

Structural considerations and modeling in the synthesis of heat integrated – thermally coupled distillation sequences

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 deals with the design of mixed thermally coupled-heat integrated distillation sequences. The approach considers from conventional columns (each distillation column with a condenser and a reboiler) to fully thermally coupled systems (only one reboiler and one condenser in the entire system). A discussion about superstructure generation and the convenience of using a representation based on separation tasks instead of equipment is presented, as well as a set of logical rules in terms of boolean variables which allow to systematically generate all the feasible structures. Based on the logical rules an algorithm is developed for generating valid sequences (even by hand) without explicitly solving the logical equations. All the specific aspects related with inter-column heat integration when partially thermally coupled systems are considered. A disjunctive programming formulation for extracting the optimal solution is presented. The model is based on the Fenske, Underwood Gilliland equations. However, the disjunctive formulation allows easily the use of any other shortcut, aggregated or even rigorous model without almost modifying the structure of the formulation. Finally three examples are presented.

Keywords: Distillation; Thermally Coupled Distillation; Heat integration; Disjunctive Programming; Superstructures.

[†] Author to whom correspondance should be addressed: caballer@ua.es

Introduction

Distillation is likely the most studied unit operation in the history of Chemical Engineering. This research effort is amply justified because distillation has been and continues to be the most widely used separation technique. The main disadvantage of distillation is the high energy requirement. Integration of distillation with the overall process can result in important energy savings^{1,2}. However, the heat integration between distillation and the rest of the process is often limited.

From the point of view of energy requirements, separation sequences using conventional columns (a single feed with two product streams, condenser and reboiler) suffer from an inherent inefficiency produced by the thermodynamic irreversibility during the mixing of streams at the feed, top and bottom of the column³. This remixing is inherent to any separation that involves an intermediate boiling component and can be generalized to an N component mixture. Theoretical studies developed by Petlyuk and coworkers³, 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. A fully thermally coupled configuration (FTC) is reached when the entire vapor load is provided by a single reboiler and all the reflux by a single condenser. Different researchers^{4, 5, 6} have shown that thermally coupled configurations are capable of typically achieving 30% in energy reduction when compared to conventional systems. Halvorsen and Skogestad^{7,8,9} proved that the minimum energy consumption for an N component mixture is always obtained for the FTC configuration.

In spite of the reduction in energy consumption, there is a price to be paid when using thermally coupled systems: 1. The energy must be 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 uses of utilities like medium or low pressure steam. 2. When using conventional columns it is common to constrain the alternatives to sharp separations, for example in a three component mixture (ABC) –sorted by volatilities-, we postulate initially separations A from BC (A/BC) and AB from C (AB/C). However, in fully thermally coupled distillation we could introduce sloppy separations –an intermediate product is allowed to distribute along the column- and therefore, we are increasing the number of column sections. This increase does not imply an increase in the number of columns, but usually an increase in the total number of trays. A detailed discussion on number of columns section needed for a given separation can be found in Agrawal¹⁰ and Caballero and Grossmann¹¹. 3. In FTC systems, the minimum vapor flow is that of the most difficult separation^{8,9} and therefore some column sections will have large diameters. 4. Operation is more difficult due to the large number of interconnections between columns. Therefore, it cannot be concluded that complex configurations are always superior compared with sequences of simple columns. Instead, the optimum configuration will depend on the specific mixture and feed conditions.

A different situation appears when heat integration is considered. Rev et al¹² demonstrated, based on theoretical considerations and case studies, that for ternary mixtures the Petlyuk configuration is usually not superior to energy integrated systems even in terms of energy savings. The situation is much more complex for systems with more than three components. In such cases, the simultaneous design of thermally coupled and heat integrated distillation

systems is expected to produce solutions in which the optimum is a mixture of thermal links and heat integrated columns.

From a structural point of view, thermally coupled configurations are much more complex than sequences of conventional columns. Agrawal¹⁰ established the basis of fully thermally coupled systems showing that some configurations were missing from the known superstructures at that moment. Caballero and Grossmann¹¹ showed that slight modifications in those superstructures could include all the alternatives presented by Agrawal. Also Agrawal¹⁰ established that, in contrast to systems with conventional columns, the number of column sections is not fixed. Therefore, there is a trade off between the energy consumption and the extra number of column sections. In partially thermally coupled systems generation of alternatives is even more complex and different researchers have proposed alternatives that were not previously considered: structures with reduced number of column sections¹³, structures with duplication of key components^{14, 15}, structures with duplication of separation tasks¹⁶, and modifications in order to get better control characteristics with almost the same performance in a large range of operational conditions^{17, 18, 19}.

From the above discussion it follows that the systematic generation of sequences including thermal links continues to be an open ended question. In the rest of the paper we propose a methodology for synthesizing simultaneously heat integrated and thermally coupled distillation systems. First we present a discussion about superstructure generation and the convenience of a representation based on tasks instead of equipment. Then we will comment different aspects related to the generation of alternatives: structures with reduced number of column sections, structures with duplication of key components in separation tasks, structures with duplication of separation tasks, and structures with reduced number of inter-column connections. Later we introduce a set of logical rules in order to systematically generate all those previous structures. The solutions of the set of logical equations are the feasible sequences of separations tasks. Based on these logical rules an algorithm is presented for generating valid sequences (even by hand) without explicitly solving the logical equations. Then, all the aspects related with inter-column heat integration will be commented, and finally a disjunctive programming formulation for extracting the optimal solution is presented.

2 Problem statement.

The problem we are dealing with can be stated as follows: given is a mixture of N components that do not form azeotropes, the objective is to generate a separation sequence to get the N pure components, considering simultaneously inter column heat integration and systems ranging from conventional to fully thermally coupled sequences.

Note that the problem could be extended to an M component mixture in which we select N components to be separated. The objective is then to obtain N streams, in such a way that only one component of the N previously selected is present in each of the final streams. However, we do not lose generality if we constrain to the original case and therefore this will be the criteria we will follow hereinafter.

3. Basic concepts and superstructure generation.

In the synthesis of distillation sequences using complex columns it is convenient to separate the concept of separation task from the equipment in which a separation task is performed. In fact, in complex columns, a single column usually performs more than a separation task. This aspect can be illustrated with a simple three component mixture (ABC) –where A is the most volatile and C the less, components are sorted by relative volatilities. -We follow this convention along the paper-. Using conventional columns we have two options. The direct sequence: separate first A (A/BC) and then B from C (B/C) or the indirect sequence separate first AB from C (AB/C) and then A from B (A/B). See [Figures 1a,b](#). Note that in this case there is a one to one relationship between tasks and columns. However, in a fully thermally coupled configuration (sequence of tasks AB/BC, indicating that the component B distributes along the column, A/B and B/C), the distribution of tasks in columns depends on the alternative chosen among all the thermodynamically equivalent. [See Figure 2](#).

Of course, a sloppy separation is not constrained to columns with thermal links. The classical pre-fractionation arrangement, see [Figure 3](#), shows this last case. However, having established that we have a source for the vapor load (i.e. a reboiler or a vapor side stream from another column) and a source for the reflux, the model of the first column in the pre-fractionation configuration ([Figure 3](#)) is identical to the model of the first column in the Petlyuk arrangement. Two important consequences follow for the modeling of the problem:

1. *We can separate the heat exchange from the separation task.* In fact the heat exchange can be defined as a new task. Note that in systems with no heat integration, there is a one to one relationship between the heat exchange task and the physical device that performs that task (the heat exchanger). However, in heat integrated systems, two heat exchange tasks are able to be joined in a single device.
2. *We can study the separation structure (sequence of tasks) without taking into account the presence or not of heat exchangers (except those related to the streams that leave the systems, as we will comment latter).*

A column section can be defined as the portion of a distillation column which is not interrupted by entering or exiting streams or heat flows. A separation task is formed by two column sections, a rectifying and a stripping section, and therefore, it is convenient to consider a separation task as a pseudo-column by similarity with conventional distillation columns, although in the final assignment of column sections to actual columns the two sections of a given separation task do not necessarily belong to the same column.

A 'state' can be defined as the set of physical and chemical properties of a stream. They can be quantitative like composition, temperature or pressure or qualitative like phase (liquid or vapor or a mixture)²⁰. When we are generating sequences for distillation, the states are defined qualitatively by the composition (i.e. state BCD indicates that there is a mixture of compounds B, C and D inside some previous specifications but the particular composition of the mixture is not important) and in some situations by the phase (liquid or vapor).

Once all the possible separation tasks have been generated and the states identified generating a superstructure is straightforward using the State Task Network formalism of [Yeomans and Grossmann](#)²⁰ [Figure 4](#) shows such a superstructure for a four component mixture. This last approach was followed by [Caballero and Grossmann](#)¹¹ for the design of fully thermally coupled systems. The major drawback of this approach is that the number of separation tasks grows very quickly with the number of components and so does the size of the resulting mathematical

programming problem. Alternatively [Yeomans and Grossmann](#) also proposed generating a superstructure by defining first the equipment and then assigning the tasks to that equipment (State Equipment Network). However, while in sequences using conventional columns and sharp separations the later approach works fine, in complex columns there are at least two problems: 1. Given a set of separation tasks with thermal links there are different possibilities of assignments of tasks to columns (thermodynamically equivalent configurations, see [Figure 2](#)); 2. In order to take into account all the possibilities of separation the same separation tasks should be assigned to more than one column, increasing the complexity of the combinatorial part of the problem.

A good approach is to generate a superstructure in which no pre-definition of columns is required so that we can aggregate as much separation tasks as possible. Note that a given state (stream defined qualitatively by its composition) gives rise to a subset of separation tasks; i.e. from the state ABCD we can generate the following separation tasks A/BCD; AB/BCD, AB/CD; ABC/BCD; ABC/CD; ABC/D; in which all the alternatives have been explicitly enumerated. Note also that for that particular mixture, at most one of the previous tasks should be selected. Therefore, we can assign all these tasks to a pseudo-column. We have used here the word pseudo-column to differentiate it to the actual column; in fact it is possible to group all previous tasks by defining the new task "separate A from D", this new definition could be enough if the system is modeled using a rigorous model, but in a short cut model like the method of Underwood, the explicit specification of the separation task is mandatory in order to determine the active roots in the Underwood equations, and maintain the explicit definition of tasks is usually a better option. The resulting superstructure is shown in [Figure 5](#).

The first version of this superstructure was due to [Sargent and Gaminibandara](#)²¹. The main difference is that all bypasses are removed, but as [Agrawal](#)¹⁰ remarked, the superstructure of Sargent and Gaminibandara does not include all the alternatives. However, the superstructure of Sargent and Gaminibandara can still be used simply assuming that if a given state is selected then it behaves like a bypass of liquid and vapor flows. In other words the bypasses are not explicitly included in the superstructure but they are implicitly included at the modeling level. The resulting superstructure, which we will use in this paper, is shown in [Figure 6](#).

4. Structural consideration in thermally coupled systems

The superstructure of [Figure 6](#), or in general any state-task based representation, has the important advantage of allowing the study of feasibility or structural aspects without any assumption on the final arrangement of the actual columns. But the superstructure by itself is not enough. In contrast to the case of using only conventional columns with sharp splits, in systems with thermal links there are some important considerations to take into account. The number of column sections is not fixed. It is possible to generate structures in which two separation tasks have the same key components, and some researchers have proposed sequences with duplication of states that apparently are not included in the superstructure of [Figure 6](#). We analyze below these aspects in detail.

The minimum number of column sections (or tasks, each task produces two column sections) is related to the number of heat exchangers associated to final products (or more in general to streams that leave the system)^{10,22}. In an N component mixture in which all the final products have a heat exchanger there are $2(N-1)$ column sections $-(N-1)$ separation tasks- the previous relationship is always true independently of the existence or not of heat exchangers associated to intermediate streams (states). The heat exchangers associated to final products (pure

components or streams that leave the system) of intermediate volatilities can be removed, but in this case we have to add two more sections for each heat exchanger removed. In fully thermally coupled systems the minimum number of separation tasks is $(4N-6)/2$ ¹⁰. However, it is possible to generate structures with up to $N(N-1)/2$ separation tasks. In general, in systems with neither duplication of states nor duplication of key components in separation tasks (we will comment these aspects below) the number of separation tasks is related to the heat exchangers associated to final products through the following equation²²

$$2N - NHE_f - 1 \leq \text{number of separation tasks} \leq N(N-1)/2 \quad (1)$$

where NHE_f is the number of heat exchanges associated to the final products.

There is an exception in which it is possible to generate sequences with fewer number of column sections than the minimum given by previous expression. It is the case of columns with vertical partitions or “Kaibel” columns¹³. Figure 7 shows an example of this configuration. The major advantage of this structure is that it allows the integration of tasks in a single shell with a vertical partition, but from the energy point of view these structures are almost always outperformed by thermally coupled systems. Their performance is similar to separating a three component mixture using a single column by withdrawing a liquid or vapor stream with the component of intermediate volatility.

Sequences with duplication of key components in separation tasks are another class of structures which deserve comment. Figure 8 shows an example where the separations AB/C and B/C have the same key components (B light key and C heavy key). As a consequence the state C is produced by three contributions one coming from the rectifying section of the pseudo-column (task) C/D and two coming from the stripping sections of the pseudo-columns (tasks) AB/C and B/C respectively. The problem appears when this sequence of tasks is converted to actual columns. We have basically two alternatives: 1. Assigning a heat exchanger (a reboiler in this case) to any of the pseudo-columns that produce C from a stripping section, Figures 9a and 9b (Configurations similar to those in Figures 9a and 9b were presented by Rong et al^{14,15}); 2. Generating a structure in which the vapor load to pseudo-columns AB/C and B/C is provided by task C/D. This can be accomplished by a structure like that presented in Figure 10a. Note that the “apparently strange” structure of Figure 10a can be converted in a column with an internal wall like that in Figure 10b.

Let us go back to Figure 8 and introduce a small modification. If state ABC instead of producing the separation task AB/C produces the separation task AB/BC, we get the structure of Figure 11a. Figure 11a is a fully thermally coupled structure. Halvorsen and Skogestad⁹ proved that this is the structure with minimum energy consumption. Eventually a configuration with a divided wall similar to that in Figure 10b, can be synthesized, see Figure 11b. Besides, it is not necessary to include new heat exchangers. The separation AB/BC, letting the component B to distribute along the column, is easier than separating AB/C, and then the number of trays is also lower. Therefore, the sequence in Figure 11 outperforms the sequence of Figure 8. The major consequence of previous discussion is that we should constrain ourselves to configurations in which a state is generated by at most two contributions –One coming from a rectifying section and another from a stripping section-. (Sequences like those presented in Figure 8 could however be justified in some cases when heat integration is considered). Note that, if we allow a state to be produced by more than two contributions, in systems with more than 4 components states produced by 4, 5 or even more contributions could appear. Note also that for systems

with more than 4 components the states with more than two contributions could also be intermediate states and not necessarily final products, producing rather complex systems. But, the analysis of the previous example continues to be valid and there should be a thermally coupled configuration with at least the same or better characteristics in terms of energy and capital cost.

