E	ABCD/BCDE AB/BCD BCD/DE A/B B/C C/D D/E	ABCD/BCDE AB/BCD BCD/DE A/B B/C C/D D/E
Tasks with condenser	AB/BCD A/B	AB/BC A/B (D/E)*	AB/BCD A/B	AB/BCD A/B	ABC/BCDE AB/BC A/B (D/E)*	A/B	A/B	A/B	A/B
Tasks with Reboiler	BCD/DE D/E (A/B)* (B/C) (C/D)	ABC/BCDE D/E (A/B)* (B/C)	D/E (A/B)* (B/C) (C/D)	BCD/DE D/E (A/B)* (B/C) (C/D)	ABC/BCDE D/E	D/E (A/B)* (B/C) (C/D)	BCD/DE D/E (A/B)* (B/C) (C/D)	D/E (A/B)* (B/C) (C/D)	BCD/DE D/E (A/B)* (B/C) (C/D)
DWC	C1 BCD1++	CD1+++	BCD1++	BCD1++	CD1+++	C1 + BCD1++	C1 + BCD1++	BCD1++	BCD1++
Total Vessels cost (k$)	563.4	586.7	638.9	608.1	562.2	653.7	622.9	698.4	676.6
Total tray cost (k$)	260.7	270.0	267.9	260.7	264.5	281.5	274.3	281.5	274.3
Total heat exchangers (k$)	681.8	680.9	619.4	681.8	746.1	560.8	623.3	560.9	623.3
Total investment (k$)	*1505.9*	*1537.6*	*1526.3*	*1550.7*	*1572.7*	*1496.1*	*1520.5*	*1540.8*	*1564.2*
Total steam cost (k$/year)	760.3	757.3	763.4	760.3	762.6	780.1	777.1	780.1	777.1
Total cooling water cost (k$/year)	29.0	28.9	29.0	29.0	29.2	29.4	29.4	29.4	29.4
Total Energy (k$/year)	*789.3*	*786.2*	*792.4*	*789.3*	*791.8*	*809.5*	*806.5*	*809.5*	*806.5*
TAC (c.f = 0.18) (k$/year)	**1060.4**	**1063.0**	**1067.1**	**1068.5**	**1074.9**	**1078.8**	**1080.1**	**1086.5**	**1088.2**

*. In parenthesis: reboilers/condensers in the connection points to compensate the mass imbalance.

+ C1 = BC/CD – B/C – C/D; ++ BCD1 = ABCD/BCDE – AB/BCD – BCD/DE; +++ CD1 = BCD/CDE – BC/CD – CD/DE

Table 4 Data for example 2.

Component	Feed composition (mol fraction)		
(A)- n-Pentane		Feed Total Flow	200 kmol/h
(B)- n-Hexane		Pressure	atm
(C)- n-Heptane		Feed Liquid Fraction	1
(D)- n-Octane			
(E)- n-nonane			
Steam cost	220.8 $/(kW year) (8000 h/year of operation)		
Cold water cost	9.216 $/ (kW year)		
Charging factor for annualizing investment costs.	0.18 (8% interest for 10 years)		
Recovery	0.99 of light and heavy key in each separation		
Thermodynamics	Peng Robinsong Equation of State. Default Hysys parameters: estimation of relative volatilities and energy balances in condensers and reboilers		

Table 5. Results and model statistics for example 2.

Separation Task	Number of actual trays		Condenser	Reboiler
	NR	NS	(kW)	(kW)
ABCD/CDE	8	6	---	---
ABC/CD	12	3	---	---
CD/DE	10	8	---	---
AB/BC	8	5	---	---
A/B	10	11	1780	360*
B/C	13	15	---	---
C/D	22	13	481*	160*
D/E	17	19	---	2403
DWC:	ABCD/CDE – AB/BCD – BCD/DE			