Another interesting situation appears when an intermediate state is generated by two contributions (necessarily, as commented above, one coming from a rectifying section and another coming from a stripping section), for example state BC in Figure 11. In this case we have basically three alternatives, see Figure 6b. 1. Mixing these two streams previous to the separation. This approach is only optimal if all previous separations are performed at the preferred split (also called transition split) and all these previous separations form a fully thermally coupled sub-system. In such a case there is no back-mixing⁹, in the other case we are introducing inefficiency because we are mixing streams previously separated. 2. Introduce a two feed column. Here there is the additional problem of determining the relative position of these two feeds. 3. Duplicate the separation task. However, this last case introduces a new separation column. From an energy point of view a two feed column is more effective than two columns, and from the point of view of investment the increase in diameter of the column does not justify the separation in two different columns –except, maybe, in some extreme situation.

In order to avoid some control problems related with interconnectivity Agrawal and Fidkowski¹⁷ proposed changing some of the thermal links by direct liquid or vapor connections, see Figure 12. In some situations depending on the volatilities and the composition the total energy consumption is similar to that in thermally coupled system. However, as commented above, including or not a heat exchanger –total or partial- does not modify the structure of tasks. i.e. A pre-fractionation configuration like that in Figure 3 and the Petlyuk column perform the same sequence of separation tasks. If the effect of these changes on the total annual cost is only marginal they can usually be ignored in preliminary designs.

5. Logic rules for generating structural distinct sequences of distillation columns.

With the previous discussion in mind it is possible to develop a set of logical rules for generating all the possible sequences for an N component mixture. These logic propositions can be transformed into a set of algebraic equations in terms of binary variables in order to be included in an MI(N)LP optimization model. Due to the interest of this last approach Table 1 shows both the logic expression and the equivalent algebraic equations but in the text only the Boolean expression is presented. (A similar set of logic expressions, but only for fully thermally coupled systems has been previously presented by Caballero and Grossmann¹¹).

It is worth noting that even in the case in which we do not use an MI(N)LP approach, and we are interested in only screening the alternatives, the following logical rules are still valid because they allow generating all the structurally different alternatives in a systematic way. However, in this last case a systematic procedure could be of interest for generating alternatives that does not require any MILP solver. A procedure for generating alternatives or simply for checking if a sequence is feasible will be presented in next section.

Let us define the following index sets:

TASKS = {t | t is a given tasks}

STATES = {s | s is a state}

COL = {s | s is a state that produces a separation task (all states except products. It is a pseudo-column in superstructure of Figure 6)}; (COL \subseteq STATES.)

OUT_ST_s = {tasks t that state s is able to produce}

IN_ST_s = {tasks t that are able to process state s}

RECT_s = {task t that produce state s by a rectifying section}

STRIP_s = {task t that produce state s by a stripping section}

PROD_s = { Final states –pure products or desired separated mixtures-}. (PROD \subseteq STATES)

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.}

We define the Boolean variable Y_t such the variables are True if the task t is selected and False otherwise. We will use the capital letters for Boolean variables and lower case for the corresponding binary variables. If a Boolean variable is True the corresponding binary (y_t in small letters) takes the value 1 and if it is False the value 0. We also define the Boolean W_s to take the value True if there is a heat exchanger associated with the state s.

The rules for extracting feasible sequences of tasks are the following:

1. A given state s can give rise to at most one task. i.e. the state BCD can give rise, at most, to one of the following separation tasks B/CD, BC/CD, BC/D.

$$\bigvee_{t \in \text{OUT_ST}_s} Y_t \preceq K ; s \in \text{COL} \quad (2)$$

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.

This logical relationship avoids duplication of keys in separation tasks as previously commented. If by any reason duplication of keys is allowed then next logical relationships should be relaxed.

$$\left. \begin{array}{l} \bigvee_{t \in \text{RECT}_s} Y_t \preceq K \\ \bigvee_{t \in \text{STRIP}_s} Y_t \preceq K \end{array} \right\} s \in \text{STATES} \quad (3)$$

where K has the same meaning than in equation (2). Note that if we want only systems with the minimum number of column sections 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.

$$\bigvee_{t \in (\text{P_REC}_s \cup \text{P_STR}_s)} Y_t ; s \in \text{PROD} \quad (4)$$

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. (cases a and b in Figure 6)

$$\left. \begin{array}{l} \neg \left(\bigvee_{t \in P_REC_s} Y_t \right) \Rightarrow W_s \\ \neg \left(\bigvee_{t \in P_STR_s} Y_t \right) \Rightarrow W_s \end{array} \right\} s \in PROD \quad (5)$$

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).*

In other words, the vapor load (or the reflux) of a separation task came from a reboiler (condenser) or from a vapor (liquid) stream of another separation task. In this second case a heat exchanger is not needed.

$$(Y_t \wedge Y_k) \Rightarrow \neg W_s \quad \left. \begin{array}{l} t \in RECT_s \\ k \in STRIP_s \\ s \in STATES \end{array} \right\} \quad (6)$$

This rule is also specifically forbidding sequences with duplications of key components. If under some circumstances we are interested in generating these systems we only have to relax the rule.

6. *Connectivity relationships between tasks in the superstructure*

$$\left. \begin{array}{l} Y_t \Rightarrow \bigvee_{k \in OUT_ST_s} Y_k ; \quad t \in IN_ST_s \\ Y_t \Rightarrow \bigvee_{k \in IN_ST_s} Y_k ; \quad t \in OUT_ST_s \end{array} \right\} s \in STATES \quad (7)$$

The previous relationships are enough for generating all the structurally different sequences of separation tasks for an N component mixture using distillation. However, heat exchangers associated to intermediate states (i.e. BC in superstructure shown [Figure 6](#)) can also appear, although they do not change the sequence of tasks; therefore the following logical relationship is needed.

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

$$W_s \Rightarrow \bigvee_{t \in IN_ST_s} Y_t ; \quad s \in STATES \quad (8)$$

6. An algorithm for generating structurally different distillation sequences.

Solving the previous equations either by an MILP solver or by solving the Boolean equations allows to generate all the structurally different distillation sequences, (remember that we defined two sequences to be structurally different if the subset of states that appear in each sequence is different, independently of the heat exchangers). Once a feasible structure is obtained we only need to add a binary cut^{23, 24} and re-solve the equations in order to get a new structure and continuing with the procedure until an infeasible solution is obtained or if we have access to the binary tree of the solution procedure to continue with the search until there are no more feasible solutions. The solver BARON²⁵ includes this option. Alternatively, we could use constraint programming²⁶ for finding all solutions in the previous logical relationships. However, it could be of interest to develop a procedure to systematically generate alternatives without solving the previous equations. An efficient and easy implementation algorithm could be as follows:

1. Start with the fully thermally coupled configuration with the maximum number of states ([Figure 13a](#) shows that configuration for a 5 component mixture).
2. Chose one of the intermediate states (intermediate states are all except the first that correspond to the initial mixture and those that are final products), remove it from the base structure and check if the configuration is feasible (see next paragraphs for a fast way of checking feasibility). If it is feasible add the sequence to the list of feasible sequences. Starting again from the base structure, select another internal state, remove it and repeat the procedure until all the intermediate states have been selected.
3. Repeat the procedure in step 2 but now deleting two states simultaneously until all the possible combinations have been tested. Then repeat deleting three states simultaneously and so on.
4. The minimum number of intermediate states is equal to $N-2$ (N is the number of components). Therefore, the procedure stops when the number of intermediate states that remain in the structure is lower than $N-2$. [Figures 13b-e](#) show some examples.

Checking if a sequence of tasks is feasible is straightforward. We need to check two conditions:

1. Check if all the states in the sequence have a precursor, for example in a 5 component mixture if the state BC appears then at least one of the following states should appear (ABC, BCDE, BCD). In other cases the state BC never could be formed.
2. Check if the separation produced by the each of the states in the sequence is a feasible separation task. Let us consider some examples: in [Figure 13a](#) state ABCDE produces states ABCD and BCDE so the separation is task is ABCD/BCDE. In [Figure 13b](#), the state ABCD produces states ABC and CD so the separation is ABC/CD. In [Figure 13c](#) the state ABCD produces states A and BCD and therefore the separation task is A/BCD.

However, if in [Figure 13a](#) we remove states AB and BC simultaneously, the state ABC should separate A from B and from C and therefore the sequence is infeasible, (see [Figure 13f](#)).

It should be noted that special cases like structures with reduced number of column sections, structures with duplication of key components in separation tasks and structures with duplication of separation tasks could be eventually generated. Simply by ignoring the second validation rule separations with reduced number of column sections are generated. Consider again [Figure 13f](#) separate A from B and from C in a mixture ABC in a single column is possible simply by withdrawing a side stream, although the energy consumption is so large that this option is only used in very especial cases. (Theoretically it would be possible to separate an N component mixture without azeotropes in a single column, although the cost is so large that this alternative is not even considered).

By duplicating in the initial superstructure some of the states it is possible generate sequences with duplication of key components or duplication of separation task. For example, in a superstructure with the state C duplicated sequences like that shown in [Figure 9](#) could be generated. Although, these particular cases have not been taken into account in this work.

This algorithm has been implemented in MatlabTM ²⁷. For a mixture of 3 components there are only three structurally different sequences (It is worth insisting that configurations like pre-flash and Petlyuk have the same sequence of tasks and therefore are considered structurally the

same. Configurations with side columns have the same sequence of tasks than the direct or indirect sequence). In a 4 component mixture there are 18 structurally different feasible sequences (it is possible generate 26 different combinations of states but only 18 are feasible). The number of feasible sequences is much larger than when only conventional columns are considered -There are only 5 configurations using conventional columns-. Matlab took 0.07 CPU seconds in generating these 18 configurations (PC Pentium IV 2800 Mhz). In a 5 component mixture there are 203 feasible structurally different sequences (It was necessary to generate and check the 466 possible configurations). In a 6 component mixture there are 4373 feasible configurations (it was necessary to generate and check 15914 sequences). If duplication of separation tasks is allowed the number of alternatives is much grater. As an example [Table 2](#) shows the feasible sequences for mixtures of 3 and 4 components.

Although generating all the feasible sequences for mixtures of more than 6 or 7 components is not practical, checking feasibility by two previous rules continues to be very fast (and in general faster than prove feasibility/infeasibility by solving the MILP problem), which could be very useful in algorithms like genetic or evolutionary algorithms where, once a sequence is generated, the first step is checking its feasibility. We should note also that the logic inequalities in [Table 1](#) are still useful for MINLP or GDP models where these constraints must be included.

7. Heat Integration

Thermally coupled designs have important savings in energy and capital costs when compared with conventional column designs. However, as commented in the introduction [Rev et al](#)¹² showed that for ternary mixtures the Petlyuk configuration is usually not superior to energy integrated systems even in energy savings. The situation is much more complex in multi-component mixtures, again depending on the feed composition, available utilities, difference in volatilities etc; the optimal solution is expected to be an intermediate situation including thermal links as well as heat integrated columns.

From the point of view of separation tasks, in the generation of structurally different alternatives we are only interested if a heat exchanger appears associated to a product stream (remember that the presence of a heat exchanger associated to an internal state does not modify the sequence of separation tasks), but it is not important if that particular heat exchanger was a condenser or a reboiler; i.e. In [Figure 6](#) is shown that the heat exchanger associated with state B is able to be a condenser or a reboiler). In heat integrated sequences the heat is exchanged between a reboiler and a condenser, so in order to identify the possibilities for heat exchange, we must identify if in a given configuration the heat exchangers are reboilers or condensers. This can be simply done by adding the following rule (logical expression):

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

$$\begin{aligned} Y_t \wedge W_s &\Rightarrow WC_s & t \in RECT_s \\ Y_t \wedge W_s &\Rightarrow WR_s & t \in STRIP_s \end{aligned} \quad (9)$$

where WC and WR and boolean variables associated to condensers and reboilers respectively. wc and wr are their corresponding binary variables.

It is convenient to complete the pervious rule adding that:

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

$$\neg W_s \Rightarrow \neg WC_s \wedge \neg WR_s \quad s \in STATES \quad (10)$$

It is important to note that if the problem is solved as an MI(N)LP or GDP the variables wc and wr do not need to be declared as binary and they can be considered as continuous with values between 0 and 1. Previous equations (9,10) force wc and wr to take integer values as far as y and w are integer. Therefore variables wr and wc do not increase the combinatorial complexity of the problem.

To explicitly determine which are the matches between condenser and reboilers we introduce the Boolean variable $ZE_{s,ss}$ that takes the value True if there is heat integration between the condenser associated to state s and the reboiler associated to state ss . Relationships between ZE and WC or WR are the following:

$$ZE_{s,ss} \Rightarrow WC_s \wedge WR_{ss} \quad s, ss \in STATES; \quad s \neq ss \quad (11)$$

The condenser of a column can exchange heat with the reboiler of another column or vice-versa but not both simultaneously. This constrain is not strictly needed but reduces considerably the number of alternatives. In order to simplify the solution of the set of logical expressions or eventually the MI(N)LP problem, we can add that relationship explicitly:

$$ZE_{s,ss} \vee ZE_{ss,s} \vee K \quad s, ss \in STATES \quad (12)$$

where again, K is a dummy boolean variable that means “do not choose any of the previous options”.

Due to safety, start-up and controllability operational constraints are usually added. The most frequent are: 1. Some matches are forbidden due to safety reasons, which can be accomplished simple by fixing to False the variable associated with those matches; 2 A given condenser (or reboiler) is constrained to exchange heat with a maximum number of reboilers (condensers) –usually one; 3 In a column either the reboiler or the condenser can be integrated, but not both. All these relationships can easily be converted in algebraic expressions and added to the model if desired.

8. Mathematical model

In this section we propose a disjunctive formulation for determining the optimal sequence for the separation of an N component mixture in their pure constituents. The basis for modeling these systems were presented by Caballero and Grossmann²² but for the sake of rigor and because that model did not include aspects like heat integration, which produces significant modifications, we have decided to include the complete description. The model has the following features:

1. The model allows designing systems with or without heat integration. It allows controlling the complexity of the heat integration through simple logical rules, including forbidden matches, multiple integration of a reboiler or condenser etc. Double-effect columns are not considered. Different utilities at different prices and different temperature levels can be considered.