Economic results
Total vessels cost (k$)	478.8
Total tray cost (k$)	167.1
Total heat exchangers cost (k$)	502.4
Total investment (k$)	*1148.3*
Total steam cost (k$/year)	568.8
Total cooling water cost (k$/year)	20.3
Total energy cost (k$/year)	*589.2*
TAC (charging factor = 0.18) (k$/year)	**795.9**

Model statistics.
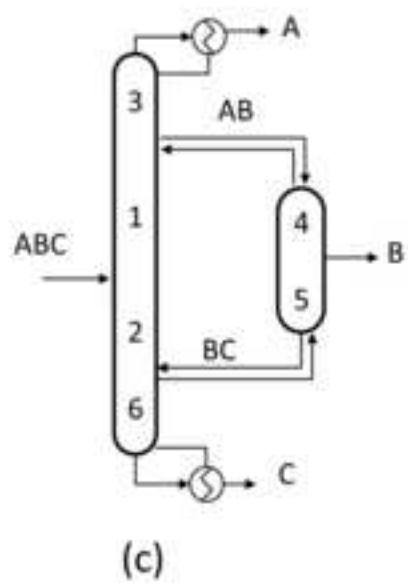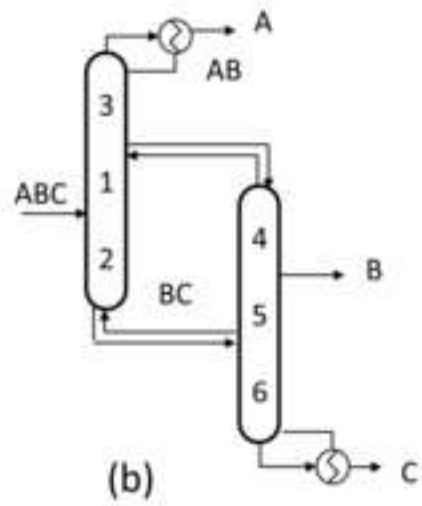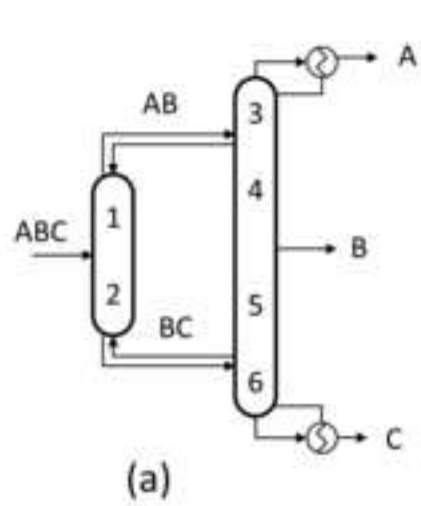|	
CPU time (s)**	12.8
Nº equations	12064
Nº Variables (total)	3142
Nº binary variables	2563

NR = Number of trays in the rectifying section; NS = Number of trays in the stripping section.
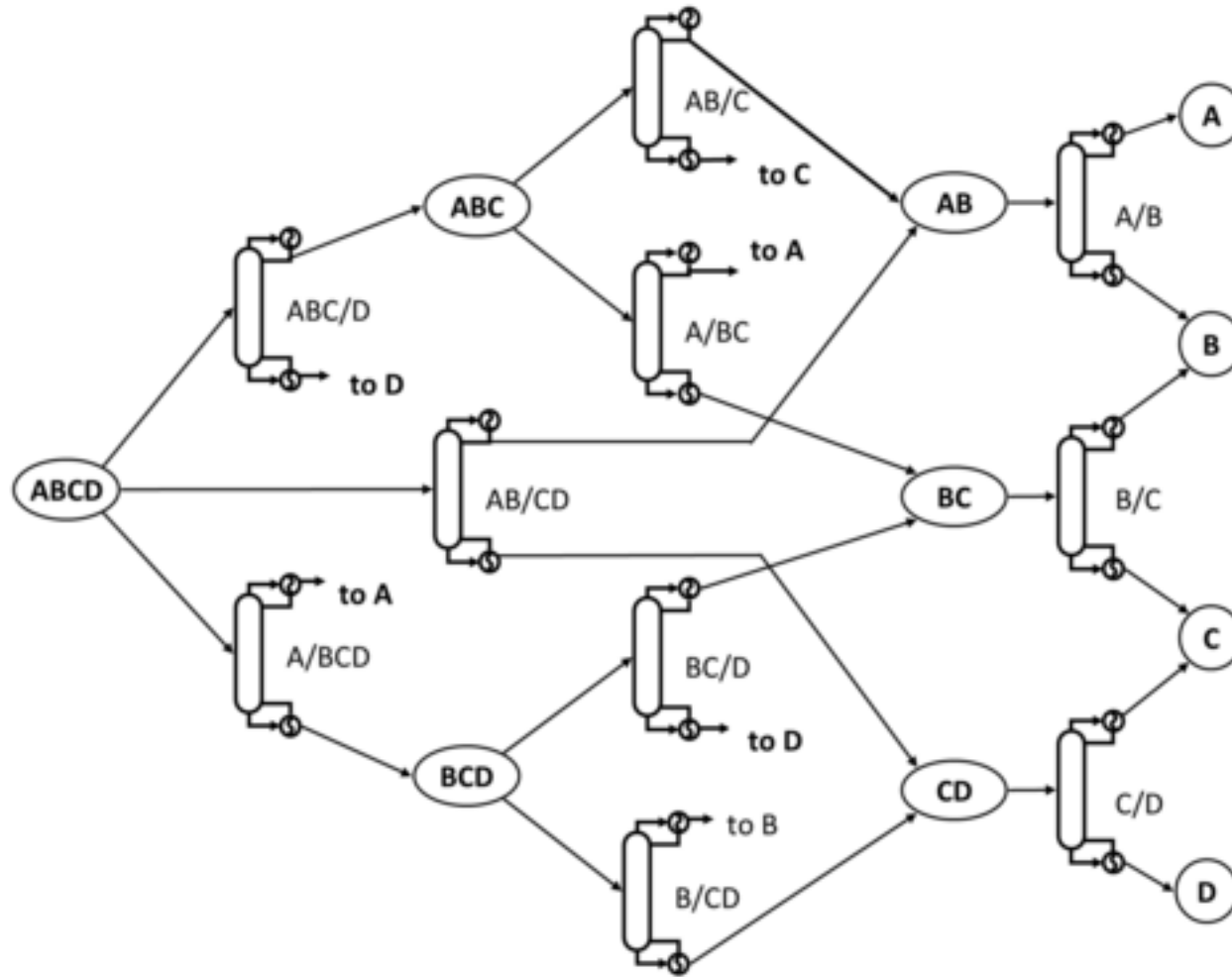*. Heat exchangers in the connecting points (see text)
++ Using Cplex 12.5, no parallel