2. The model allows controlling the degree of thermal coupling. Without any extra constraint, it allows designing systems from conventional columns to fully thermally coupled systems with only two heat exchangers and the maximum number of column sections ($N(N-1)$). However, in order to reduce the complexity of the resulting structure it is possible to consider almost any particular case. Some cases of interest are:
 - a. Fully thermally coupled systems. This can be accomplished by simple fixing all the Boolean (binary) variables associated with intermediate heat exchangers to False (zero).
 - b. Systems with the minimum number of column sections. This can be accomplished by avoiding that any internal state be produced by more than one contribution –see logical rule number 2, or simply enforcing the terms in the left of [equation \(1\)](#) as equality. Note that although the minimum energy consumption is only guaranteed for the FTC configuration with the maximum number of column sections, usually a configuration with the minimum number of column sections has similar performance. Besides, all the problems related to internal states are avoided.
 - c. Sequences with only heat exchangers associated to final products. These structures are, from the point of view of the sequence of separation tasks, equivalent to sequences with conventional columns.
 - d. Although we previously mentioned that we would try to avoid structures with duplication of keys, it is possible to allow those structures by simple relaxing rule 2 and letting a state to be formed by more than two contributions.
3. Special structures like the Kaibel arrangement are not considered.
4. Integration of columns in a single column with internal walls is not considered. However, the best (or a set of the more promising configurations) can be used as starting point for generating all the thermodynamically equivalent configurations where columns with internal walls can be included.
5. Thermodynamically equivalent configurations are not explicitly considered. A procedure for generating all the thermodynamically equivalent configurations from a given sequence of separation tasks and extract the best one was previously presented by [Caballero and Grossmann²⁸](#), [Agrawal and Fidkowski²⁹](#), [Agrawal³⁰](#). Note however, that except in the case of columns with internal walls, the different arrangements in thermodynamically equivalent configurations have small differences in the total cost.
6. Configurations in which the thermal links are changed by direct liquid or vapor connections in order to favor controllability or other similar modifications are not considered, see the works by [Agrawal and Fidkowski¹⁷](#) or [Agrawal³¹](#), although they could be easily implemented. The reason is that those alternatives try to improve controllability usually with a marginal worsening of the cost or energy consumption. Including all these alternatives would produce a large number of very similar solutions from a structural point of view –same sequence of separation tasks-. Since we are dealing with the preliminary design, it is better (and computational more efficient) to determine the more promising alternatives and then perform a detailed study of them.
7. The model is based on the Underwood-Fenske-Gilliland equations^[32]. Given the disjunctive formulation of the problem other models (aggregated³³, Modular

framework³⁴, or rigorous tray by tray calculations³⁵ could be readily implemented, although the difficulty in the solution could increase.

According to the superstructure of Figure 6, a given state can produce a separation tasks among a set of candidates. Therefore, as mentioned in the superstructure generation section, we can group all those separation tasks and model the system in terms of states: “If a given state exists, it produces a pseudo-column”. Note that until this point we have considered specific separation tasks, and defined a Boolean variable for each of them, but not for the states. It is convenient to define a Boolean variable associated to the states. This variable (Z_s) takes the value of True if a given state (and then a pseudo-column) exists and False otherwise.

It is worth mentioning that the set of logical rules previously presented in terms of separation tasks could 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*”. Adding the relationship between tasks and states is straightforward:

$$Y_t \Rightarrow Z_s; \quad t \in OUT_ST_s \quad (13)$$

$$Z_s \Rightarrow \bigvee_{t \in OUT_ST_s} Y_t \quad (14)$$

Equation (13) could be read as: “if the task t , that belongs to the set of task produced by the state s , exists then the state s must exist”. And equation 14a as: “If the state s exists at least one of the tasks that the state s is able to produce must exist”

We should note that if the problem is solved as an MI(N)LP it is only necessary declare as binary either y_t or z_s , but not both. Whether y_t is declared as binary z_s can be declared as continuous between zero and one and vice-versa. It is also worth noting that, even though the number of tasks is larger than the number of states, numerically the behavior of the model is similar declaring either the tasks or the states as binary. Curiously in the few cases in which we found differences, declaring the tasks as binary produced lower computing times.

With the previous equations the set of logical relationships is complete. For the rest of the model we define the following index sets,

COMP = { i | i is a component in the initial mixture }

Note that components (set COMP) and products (set PROD) are not the same. In a mixture where there are M components and we separate N of these components, the set COMP include all the M components of the original mixture. However, the set PROD only include the N final streams.

FEED = { State s is the feed to the system }

TOP = { States s in the upper line of the superstructure } (TOP \subseteq STATES)

DOWN = { States s in the lower line of the superstructure } (DOWN \subseteq STATES)

COLD _{s} = { State ss that are connected to state s through a rectifying section }

COLB _{s} = { State ss that are connected to state s through a stripping section }

COLT _{s} = COLD _{s} \cup COLB _{s}

FP _{s} { State ss can produce a pure product (without heat exchanger) together with state s }

$LK_T = \{\text{Light key component in a given separation task}\}$

$HK_T = \{\text{Heavy key component in a given separation task}\}$

$RUD = \{\text{Underwood roots}\}$

This set includes the possible Underwood roots.

$RUA_s = \{\text{Possible active Underwood roots in a pseudo-column (state) } s\}$

The variables in the problem are:

$F_s = \text{Molar feed flow rate to pseudo-column (state) } s.$

$D_s = \text{Net distillate flow rate of pseudo-column } s.$

$B_s = \text{Net bottoms flow rate of pseudo-column } s.$

$FI_{s,i} = \text{Molar flow rate of component } i \text{ in the feed stream of pseudo-column } s.$

$DI_{s,i} = \text{Molar flow rate of component } i \text{ in the distillate of pseudo-column } s.$

$BI_{s,i} = \text{Molar flow rate of component } i \text{ in the bottoms of pseudo-column } s.$

$V1_s = \text{Molar vapor flow rate in the rectifying section of pseudo-column } s.$

$V2_s = \text{Molar vapor flow rate in the stripping section of pseudo-column } s.$

$L1_s = \text{Molar liquid flow rate in the rectifying section of pseudo-column } s.$

$L2_s = \text{Molar liquid flow rate in the stripping section of pseudo-column } s.$

$\phi_{s,r} = \text{Possible active Underwood root (} r \text{) in section } s.$

$Ar_s = \text{Section of the pseudo-column } s.$

$Dia_s = \text{Diameter of pseudo-column } s.$

$P_s = \text{Pressure in pseudo-column } s.$

$Ntrays_s = \text{Number of trays in column state } s.$

$\rho_{v,s} = \text{Vapor density (used in diameter estimation).}$

$T_s = \text{Temperature of state } s$

$Qreb_s = \text{Heat load of reboiler associated to state } s.$

$Qcond_s = \text{Heat load of condenser associated to state } s.$

$Qheat_s = \text{Heat provided to reboiler } s \text{ from a hot utility}$

$Qcools = \text{Heat removed from condenser } s \text{ by a cold utility}$

The necessary data are:

$\lambda_i = \text{Heat of vaporization on component } i \text{ calculated at the pressure of the system.}$

$i = \text{interest rate}$

$PL = \text{Plant life (years)}$

Ff = total molar fed to the system.

zf_i = molar fraction of component i in the feed.

α_i = Relative volatility of component i respect to the heaviest one.

ρ = Liquid density. (Assumed to be constant).

CH = cost of heat utilities.

CC = cost of cold utilities.

γ = Recovery of keys in a given separation

U = Overall heat transfer coefficient.

EMAT = Exchanger minimum approach temperature.

A disjunctive representation of the model is as follows:

$$\min : TAC \quad (15)$$

Where TAC is the total annualized cost, this includes the cost of utilities and the investment and installation costs:

$$TAC = \sum_{s \in STATES} (CH Q_{heat_s} + CC Q_{cool_s}) + \frac{i(i+1)^{PL}}{(i+1)^{PL} - 1} \left[\sum_{s \in COL} (Cost Vessel_s + Cost Internals_s) + \sum_{s \in STATES} (Cost Heat Exchanger_s) \right] \quad (16)$$

$$\left[\begin{array}{l} \mathbf{Z}_s \\ \left. \begin{array}{l} FI_{s,i} = DI_{s,i} + BI_{s,i} \\ D_s = V1_s - L1_s \\ B_s = L2_s - V2_s \end{array} \right\} \text{mass balance} \\ \left. \begin{array}{l} FI_{s,i} = \gamma DI_{s,i} \quad i \in LK_t ; s \in OUT_ST_s \\ FI_{s,i} = (1-\gamma) DI_{s,i} \quad i \in HK_t ; s \in OUT_ST_s \end{array} \right\} \text{Sharp Split} \\ \left. \begin{array}{l} \sum_i \frac{\alpha_i FI_{s,i}}{\alpha_i - \Phi_{s,r}} - (V1_s - V2_s) = 0 \\ \sum_i \frac{\alpha_i DI_{s,i}}{\alpha_i - \Phi_{s,r}} - V1_s \leq 0 \\ - \sum_i \frac{\alpha_i BI_{s,i}}{\alpha_i - \Phi_{s,r}} - V2_s \leq 0 \end{array} \right\} \begin{array}{l} i \in COMP \\ r \in RUA_s \\ \text{Underwood eqs.} \end{array} \\ Ar_s = f(\rho_L, \rho_V, V1_s, V2_s, \sigma) \\ \text{Column Capital Cost} = f(D, P, N_{trays}) \\ T_s = f(P, FI_{s,i}) \end{array} \right] \bigvee \left[\begin{array}{l} -\mathbf{Z}_s \\ V1_s = \sum_{ss \in COLD_{ss,s}} V1_{ss} ; s \neq FEED \quad ss \notin DOWN \\ L1_s = \sum_{ss \in COLD_{ss,s}} L1_{ss} ; s \neq FEED \quad ss \notin DOWN \\ V2_s = \sum_{ss \in COLB_{ss,s}} V2_{ss} ; s \neq FEED \quad ss \notin TOP \\ L2_s = \sum_{ss \in COLB_{ss,s}} L2_{ss} ; s \neq FEED \quad ss \notin TOP \\ DI_{s,i} = \sum_{ss \in COLD_{ss,s}} DI_{ss,i} \quad s \neq FEED \quad ss \notin DOWN \\ BI_{s,i} = \sum_{ss \in COLB_{ss,s}} BI_{ss,i} \quad s \neq FEED \quad ss \notin TOP \\ V2_{ss} = 0 \quad ss \in TOP \\ L2_{ss} = 0 \quad ss \in TOP \\ V1_{ss} = 0 \quad ss \in DOWN \\ L1_{ss} = 0 \quad ss \in DOWN \end{array} \right] \quad (17)$$

$$\left. \begin{aligned} F_s &= \sum_{i \in COMP} F_{s,i} \\ D_s &= \sum_{i \in COMP} D_{s,i} \\ B_s &= \sum_{i \in COMP} B_{s,i} \end{aligned} \right\} \forall s \in COL \quad (18)$$

The left term in the [disjunction \(17\)](#) includes mass balances, cost and temperature calculations and the Underwood equations. The right side –state does not exist- enforces that liquid and vapor internal flows behave like simple flow bypasses.

Underwood equations deserve a special remark. Note that the second and the third Underwood equations are written as inequalities. The reason is that, due to thermal coupling, we cannot guarantee that all columns are operate at their minimum vapor flow (or 1.2 times the minimum). i.e. in [Figure 1c](#) or [Figure 2](#) the vapor flow in the stripping section of task A/B must be the same that the vapor flow in the rectifying section of task B/C. Therefore, at most only one of these pseudo-columns can be designed to operate at 1.2 times its minimum reflux ratio.

The column area (Ar) is calculated using the Fair correlation³⁶. The capital costs are estimated using the correlations for vessels and internals as presented in [Turton et al³⁷](#). To estimate the actual number of trays and the actual reflux rate we can use the following suggestion by [Douglas³⁸](#) for preliminary designs; $N_{trays} = 2 N_{min_trays}$, and reflux rate 1.2 times the minimum. The minimum number of trays was calculated using the Fenske equation³². All physical properties were obtained from [Poling et al⁴⁰](#).

Note that according to the previous definitions all properties are calculated for a state 's'. If a state s produces a pseudo-column, it means that we are calculating all the properties at the feed conditions. However, this is not a problem. For example if the state ABC produces the separation AB/C and we want to know the temperature of distillate we only have to check the temperature of state AB.

[Equation \(18\)](#) simply relates the individual component molar flows with the total molar flows. These equations do no depend on the existence of a state.

If a heat exchanger associated to a state exists, the feed to the pseudo-column that the state produce will be liquid at their bubble point (this can be easily modified changing the left term of the next disjunction). If the heat exchanger does not exist, we have to introduce a mass balance between columns in order to deal with liquid and vapor transfers. Note that in this case it is not important if the heat exchanger is a condenser or a reboiler. But if for some reason we want to differentiate between condensers and reboilers we can use the variables WR or WC, instead of W.

$$\left[\begin{array}{c} W_s \\ V1_s - V2_s = 0 \end{array} \right] \forall \left[\begin{array}{c} V1_s + \sum_{ss \in COLB_S} V2_{ss} - V2_s - \sum_{ss \in COLD_S} V1_{ss} = 0 \\ L1_s + \sum_{ss \in COLB_S} L2_{ss} - L2_s - \sum_{ss \in COLD_S} L1_{ss} = 0 \end{array} \right] \forall s \in COL \quad (19)$$

$$FI_{s,i} = \left. \begin{aligned} & \sum_{ss \in COLDS} DI_{ss,i} + \sum_{ss \in COLBS} BI_{ss,i} \\ & \forall i \in COMP \\ & \forall s \in COL / s \notin FEED \end{aligned} \right\} \quad (20)$$

Equation (20) is a mass balance between columns, similar to the one in equation (19). However, F, D and B are net flows (differences between liquid and vapor or vice-versa), and their values are the same independently if a heat exchanger exists or not and can be taken out of the disjunction.

If a heat exchanger exists then we have to calculate the heat load as well as the costs:

$$\left[\begin{array}{l} \mathbf{WC}_s \\ Q_{cond_s} D_{ss} - V1_{ss} \sum_{i \in COMP} D_{ss,i} \lambda_i = 0 \quad \forall ss \in COLDT_s \\ Cost_{condenser_s} = f(U, Ar, \Delta T_{lm}) \end{array} \right] \bigvee \left[\begin{array}{l} \neg \mathbf{WC}_s \\ Q_{cond_s} = 0 \\ Cost_{condenser_s} = 0 \end{array} \right] \quad \forall s \in STATES \quad (21)$$

$$\left[\begin{array}{l} \mathbf{WR}_s \\ Q_{reb_s} B_{ss} - V2_{ss} \sum_{i \in COMP} B_{ss,i} \lambda_i = 0 \quad \forall ss \in COLBT_s \\ Cost_{reboiler_s} = f(U, Ar, \Delta T_{lm}) \end{array} \right] \bigvee \left[\begin{array}{l} \neg \mathbf{WR}_s \\ Q_{reb_s} = 0 \\ Cost_{reboiler_s} = 0 \end{array} \right] \quad \forall s \in STATES \quad (22)$$

When a final stream (product) is formed by two contributions without heat exchanger –this is the case of a side product stream- we must include a mass balance in order to assure that the liquid (vapor) transfer between two consecutive sections is correct.

$$\neg \mathbf{W}_s \Rightarrow L2_s - L1_{ss} = Ff_{z_i} \quad ss \in FP_s \quad \forall s \in PROD \quad (23)$$

In the previous implication it has been assumed that products are liquid streams. In the case that those heat exchangers exist the liquid and vapor flows of consecutive columns are not related.

In the preliminary design of thermally coupled distillation systems it is usually assumed that the pressure in the entire system is the same (or that there is only a slight difference of pressures in order to assure the vapor flow transfer between columns). However, in heat integrated distillation systems the pressure in each column is set to accommodate the temperature that makes feasible the heat exchange between condensers and reboilers. In mixed systems we must force the tasks with a thermal link joining them, to be at the same nominal pressure. In other words, the presence of a heat exchanger associated to any intermediate state is a point for a pressure change. Therefore, we must explicitly add that if a heat exchanger does not appear, the pressure should propagate through that state, even in the case in which that state (pseudo-column) neither exists.

$$\neg \mathbf{W}_s \Rightarrow P_s - P_{ss} = 0 ; ss \in COLT_s \quad \forall s \in COL \quad (24)$$

Equation (23) can be included in the right term of equation (19), but it has been written separately for clarity.