processing, under GAMS in Windows 7; Processor Intel(R) Core(TM)2Q Quad CPU 2.40GHz 2.39 GHz; RAM 8.00GB.
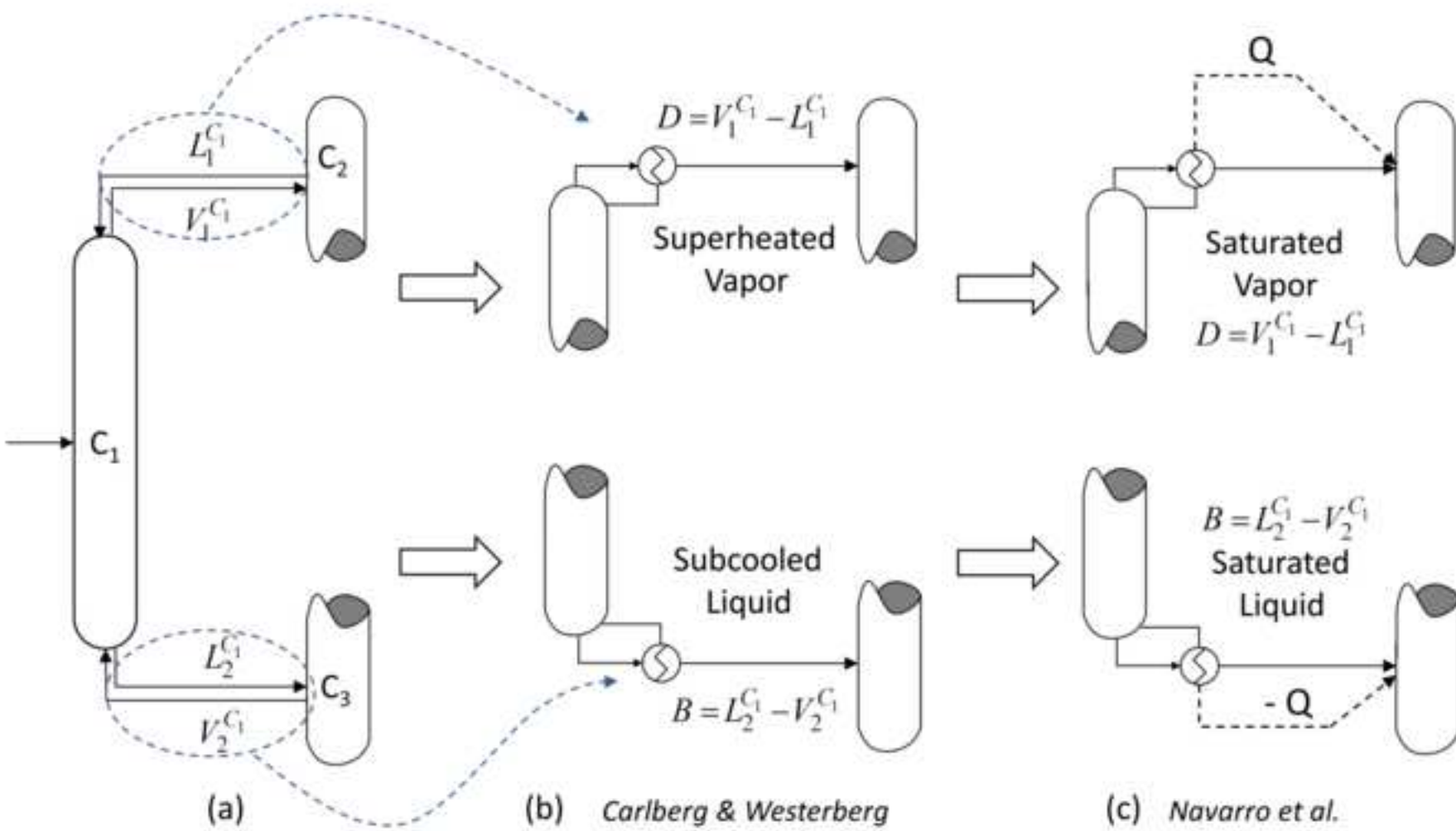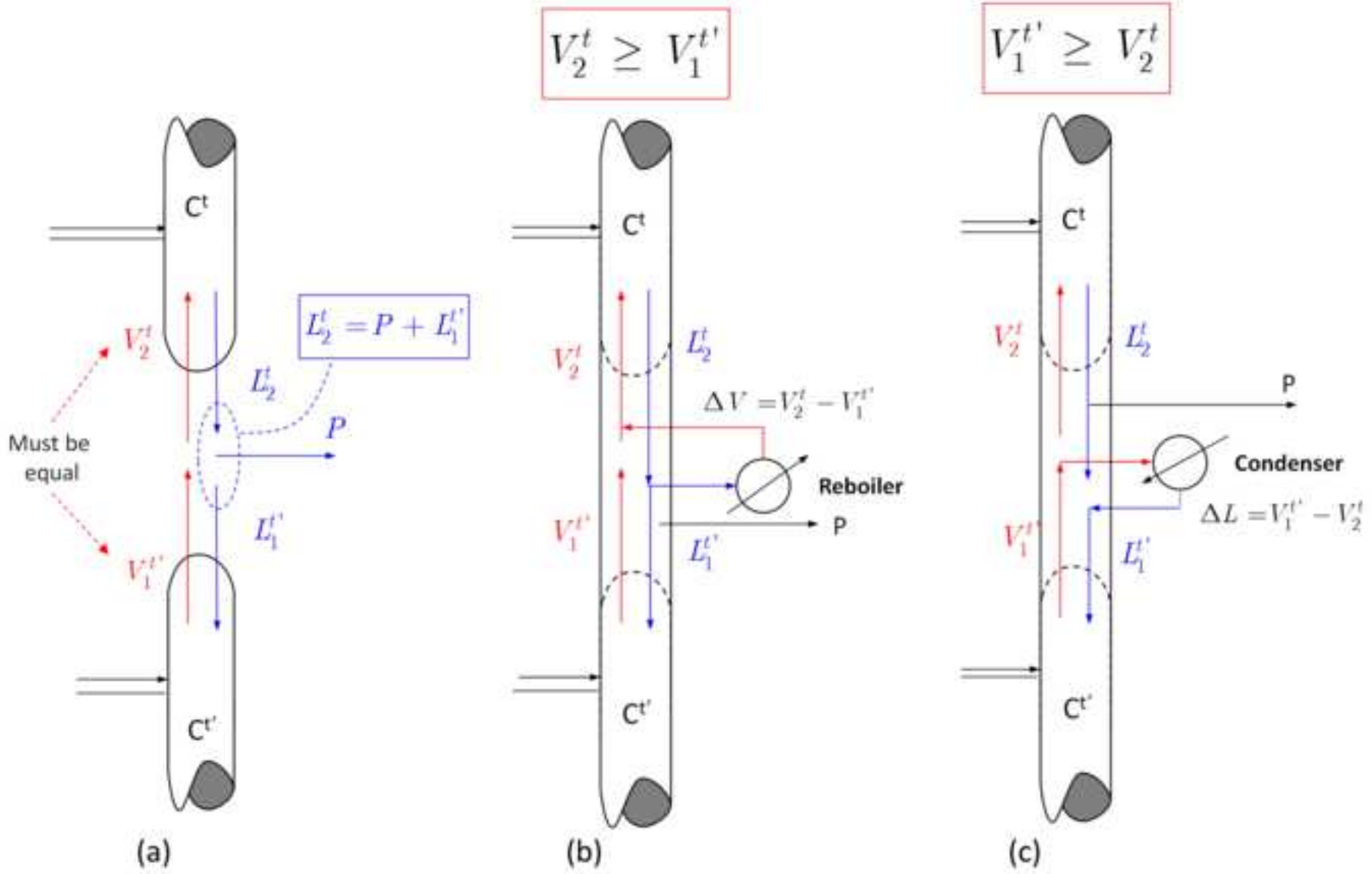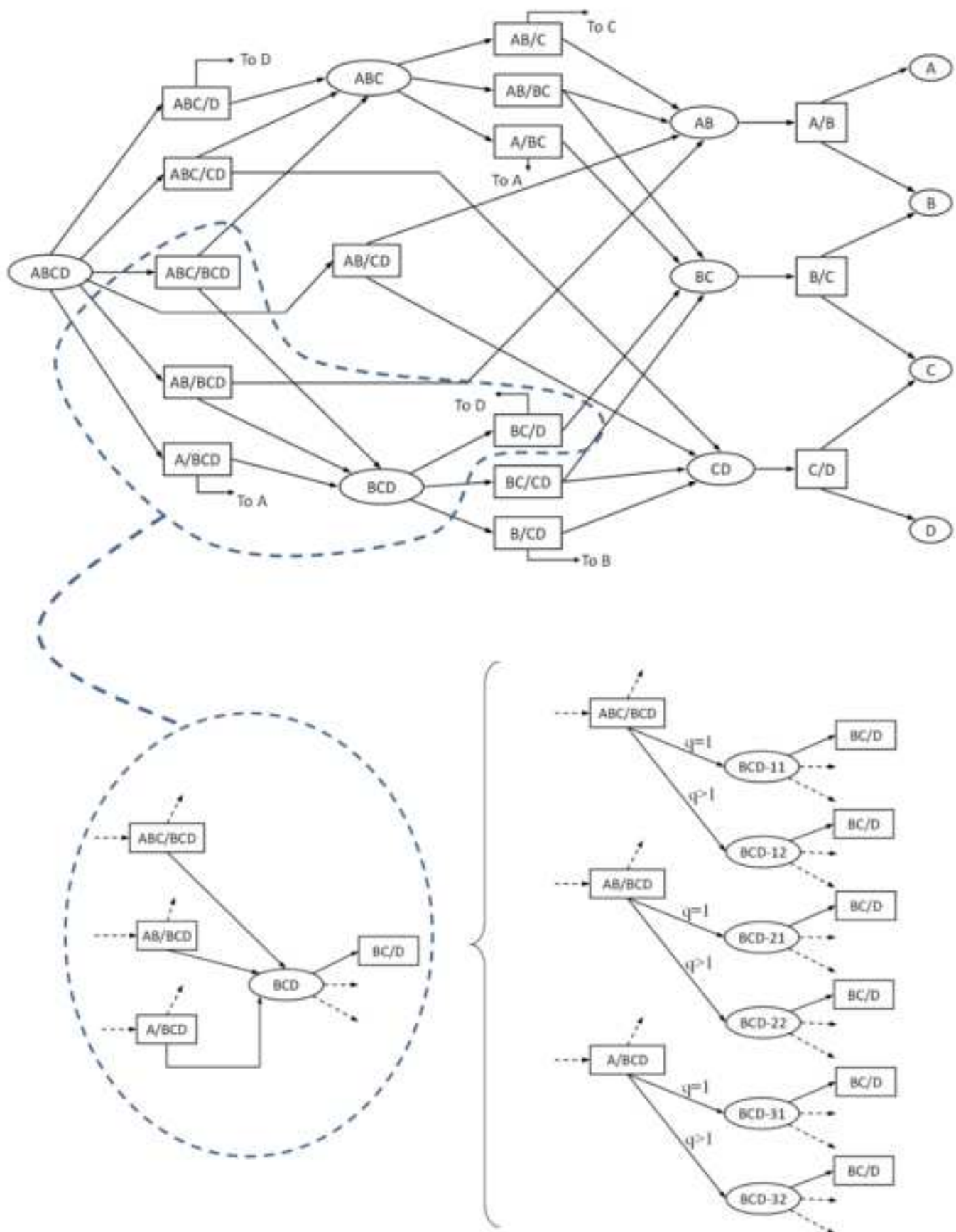