Besides, if there is the possibility for heat integration we must assure that the exchange is feasible by defining an exchange minimum approach temperature (EMAT) and establishing the corresponding energy balances.

$$\left[\begin{array}{c} \mathbf{ZE}_{s,ss} \\ T_s \geq T_{ss} + EMAT \end{array} \right] \bigvee \left[\begin{array}{c} \neg \mathbf{ZE}_{s,ss} \\ Qex_{s,ss} = 0 \end{array} \right] \quad s, ss \in STATES; s \neq ss \quad (25)$$

$$\begin{aligned} \sum_{ss \neq s} Qex_{s,ss} + Qcool_s &= Qcond_s ; s \in STATES \\ \sum_{s \neq ss} Qex_{s,ss} + Qheat_{ss} &= Qreb_{ss} ; ss \in STATES \end{aligned} \quad (26)$$

In equations (25) and (26) 's' implicitly references to a condenser and ss to a reboiler. As commented previously this is explicitly done by logical relationships.

Finally, we must include all the logical relationships previously mentioned.

9. Solution algorithm.

The disjunctive model shown in previous section, given by equations (15-26) and the logic constraints (2-14), was reformulated as a Mixed Integer Non Linear Programming Problem (MINLP) using a big M formulation, and written in GAMS⁴¹. Then the problem can be solved using any standard solver. However, the non-convexities and the large number of local solutions in this kind of problems often leads to suboptimal solutions.

However, based on the following observations, it is possible develop an algorithm that allows finding, if not the global optimum, a near optimal solution. 1. Problems with a fixed topology (fixed binary variables for separation states) produce the optimal solution and rarely get trapped in local solutions. 2. Given a sequence of states (or separation tasks), a simple branch and bound based solver -like the SBB⁴² included in GAMS - usually finds the optimal solution for the heat integrated sequence. Although a branch and bound algorithm for these kind of problems is slower than a decomposition method like Outer Approximation⁴³, for this particular case the branch and bound method tends to get much better results. 3. When using conventional columns usually the best sequence with no heat integration is also the best when the heat integration is considered. , although there are some counterexamples. In thermally coupled distillation the best sequence with no heat integration is also among the best when heat integrated is considered although the correlation is not so strong as in the case of conventional columns it is a good starting point.

The steps of the proposed algorithm are as follows

1. Solve a first MINLP using DICOPT⁴⁴ fixing the values of the variables related to the heat integration to False. This is the best non heat integrated solution and is likely to be among the bests heat integrated sequences.
2. Fix the sequence of states obtained in step 1 and solve the heat integration problem using SBB, which uses a branch and bound strategy.
3. Generate an MILP master problem⁴⁴ from the outer approximation of problem in step 2. The idea is not only transfer to the master information of the structure of separation tasks but also from the heat integration. A binary cut including only variables related to separation tasks was also added to avoid repeated solutions.

4. From the solution of the MILP obtained in step 3, which is obtained with CPLEX, fix to the values predicted by the master only the binaries related to separation tasks and let the binaries related to heat integration free.
5. Return to step 2 and continue until there is no improvement in the solution of the MINLP in step 2.

While, we cannot guarantee optimality, numerical experiments have shown that the proposed algorithm usually finds good solutions. It is of course also possible to force the algorithm to continue performing iterations in order to continue the search for the optimal solution. However, even in the case in which the algorithm did not find the optimal solution with the stopping criteria mentioned above, usually no more than 5-6 major iterations are needed to obtain it (see Table 7).

10. Examples

Example 1.

The first example consists of the separation of a 5 lineal hydrocarbons, from n-hexane to n-decane. All specific data for this example is shown in Table 3. In order to obtain realistic configurations some constraints have been added to the problem, only configurations with minimum number of column sections are considered. In other words, a given state can be produced at most by one contribution (as was commented in the 'structural considerations section'). In order to avoid controllability problems, we have constrained ourselves to systems in which a given condenser (reboiler) can exchange heat with a single reboiler (condenser). And to systems in which in a column either the reboiler or the condenser can be heat integrated, but not both.

The best solution obtained is shown in Figure 14, with a TAC \$920,000/year. The algorithm starts solving an MINLP in which the binary variables related with heat exchange are fixed to false. This allows determining an initial sequence of tasks and produce the best non heat integrated sequence (TAC \$1221000/year). The best heat integrated sequence for this initial solution (TAC \$1199000/year) is around 30 % worse than the best obtained solution. If we continue performing iterations we observe that there is an important number of solutions with differences around 6%. These small differences explain the difficulties in finding the global optimum, or even a good solution, using direct MINLP techniques, because it is not uncommon to find groups of solutions with very similar costs. Table 4 shows the main steps in the algorithm and some statistical data about the problem.

It is of interest to remark that in this first example heat exchangers only appear associated to a heat integration scheme (except, of course, those needed for provide heat and remove heat to the entire system: condenser in state A and reboiler in state E). In the rest of the system all connections are made by thermal couplings.

If we repeat example 1 but now keeping the pressure constant the best obtained configuration is slightly modified (state AB appears in the solution and state CD is removed). See Figure 15. The TAC increases to \$1,051,000/year, 14.2% higher. Possibilities for heat integration are reduced, but the optimal configuration continues including heat integration. However the most important characteristic is that an internal heat exchanger, which is not involved in the heat integration, appears in the optimal configuration. Removing that heat exchanger and introducing

a thermal link instead, is likely to produce some decrease in the total energy consumption. However, the thermal links also produce an increase in the total vapor flow through the entire system increasing the diameters of the columns. Therefore, although thermal links are favorable from the energy point of view, and even though the energy is the dominant factor, the increase in the investment costs due to large vapor flows in the entire system produces that an optimal solution that includes some internal heat exchangers.

If we consider the problem without heat integration, the best obtained solution is 32% more expensive than the best heat integrated solution (TAC \$1,221,000/year). The best obtained solution is a fully thermally coupled configuration, but the configuration of separation tasks is completely different of the previous cases. See [Figure 16](#).

Example 2. Mixture of alcohols

In this example consider the separation of 5 alcohols. All data for this example is shown in [Table 5](#), the differences in relative volatility of the compounds is lower than in previous case. Therefore in this example it is expected that, at least from the point of view of energy, the optimal sequence tends to be a fully thermally coupled configuration but this will depend on the relative importance of the investment costs. As the importance of the investment cost increases the energy benefits of thermal links are compensated by the extra vapour flowing through the system.

When heat integration is allowed the configuration showed in [Figure 17](#) is obtained. This configuration includes the integration between two reboilers and two condensers. Again, as happened in example 1, an intermediate heat exchanger appears. The reason is the same as in the previous case: reducing the vapour flow through the system and therefore reduce the column diameters. The TAC is \$1,180,000/year.

If we keep the pressure constant, differences in volatilities prevent heat integration, the TAC increases up to \$1,662,000/year. The sequence of tasks is only slightly modified respect to the heat integrated sequence, but in this case is almost a fully thermally coupled configuration. See [Figure 18](#).

Example 3. Separation of a mixture of Aromatics

In this example the objective is to separate a mixture of Benzene, Toluene, Ethylbenzene, styrene and α -methylstyrene. Data are showed in [Table 6](#).

The total annualized cost was \$1,267,000/year. In this example the differences in volatilities between benzene and toluene and the rest of the compounds is relatively large. The optimal solution follows the well known heuristic "perform first the easy separations", see [Figure 19](#). However, toluene is not sharply separated in a single column (or task) and appears in three separations; therefore some care must be taken when heuristics are applied to systems with thermal links.

If heat integration is not allowed the sequence of tasks is similar, but the degree of thermal coupling increases, see [Figure 20](#). Again some heat exchangers associated to internal states appear. Note that if only the energy costs are considered, all these internal heat exchangers disappear from the optimal configuration. The total annual cost increases up to \$1,501,000/year

Table 7 shows a summary of some data of interest in the proposed algorithm for all the previous examples.

11. Conclusions and final remarks

In this paper we have presented a superstructure approach for synthesizing heat integrated thermally coupled distillation sequences. The superstructure is based on a state-task approach instead of an equipment based system, at both levels mass and heat exchange. Calculation of all the internal parameters of the columns like flows, temperatures, is made based on considering a task like a pseudo-column formed by a stripping and a rectifying section, by similarity with conventional columns. However, no assumption is made about the final arrangement of those sections in actual columns. In fact the two sections of a pseudo-column do not necessarily belong to the same final actual column.

The discussion about structural characteristics of the sequences of columns with thermal links showed that it is still an open field of research. Situations like structures with reduced number of column sections like the '*Kaibel column*', structures with duplication of key components in separation tasks, or structures with duplication of separation tasks are in general outperformed by some thermally coupled configuration, but there are situations in where these alternatives could be of interest. For example the Kaibel column reduces the investment. However, it tends to increase the energy consumption, but in situations where some of the products are required with not too much purity, it could be an interesting alternative. Structures with duplication of key components could be of interest in some heat integrated systems.

A set of logical rules, expressed in 'colloquial language' and formally translated to Boolean and algebraic expressions in terms of Boolean and binary variables, for generating feasible alternatives was introduced. An important characteristic of these logical rules is that they have a large degree of flexibility including almost all the special cases and allowing to the designer easily to add any extra constraint. Besides, an alternative procedure to generate alternatives (even at hand) or simply to check if a given alternative is feasible was presented.

The model was formulated as a generalized disjunctive programming problem (GDP) and solved as a modified MINLP. Inherent to these kinds of systems, especially when heat integration is considered, is the large number of possible local solutions with very similar performance. The algorithm solves the problem by searching at two levels: structural level and heat integration level (for a fixed structure) using an MINLP branch and bound based search. The algorithm has proved to be very robust and reliable. However, more research is needed in order to reduce CPU calculation times for mixtures of more than 5 components.

Although the model was formulated using shortcut equations, the disjunctive structure of the formulation makes migration to any other kind of models (even rigorous tray by tray calculations) straightforward.

In general the optimal sequence is a complex structure that simultaneously includes thermal links and heat integration. Although, thermal links tend to reduce the energy consumption, they also increases the vapour flowing through the system and therefore the size of equipment. This is the reason why it is not uncommon that some intermediate heat exchangers appear in the optimal configuration breaking some of the thermal links.

Finally, an interesting observation is that, in general, the sequence of separation tasks is similar in heat integrated systems with thermal links and in systems without heat integration. However,

this observation, cannot be considered as a design rule (example 1 is a clear counter-example). Nevertheless, numerical tests showed that, in most cases, the no-heat integrated sequence with thermal links is also a good solution when the heat integration is considered.

Acknowledgements

The authors gratefully acknowledge financial support from Spanish "Ministerio de Ciencia y Tecnología" under projects PPQ2002-01734 and CTQ2005-05456/PPQ

References

- ¹ Smith, R.; Linnhoff, B. The Design of Separators in the Context of Overall Processes. *Chem. Eng. Res. Des.* **1988**, 66, May, 195.
- ² Mizsey P. and Z. Fonyo, A Predictor Based Bounding Strategy for Synthesizing Energy Integrated Total Flowsheet. *Comput. chem. Engng.* **1990**. 14(11) 1303-1310.
- ³ Peltyuk, F.B.; Platonov, V.M.; Slavinskii, D.M. Thermodynamically Optimal Method of Separating Multicomponent Mixtures. *International Chemical Engineering*, **1965**. 5, 555.
- ⁴ Rudd, H. Thermal Coupling for Energy Efficiency. *Supplement to the Chem. Eng.* S14. **1992**.
- ⁵ Triantafyllou, C.; Smith, R. The Design and Optimisation of Fully Thermally Coupled Distillation Columns. *Trans. Inst. Chem. Eng.* **1992**, 70, 118.
- ⁶ Fidkowsky, Z.T.; Agrawal, R.; Multicomponent Thermally Coupled Systems of Distillation Columns at Minimum Reflux. *AIChE Journal*. **2001**. 47(12), 2713-2724.
- ⁷ Halvorsen, I.J.; Skogestad, S.; Minimum Energy Consumption in Multicomponent Distillation. 1. Vmin Diagram for a Two Product Column. *Ind. Eng. Chem. Res.* **2003**, 42, 596-604.
- ⁸ Halvorsen, I.J.; Skogestad, S.; Minimum Energy Consumption in Multicomponent Distillation. 2. Three-Product Petlyuk Arrangements. *Ind. Eng. Chem. Res.* **2003**, 42, 605-615.
- ⁹ Halvorsen, I.J.; Skogestad, S.; Minimum Energy Consumption in Multicomponent Distillation. 3. More than Three Products and Generalized Peltyuk Arrangements. *Ind. Eng. Chem. Res.* **2003**, 42, 616-629.
- ¹⁰ Agrawal, R; Synthesis of Distillation Column Configurations for a Multicomponent Separation. *Ind. Eng. Chem. Res.* **1996**, 35, 1059-1071.
- ¹¹ Caballero, J.A.; Grossmann, I.E.; Generalized Disjunctive Programming Model for the Optimal Synthesis of Thermally Linked Distillation Columns. *Ind. Eng. Chem. Res.* **2001**, 40(10), 2260-2274.
- ¹² Rév, E. Emtir, M.; Sztikai, Z.; Mizsey, P.; Fonyó, Z.; Energy Savings of Integrated Distillation Systems. *Comput. Chem. Eng.* **2001**, 25, 119-140.
- ¹³ Kaibel, G.; Distillation Columns with Vertical Partitions. *Chem. Eng. Technol.* **1987**, 10, 92-98.
- ¹⁴ Rong, B.G.; Kraslawski, A.; Turunen, I.; Synthesis of Functionally Distinct Thermally Coupled Configurations for Quaternary Distillations. *Ind. Eng. Chem. Res.* **2003**, 42, 1204-1214.