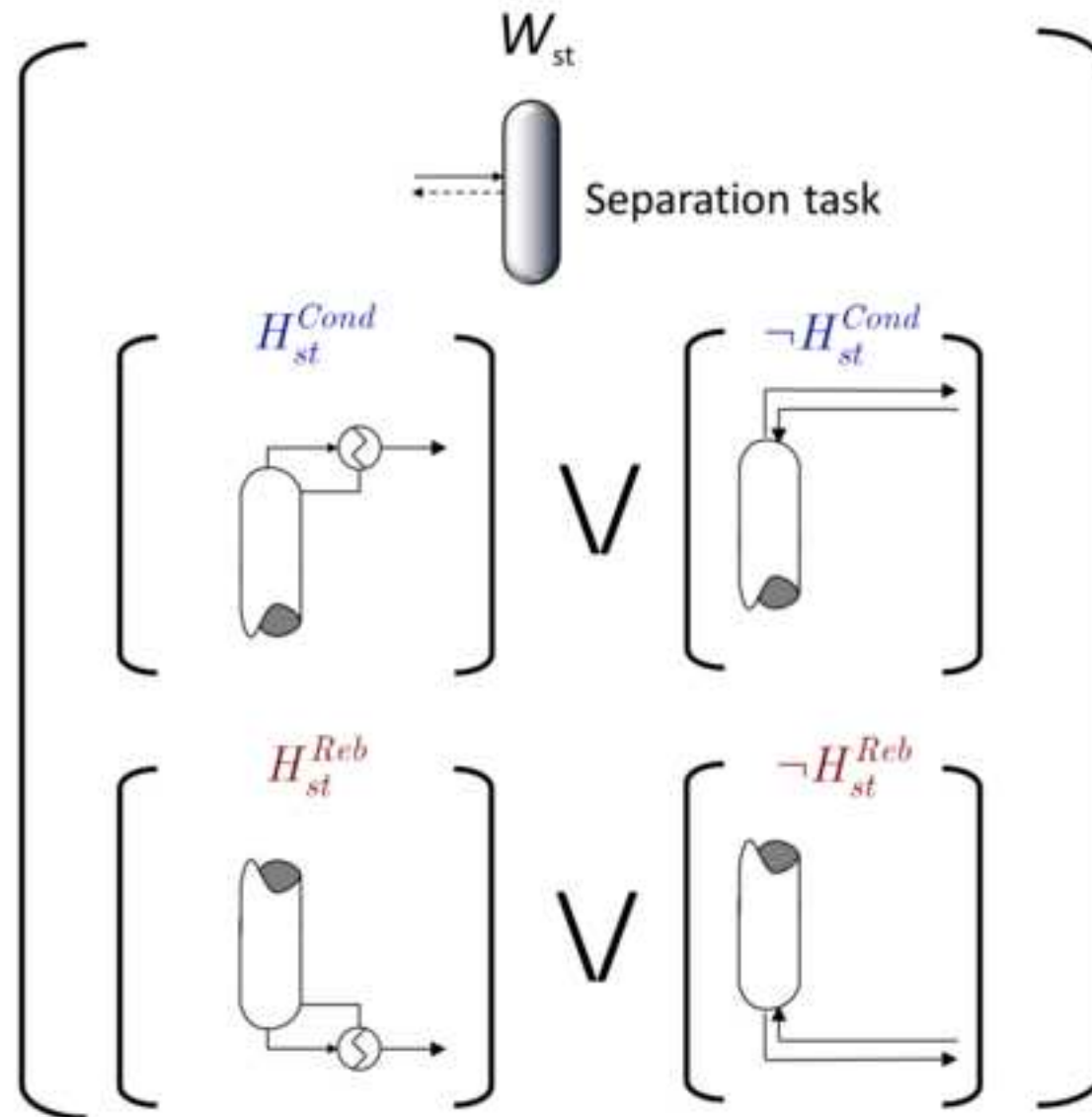
(a)   (b)

Figure(s)

Figure(s)

Figure(s)

$D = V_1^{C_1} - L_1^{C_1}$

Superheated Vapor

Saturated Vapor
$D = V_1^{C_1} - L_1^{C_1}$

Subcooled Liquid

$B = L_2^{C_1} - V_2^{C_1}$

$B = L_2^{C_1} - V_2^{C_1}$
Saturated Liquid

Q

-Q

(a)

(b)   Carlberg & Westerberg

(c)   Navarro et al.

$$V_2^t \geq V_1^{t'}$$

$$V_1^{t'} \geq V_2^t$$

$L_2^t = P + L_1^{t'}$

Must be equal

$\Delta V = V_2^t - V_1^{t'}$

Reboiler

$\Delta L = V_1^{t'} - V_2^t$

Condenser

(a)

(b)

(c)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

1780 kW

A

360 kW

B

D = 0.8 m

D = 1.7 m

F

424 kW

C

D = 1.0 m

D

160 kW

D = 1.9 m

E

2403 kW