- ¹⁵ Rong, B.G.; Kraslawski, A.; Turunen, I.; Systematic Synthesis of Functionally Distinct New Distillation Systems for Five-Component Separations. In Computer Aided Chemical Engineering 20A. European Symposium on Computer Aided Process Engineering 15. Puigjaner, L.; Espuña, A. Editors. **2005**, 823-828.
- ¹⁶ Grossmann, I.E.; Aguirre, P.A.; Bartfeld, M. Optimal Synthesis of Complex Distillation Columns Using Rigorous Models. . In Computer Aided Chemical Engineering 20A. European Symposium on Computer Aided Process Engineering 14. Barbosa-Pavoa, A.; Matos, H. Editors. **2004**, 53-74.
- ¹⁷ Agrawal, R.; Fidkowski, Z.T.; New Thermally Coupled Schemes for Ternary Distillation. *AIChE Journal*. **1999**, 45(3), 485-496.
- ¹⁸ Agrawal, R. Thermally Coupled Distillation with Reduced Number of Intercolumn Vapor Transfers. *AIChE Journal*. **2000**, 46(11), 2198-2210.
- ¹⁹ Rong, B.G.; Kraslawski, A.; Optimal Design of Distillation Flowsheets with Lower Number of Thermal Couplings for Multicomponent Separations. *Ind. Eng. Chem. Res.* **2002**, 41, 5716-5726.
- ²⁰ Yeomans, H; Grossmann, I.E.; A Systematic Modeling Framework of Superstructure Optimization in Process Synthesis. *Comput. Chem. Engng.* **1999**, 23, 709.
- ²¹ Sargent, R.W.H.; Gaminibandara, K.; Approaches to Chemical Process Synthesis. *In Advances in Chemical Engineering*. **1976**. New York Academic Press.
- ²² Caballero, J.A.; Grossmann, I.E.; Design of Distillation Sequences: from conventional to fully thermally coupled distillation systems. *Comput. Chem. Engng.* **2004**, 28, 2307-2329.
- ²³ Balas E.; Jeroslow, R.; Canonical Cuts on the Unit Hypercube. *SIAM J. Appl. Math.* **1972**, 23, 61-79.
- ²⁴ Raman, R.; Grossmann, I.E.; Relation Between MILP Modeling and Logical Inference for Chemical Process Synthesis. *Comput. Chem. Engng.* **1991**, 15(2), 73-84.
- ²⁵ Sahinidis, N. BARON: A General Purpose Global Optimization Software Package. *Journal of Global Optimization*, **1996** 8 (2), 201 -205.
- ²⁶ ILOG OPL Studio 3.5: The User's Manual, ILOG Inc., **2001**.
- ²⁷ MATLAB The language of technical computing. Mathworks **2004**.
- ²⁸ Caballero, J.A.; Grossmann, I.E.; Thermodynamically Equivalent Configurations for Thermally Coupled Distillation. *AIChE Journal*. **2003**, 49(11), 2864-2884,
- ²⁹ Agrawal R.; Fidkowski, Z.T.; More Operable Arrangements of Fully Thermally Coupled Distillation Columns. *AIChE Journal*. **1998**. 44, 2565.
- ³⁰ Agrawal, R.; A Method to Draw Fully Thermally Coupled Distillation Column Configurations for Multicomponent Distillation. *Transaction of IChemE*, **2000**. 78, 454-464.
- ³¹ Agrawal, R.; Thermally Coupled Distillation with Reduced Number of Intercolumn Vapor transfers. *AIChE Journal*. **2000**. 46(11), 2211.
- ³² King, J. Separation Processes. Chemical Engineering Series. Mc GrawHill. **1980**

- ³³ Caballero, J.A.; Grossmann, I.E.; Aggregated Models for Integrated Distillation Systems. *Ind. Eng. Chem. Res.* **1999**. 38(6), 2330.
- ³⁴ Papalexandri, K.P.; Pistikopoulos, E.K.; Generalized Modular Representation Framework for Process Synthesis. *AIChE Journal*. **1996**. 42, 1010.
- ³⁵ Barttfeld, M., P.A. Aguirre and I.E. Grossmann. A Decomposition Method for Synthesizing Complex Column Configurations Using Tray-by-Tray GDP Models. *Computers and Chemical Engineering*, 28, 2165–2188 (2004).
- ³⁶ Stichmair J.G.; Fair, J.R.; Distillation: Principles and Practice. Wiley-Liss. **1998**.
- ³⁷ Turton, R.; Bailie, R.C.; Whiting, W.B.; Shaeiwitz, J.A. Analysis Synthesis and Design of Chemical Processes. **1998**. McGraw-Hill.
- ³⁸ Douglas, J.M.; Conceptual Design of Chemical Processes. McGraw-Hill Chemical Engineering Series. **1988**.
- ⁴⁰ Poling, B.E.; Prausnitz, J.M.; O'Connell, J.P.; The Properties of gases and Liquids. (5th edition). New York McGraw Hill. **2000**.
- ⁴¹ Brooke, A.; Kendrick, D.; Meeraus, A.; Raman, R.; GAMS a user guide. Gams Development Corporation. **2004**.
- ⁴² Bussiek, M.R. Drud, A.S, In Gams Development Corporation. The Solver Manuals. SBB solver manual. Washington. **2003**.
- ⁴³ Duran, M.; Grossmann, I.E.; An Outer Approximation Algorithm for a Class of Mixed Integer Non-linear Programs. *Mathematical Programming*. **1986**. 36, 307-339.
- ⁴⁴ Viswanathan, J. and I.E. Grossmann, "A Combined Penalty Function and Outer Approximation Method for MINLP Optimization," *Computers and Chemical Engineering* **1990**. 14, 769.

Table1. Logical boolean expressions and their equivalent algebraic expression in terms of binary variables. (The number in brackets is the equation number in the text)

Boolean expression	Equivalent algebraic expression
$\bigvee_{t \in OUT_ST_s} Y_t \leq K ; s \in COL$ (2)	$\sum_{t \in OUT_ST_s} y_t \leq 1 ; s \in COL$
$\left. \begin{array}{l} \bigvee_{t \in RECT_s} Y_t \leq K \\ \bigvee_{t \in STRIP_s} Y_t \leq K \end{array} \right\} s \in STATES$ (3)	$\left. \begin{array}{l} \sum_{t \in RECT_s} y_t \leq 1 \\ \sum_{t \in STRIP_s} y_t \leq 1 \end{array} \right\} s \in STATES$
$\bigvee_{t \in (P_REC_s \cup P_STR_s)} Y_t ; s \in PROD$ (4)	$\sum_{t \in (P_REC_s \cup P_STR_s)} y_t \geq 1 ; s \in PROD$
$\left. \begin{array}{l} \neg \left(\bigvee_{t \in P_REC_s} Y_t \right) \Rightarrow W_s \\ \neg \left(\bigvee_{t \in P_STR_s} Y_t \right) \Rightarrow W_s \end{array} \right\} s \in PROD$ (5)	$\left. \begin{array}{l} \sum_{t \in P_REC_s} y_t + w_s \geq 1 \\ \sum_{t \in P_STR_s} y_t + w_s \geq 1 \end{array} \right\} i \in PROD$
$(Y_t \wedge Y_k) \Rightarrow \neg W_s \left\{ \begin{array}{l} t \in RECT_s \\ k \in STRIP_s \\ s \in STATES \end{array} \right.$ (6)	$1 - y_t + 1 - y_k + 1 - w_i \geq 1 \left\{ \begin{array}{l} t \in RECT_s \\ k \in STRIP_s \\ s \in STATES \end{array} \right.$
$\left. \begin{array}{l} Y_t \Rightarrow \bigvee_{k \in OUT_ST_s} Y_k ; t \in IN_ST_s \\ Y_t \Rightarrow \bigvee_{k \in IN_ST_s} Y_k ; t \in OUT_ST_s \end{array} \right\} s \in STATES$ (7)	$\left. \begin{array}{l} 1 - y_t + \sum_{k \in OUT_ST_s} y_k \geq 1 ; t \in IN_ST_s \\ 1 - y_t + \sum_{k \in IN_ST_s} y_k \geq 1 ; t \in OUT_ST_s \end{array} \right\} s \in STATES$
$W_s \Rightarrow \bigvee_{t \in IN_ST_s} Y_t ; s \in STATES$ (8)	$1 - w_s + \sum_{t \in IN_ST_s} y_t \geq 1 ; s \in STATES$
$\begin{array}{l} Y_t \wedge W_s \Rightarrow WC_s \quad t \in RECT_s \\ Y_t \wedge W_s \Rightarrow WR_s \quad t \in STRIP_s \end{array}$ (9)	$\begin{array}{l} 1 - y_t + 1 - w_s + wc_s \geq 1 \quad t \in RECT_s \\ 1 - y_t + 1 - w_s + wr_s \geq 1 \quad t \in STRIP_s \end{array}$
$\neg W_s \Rightarrow \neg WC_s \wedge \neg WR_s \quad s \in STATES$ (10)	$\left. \begin{array}{l} w_s - wc_s \geq 0 \\ w_s - wr_s \geq 0 \end{array} \right\} s \in STATES$
$ZE_{s,ss} \Rightarrow WC_s \wedge WR_{ss} \quad s, ss \in STATES ; s \neq ss$ (11)	$\left. \begin{array}{l} ze_{s,ss} \leq wc_s \\ ze_{s,ss} \leq wr_{ss} \end{array} \right\} s, ss \in STATES ; s \neq ss$
$ZE_{s,ss} \leq ZE_{ss,s} \leq K \quad s, ss \in STATES$ (12)	$ze_{s,ss} + ze_{ss,s} \leq 1 \quad s, ss \in STATES$
$Y_t \Rightarrow Z_s ; t \in OUT_ST_s$ (13)	$1 - y_t + z_s \geq 1 ; t \in OUT_ST_s$
$Z_s \Rightarrow \bigvee_{t \in OUT_ST_s} Y_t$ (14)	$1 - z_s + \sum_{t \in OUT_ST_s} y_t \geq 1$

Table 2. Different feasible structural sequences for 3 and 4 component mixtures.

<p><i>3 component mixtures: 3 different feasible structural sequences.</i></p> <p>ABC AB BC A B C ABC AB A B C ABC BC A B C</p>
<p><i>4 Component mixtures: 18 different feasible structural sequences.</i></p> <p>ABCD ABC BCD AB BC CD A B C D ABCD ABC BCD AB BC A B C D ABCD ABC BCD AB CD A B C D ABCD ABC BCD BC CD A B C D ABCD ABC AB BC CD A B C D ABCD BCD AB BC CD A B C D ABCD ABC BCD BC A B C D ABCD ABC AB BC A B C D ABCD ABC AB CD A B C D ABCD ABC BC CD A B C D ABCD BCD AB BC A B C D ABCD BCD AB CD A B C D ABCD BCD BC CD A B C D ABCD ABC AB A B C D ABCD ABC BC A B C D ABCD BCD BC A B C D ABCD BCD CD A B C D ABCD AB CD A B C D</p>

Table 3. Data for example 1.

Component	Feed Composition (mol fraction)	$\alpha_{i,j}^*$
(A) n-Hexane	0.1	8.90
(B) n-Heptane	0.1	5.70
(C) n-Octane	0.4	3.20
(D) n-Nonane	0.3	1.55
(E) n-Decane	0.1	1.00
Total Flow	200 kmol h ⁻¹	
Pressure	2-4 atm.	
Steam cost	5.09 \$ GJ ⁻¹ (8000 h/year operation)	
Cold water cost	0.19 \$ GJ ⁻¹	
Recovery:	0.999 of light key and heavy key in each separation.	

* Relative volatility of component (i) respect to the heaviest one (n-decane (j))

Table 4. Some statistics and evolution in the solution of example 1.

Iteration	T.A.C (\$/year 10 ⁻³)	Structural Configuration (sequence of states)		CPU time (s)
		States with heat exchangers	Integrated heat exchangers	
Initial	1221	ABCDE – ABCD – BCD – CDE – BC – DE – A – B – C – D – E		79.5
1	1199	ABCDE – ABCD – BCD – CDE – BC – DE – A – B – C – D – E	ABCD, BCD, BC, A, B, E, BC-BCD	209.8
2	1130	ABCDE – ABCD – ABC – CDE – BC – DE – A – B – C – D – E	ABC, CDE, BC, A, B, E B-BC;	255.9
3	920	ABCDE – ABC – CDE – BC – CD – DE – A – B – C – D – E	CDE, BC, CD, A, B, E B-BC; CD-CDE	185.3
4	1176	ABCDE – ABCD – ABC – CDE – BC – DE – A – B – C – D – E	ABC, CDE, BC, A, B, E B-BC	180.7
TOTAL				911.2
Number of equations	2681			
Number of Variables	1198			
Discrete Variables	275			

* New best solution.

Table 5. Data for example 2.

Component	Feed Composition (mol fraction)	$\alpha_{i,j}^*$
(A) Ethanol	0.1	4.1
(B) Isopropanol	0.1	3.6
(C) 1-Propanol	0.4	2.1
(D) Isobutanol	0.3	1.42
(E) 1-butanol	0.1	1
Total Flow	200 kmol h ⁻¹	
Pressure	1-4 atm.	
Steam cost	5.09 \$ GJ ⁻¹ (8000 h/year operation)	
Cold water cost	0.19 \$ GJ ⁻¹	
Recovery:	0.98 of light key and heavy key in each separation.	

* Relative volatility of component (i) respect to the heaviest one (1-butanol (j))

Table 6. Data for example 3

Component	Feed Composition (mol fraction)	$\alpha_{i,j}^*$
(A) Benzene	0.15	10.5
(B) Toluene	0.15	4.04
(C) Ethylbenzene	0.4	1.76
(D) Styrene	0.2	1.31
(E) α -methyl styrene	0.1	1
Total Flow	200 kmol h ⁻¹	
Pressure	0.3 – 1 atm.	
Steam cost	5.09 \$ GJ ⁻¹ (8000 h/year operation)	
Cold water cost	0.19 \$ GJ ⁻¹	
Recovery:	0.98 of light key and heavy key in each separation.	

* Relative volatility of component (i) respect to the heaviest one (α -methyl styrene)

Table 7. Summary of computational results.

Example	1	2	3
Initial MINLP (DICOPT) no heat integration (\$/year 10^{-3})	1221	1662	1501
First Heat integrated solution (SBB) (\$/year 10^{-3})	1199	1406	1364
Best obtained solution (\$/year 10^{-3})	920	1180	1267
Total CPU time (s)	911.2	2248	2777
Major Iterations	4	5	6

Figure Captions

Figure 1. Column sequences and state-task representation for the direct (a) and indirect (b) three component separation using conventional columns. Ellipses = states; rectangles = separation tasks.

Figure 2. State-task representation and thermodynamically equivalent column configurations for the fully thermally coupled configuration in the separation of a three component mixture.

Figure 3. Separation of a three component mixture using pre-fractionation. State-task representation and column arrangement.

Figure 4. STN (state task network) superstructure for a four component mixture.

Figure 5. STN superstructure with aggregation of tasks.

Figure 6.(a) Detailed superstructure for a four component mixture.(b) Detailed of alternatives in internal states.

Figure 7. Kaibel's arrangement. Thermally coupled structure with reduced number of column sections.

Figure 8. Sequence with duplication key components (B light key; C heavy key) in the separations AB/C and B/C. Component C is produced by three contributions.

Figure 9. Arrangements for the sequence with duplication of key components adding a heat exchanger. (a) Reboiler added to the separation AB/C. (b) Reboiler added to the separation B/C.

Figure 10. . Arrangements for the sequence with duplication of key components using an internal wall.

Figure 11. Fully thermally coupled configuration and possible rearrangement using internal walls.

Figure 12. a) Side rectifier with direct vapour connection. b) side stripper with direct vapour connection.

Figure 13. a-e) Examples of structural feasible sequences for a five component mixture. f) Structural Infeasible sequence.

Figure 14. Best obtained solution in example 1. In state-task representation dashed lines show heat integration. Only one out of 4 possible thermodynamically equivalent configurations using four distillation columns is presented.

Figure 15. Best obtained solution in example 1. Pressure is kept constant. In state-task representation dashed lines show heat integration. Only one out of 8 possible thermodynamically equivalent configurations using four distillation columns is presented.

Figure 16. Best obtained solution in example 1. No heat integration. Only one out of 64 possible thermodynamically equivalent configurations using four distillation columns is presented.

Figure 17. Best obtained solution in example 2. In state-task representation dashed lines show heat integration. Only one out of 4 possible thermodynamically equivalent configurations using four distillation columns is presented.

Figure 18. Best obtained solution in example 2. Constant pressure. Only one out of 32 possible thermodynamically equivalent configurations using four distillation columns is presented.

Figure 19. Best obtained solution in example 3. In state-task representation dashed lines show heat integration. Only one out of 2 possible thermodynamically equivalent configurations using four distillation columns is presented.

Figure 20. Best obtained solution in example 3. Constant pressure. Only one out of 16 possible thermodynamically equivalent configurations using four distillation columns is presented.

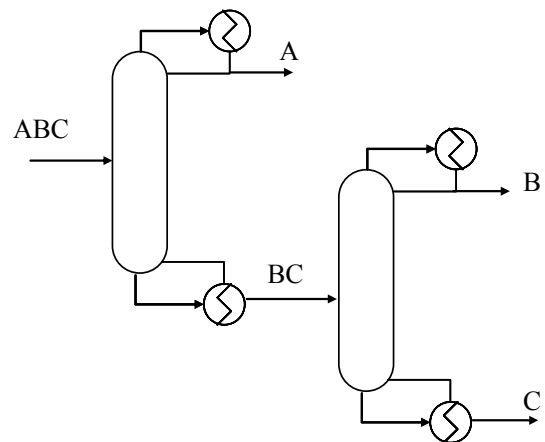


Figure 1a

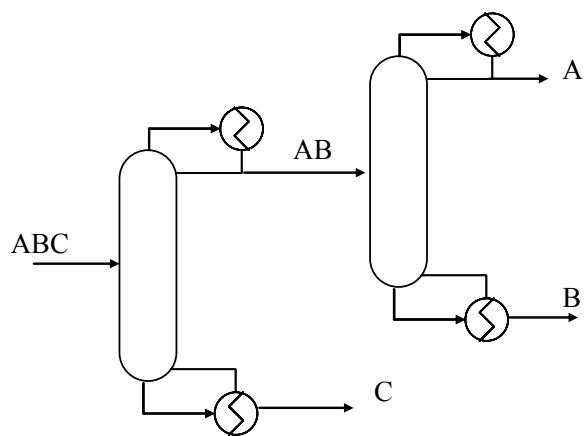
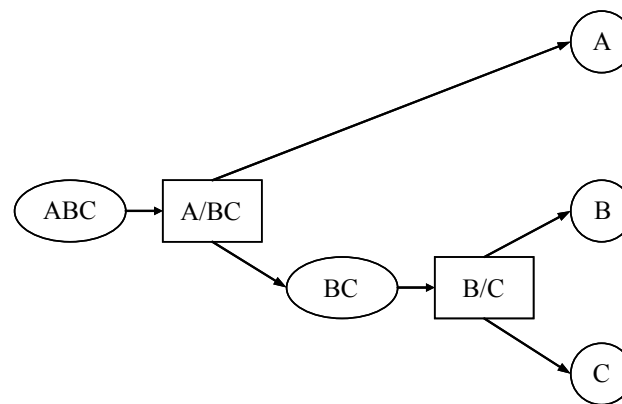


Figure 1b

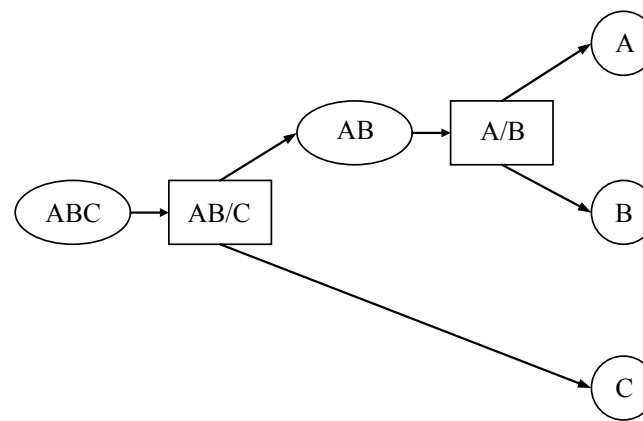


Figure 1

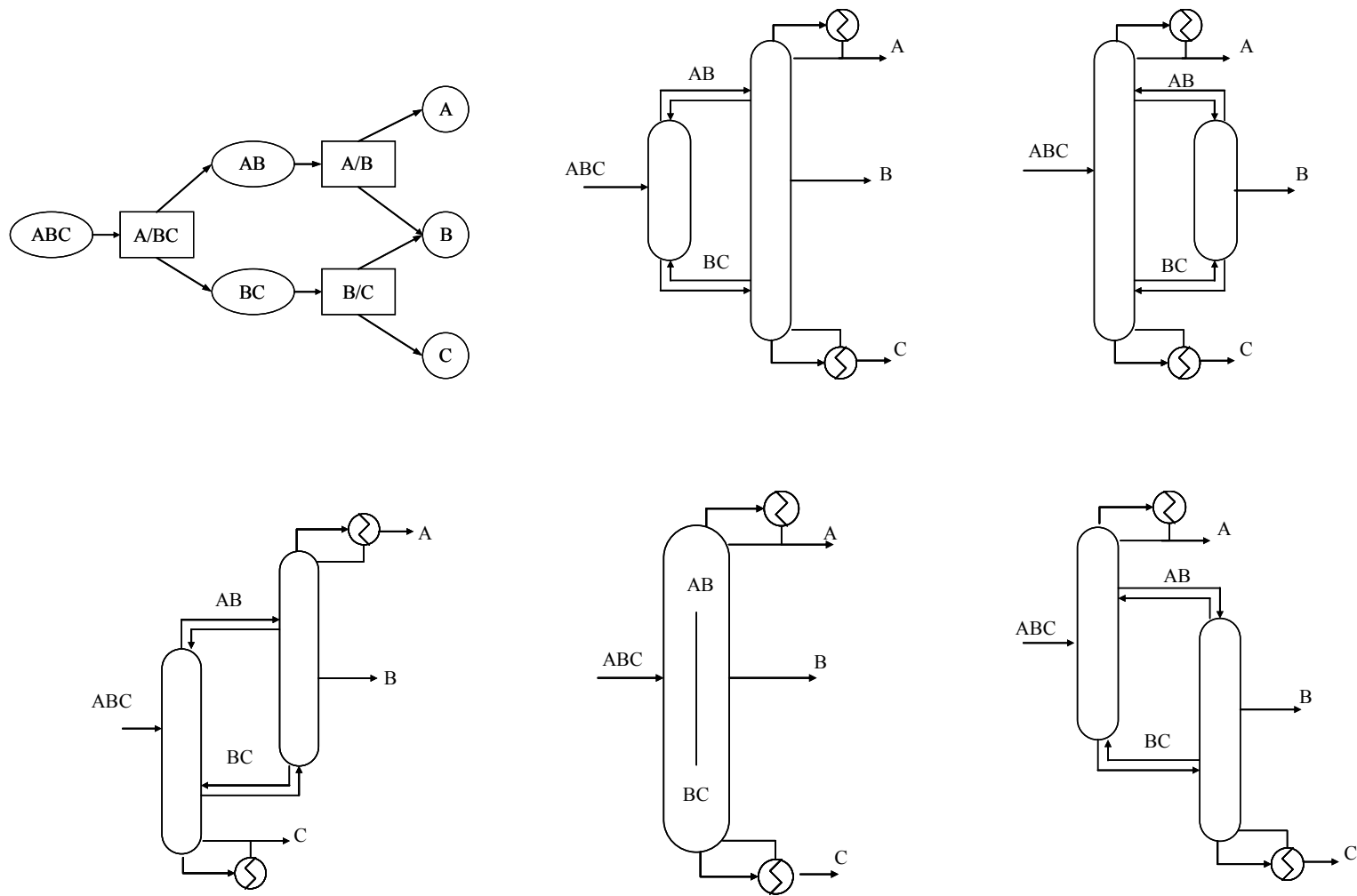


Figure 2

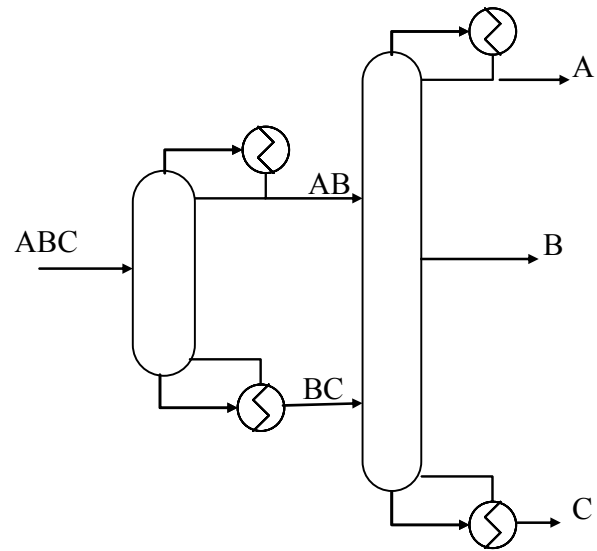
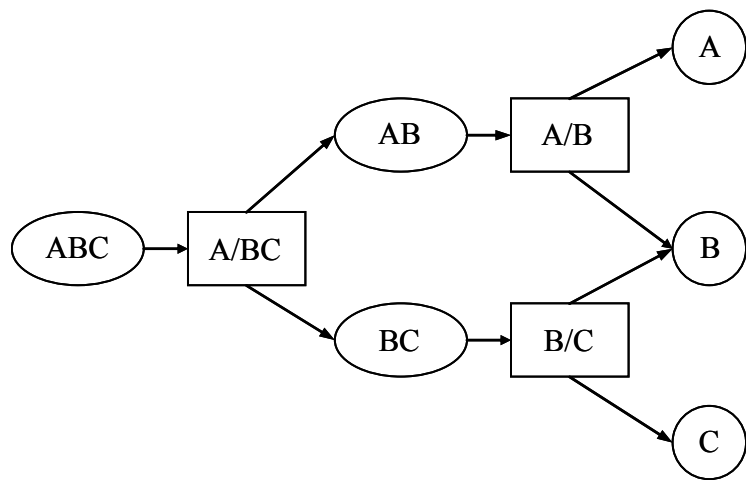


Figure 3

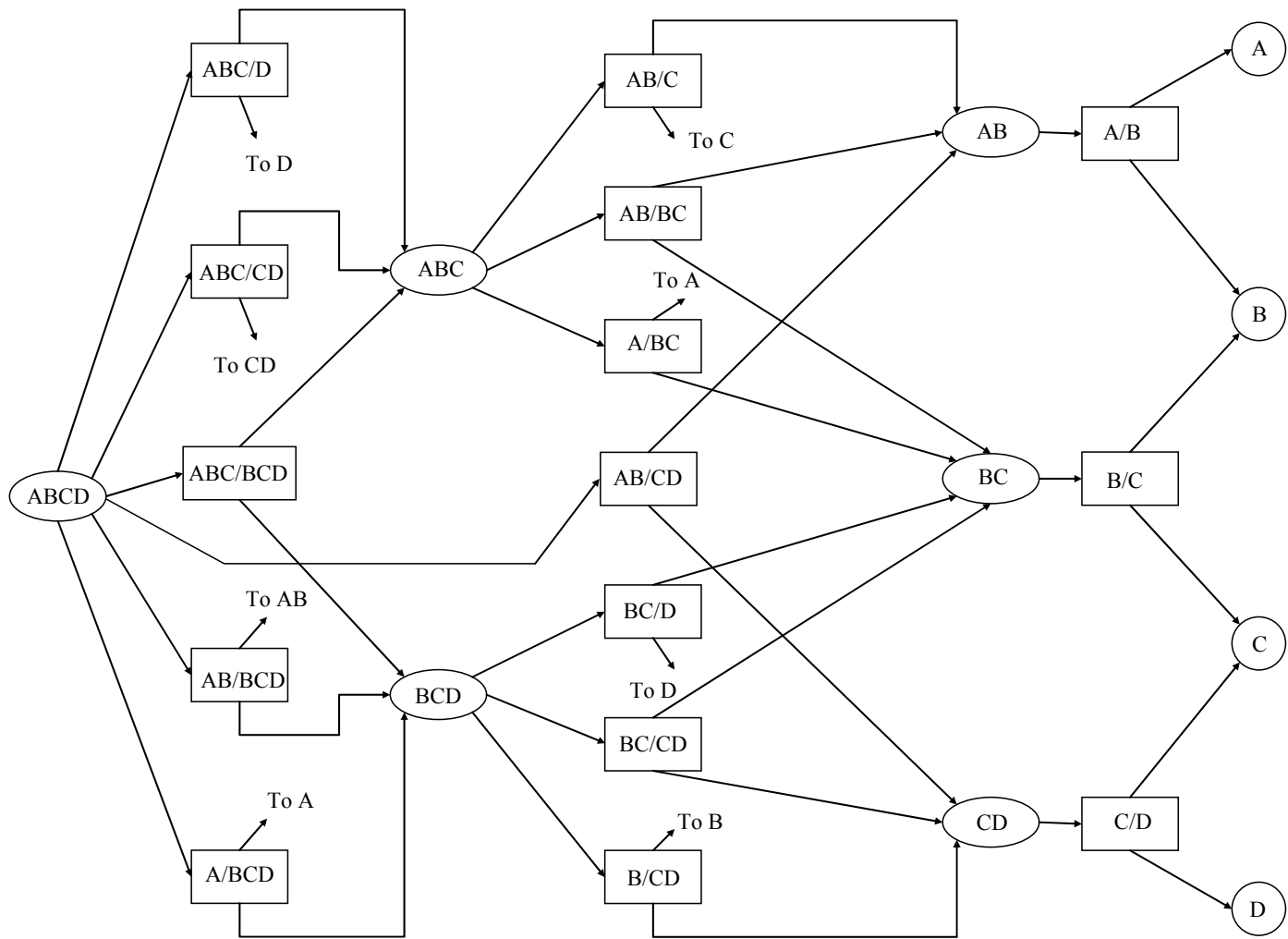


Figure 4

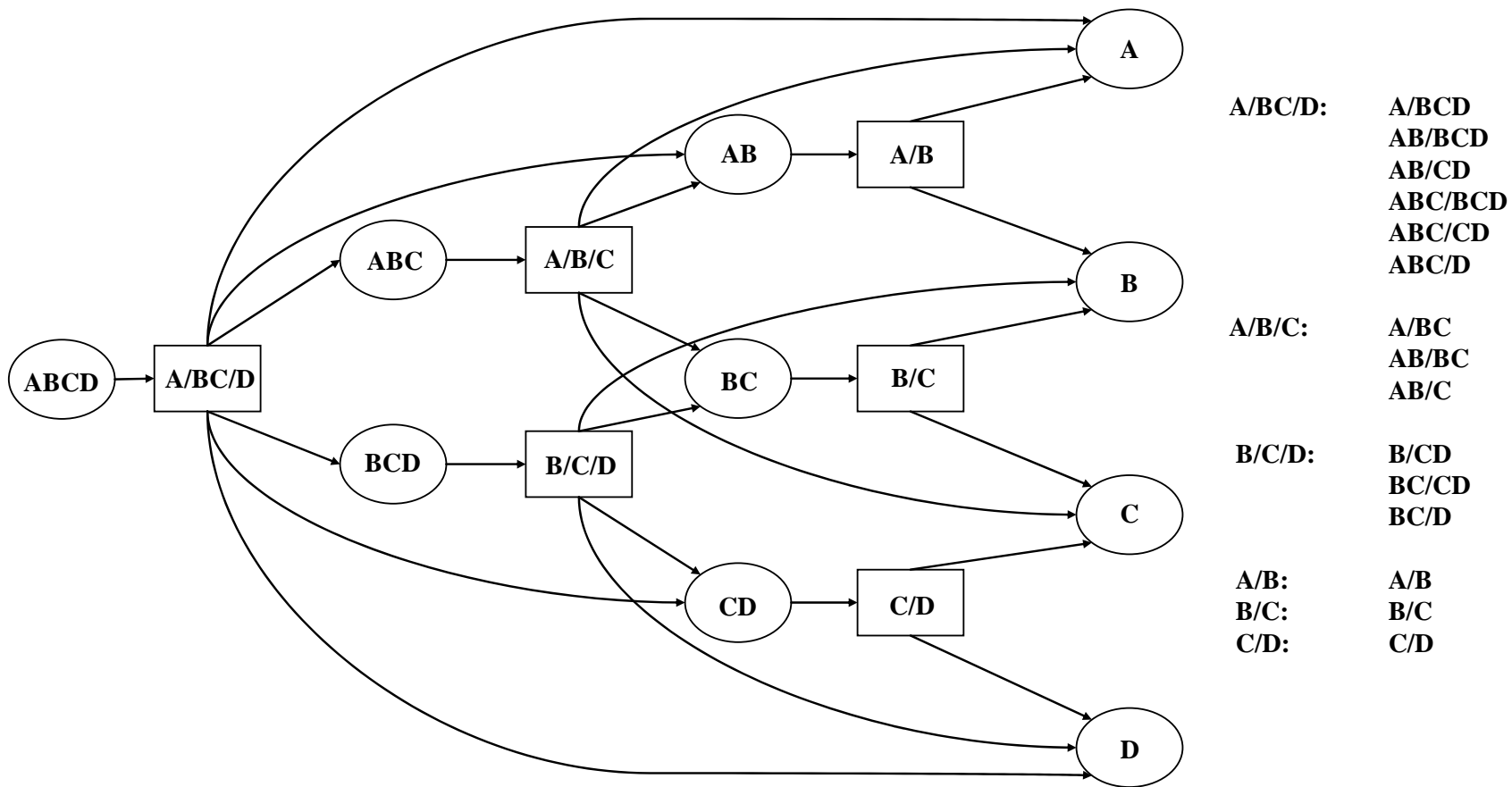


Figure 5

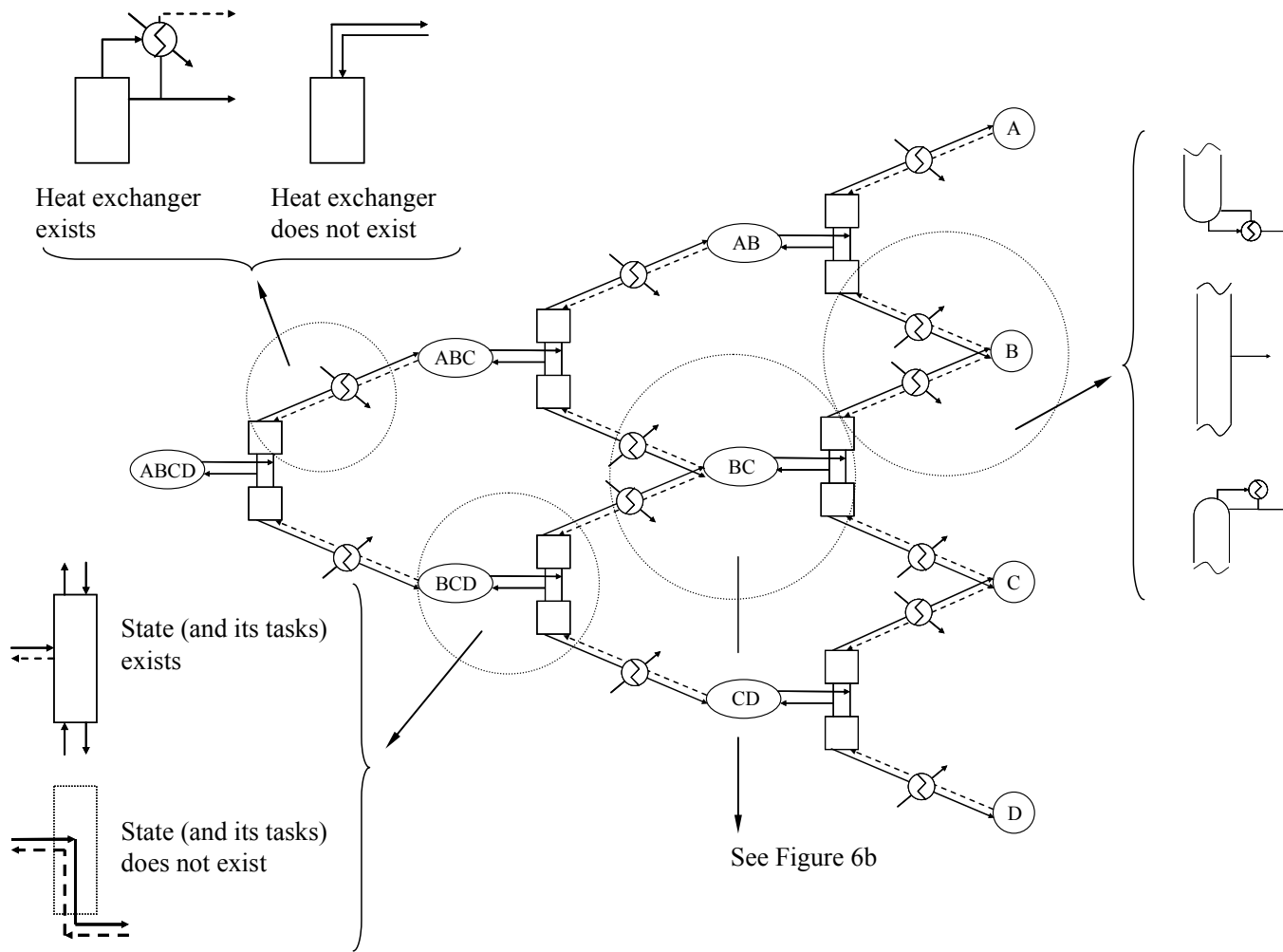


Figure 6a

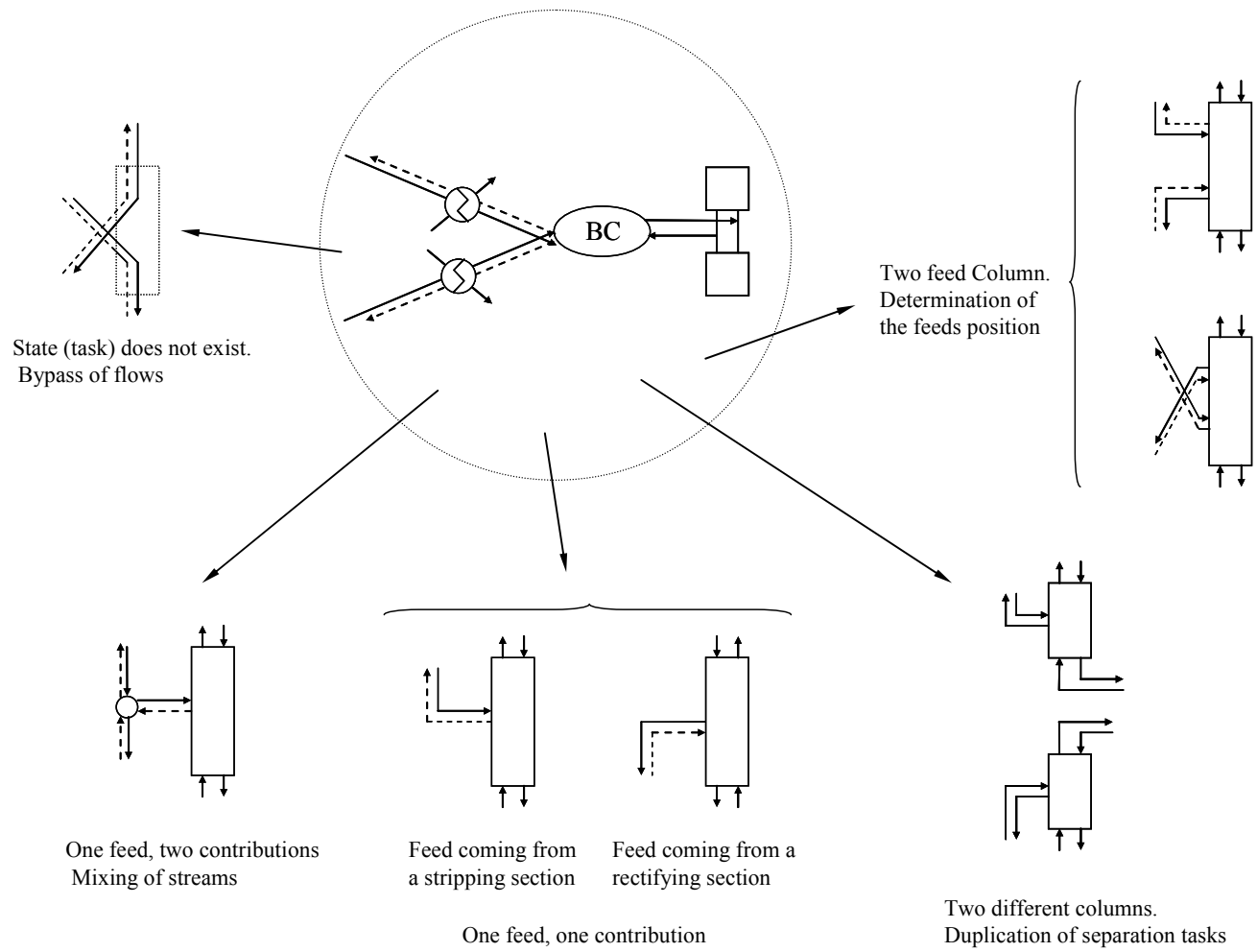


Figure 6b

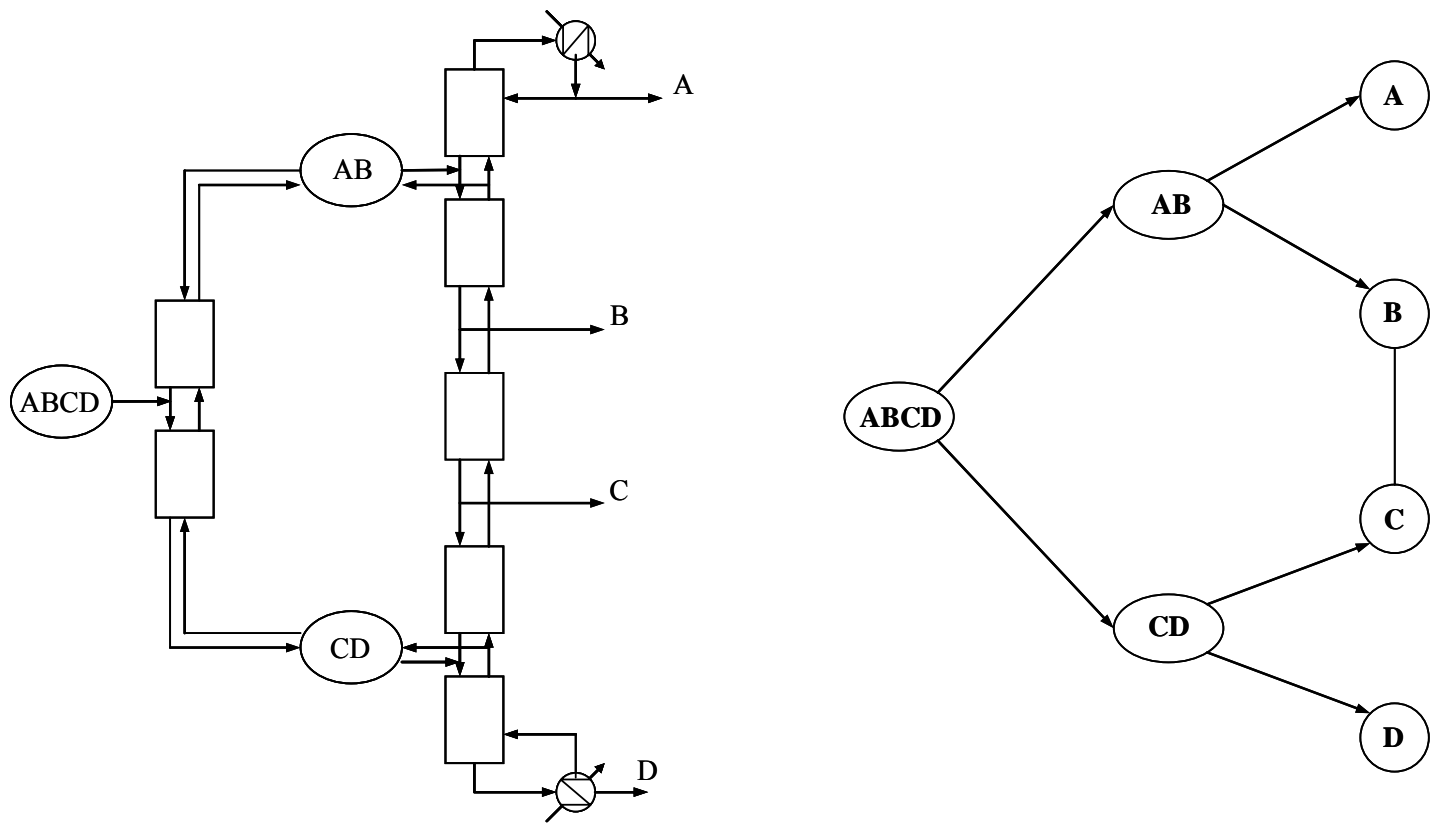


Figure 7

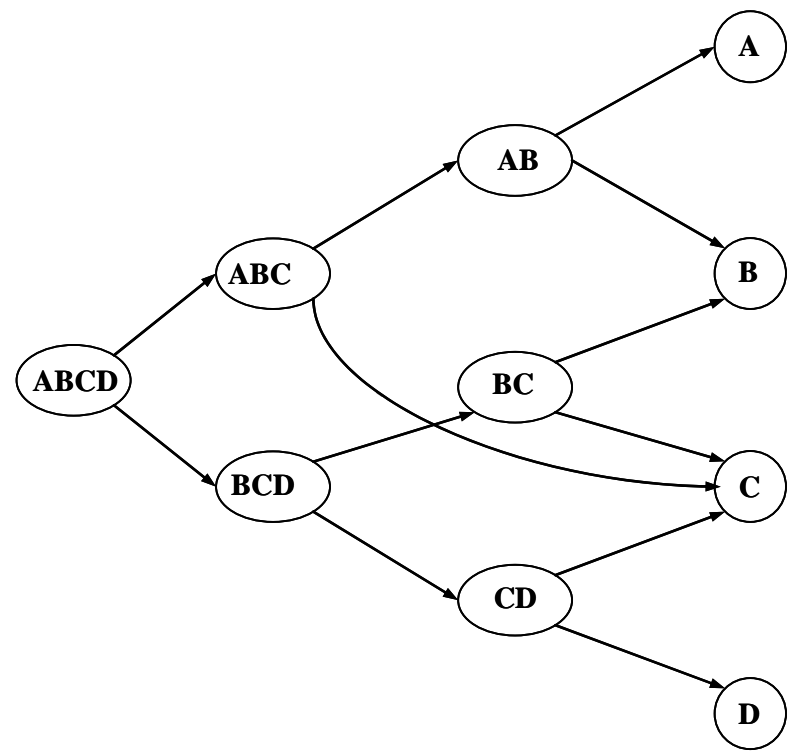
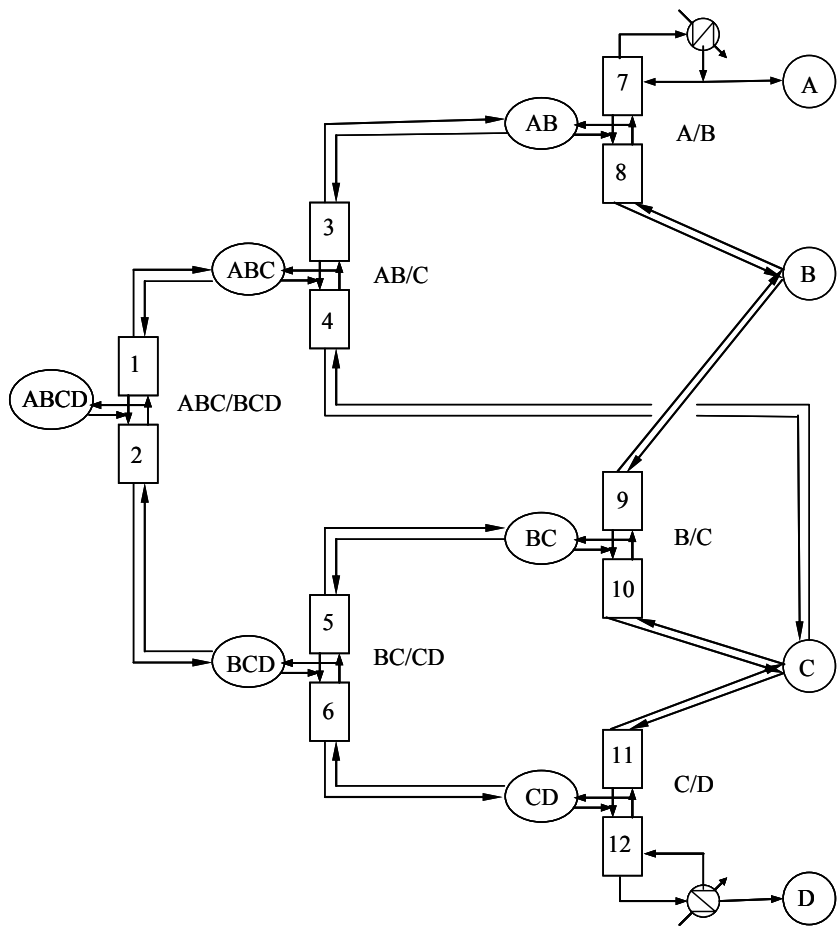


Figure 8

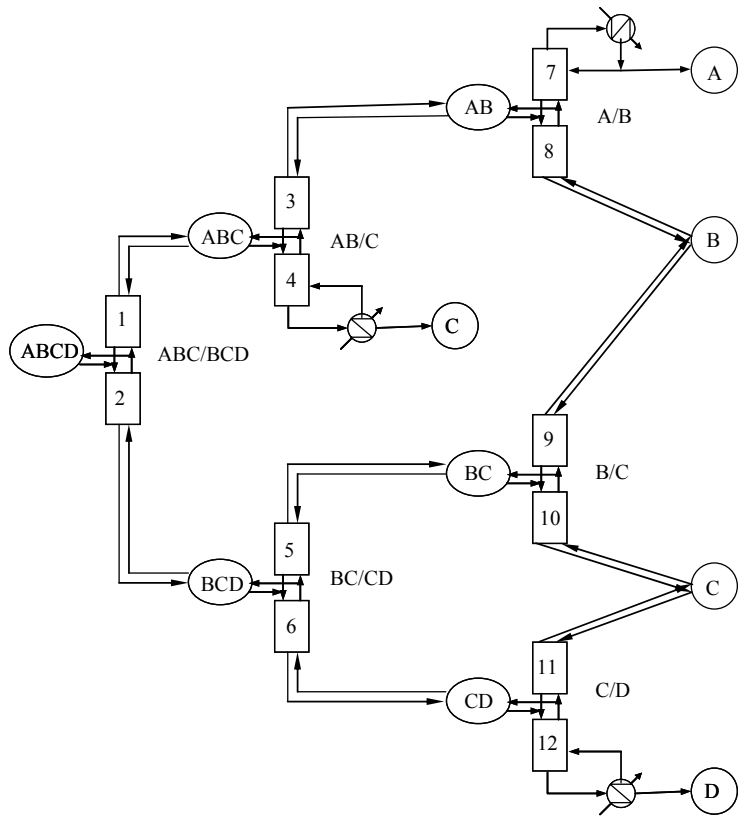


Figure 9a

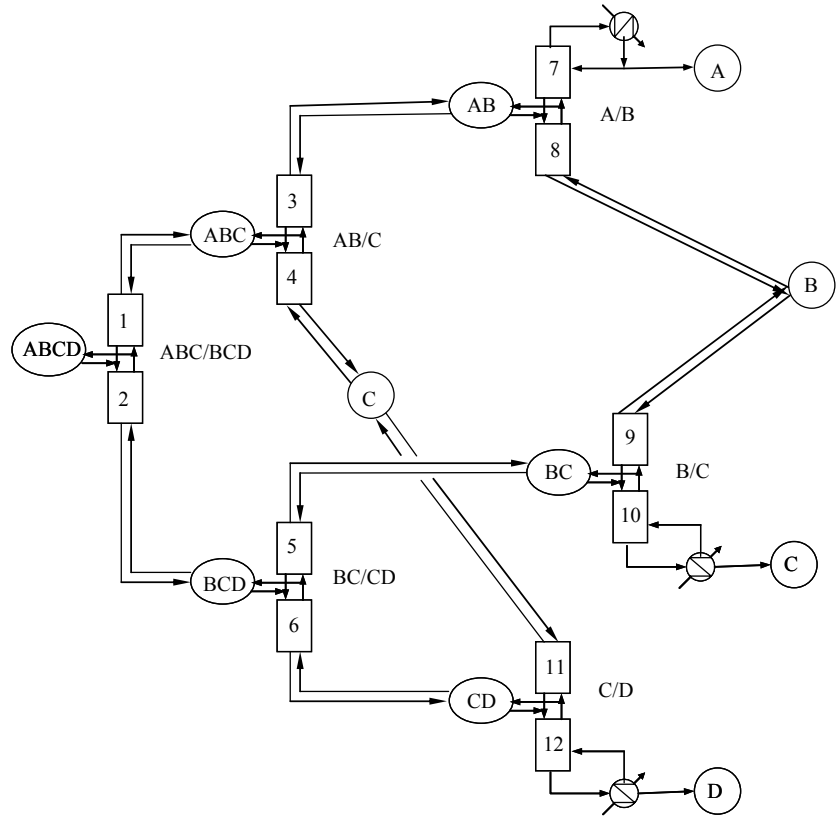


Figure 9b

Figure 9

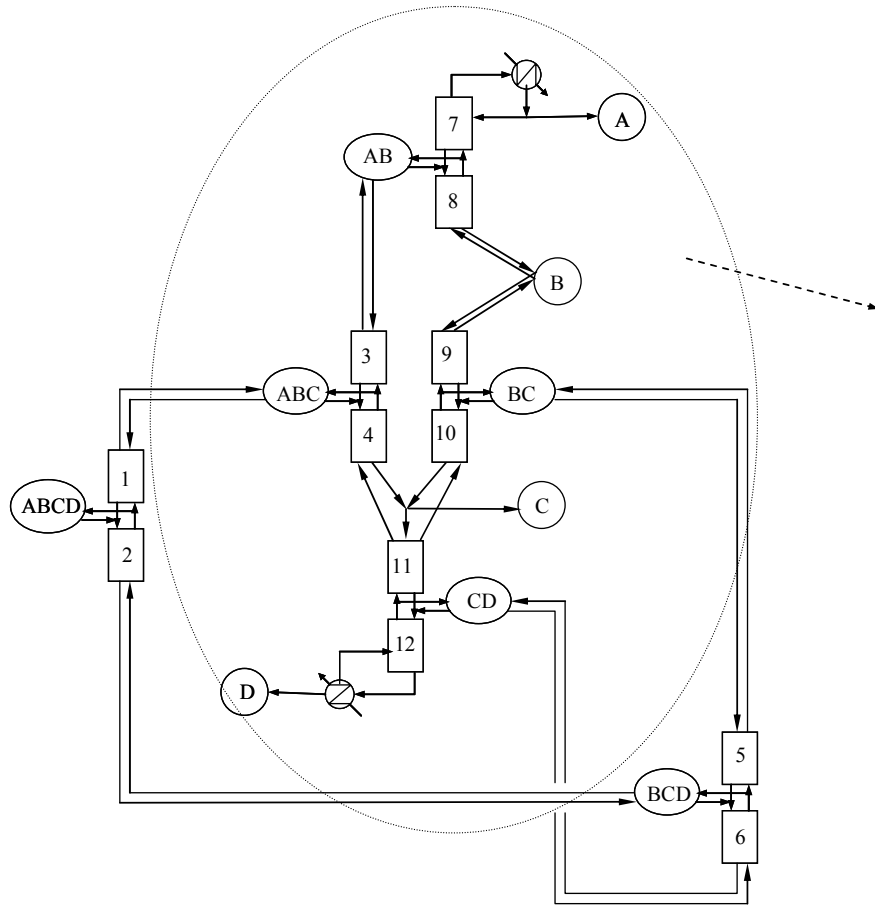


Figure 10a

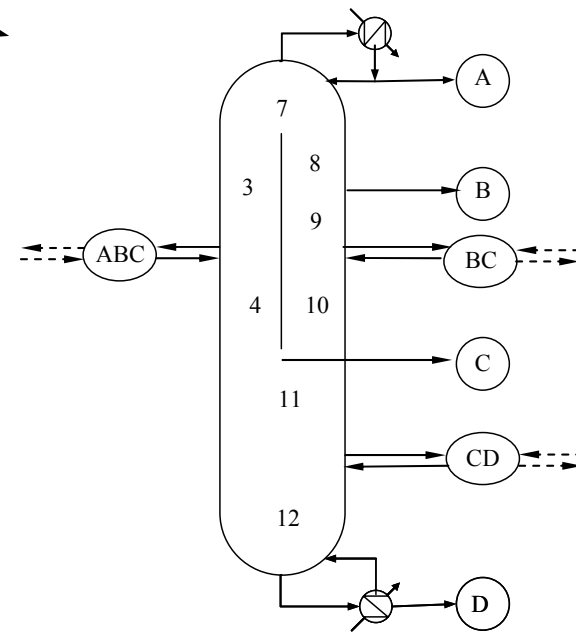


Figure 10b

Figure 10

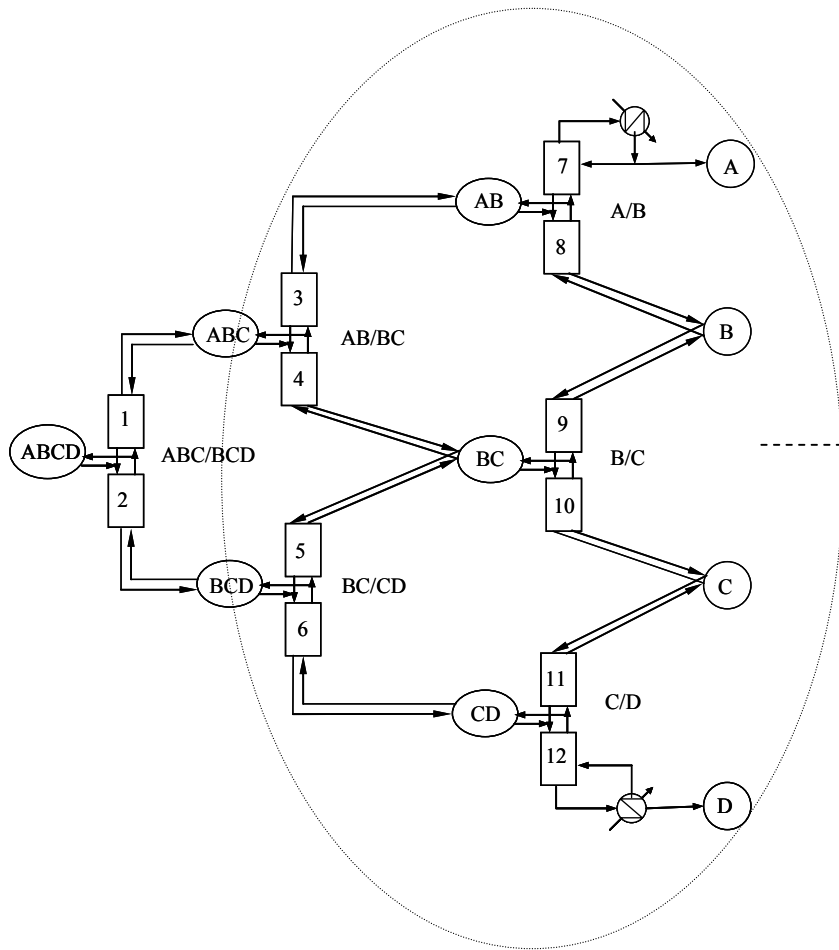


Figure 11a

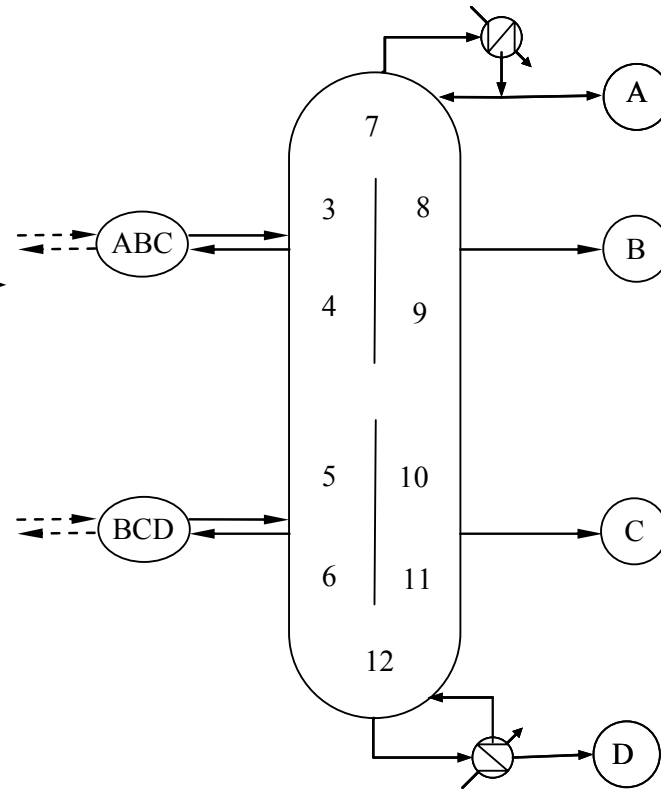


Figure 11b

Figure 11

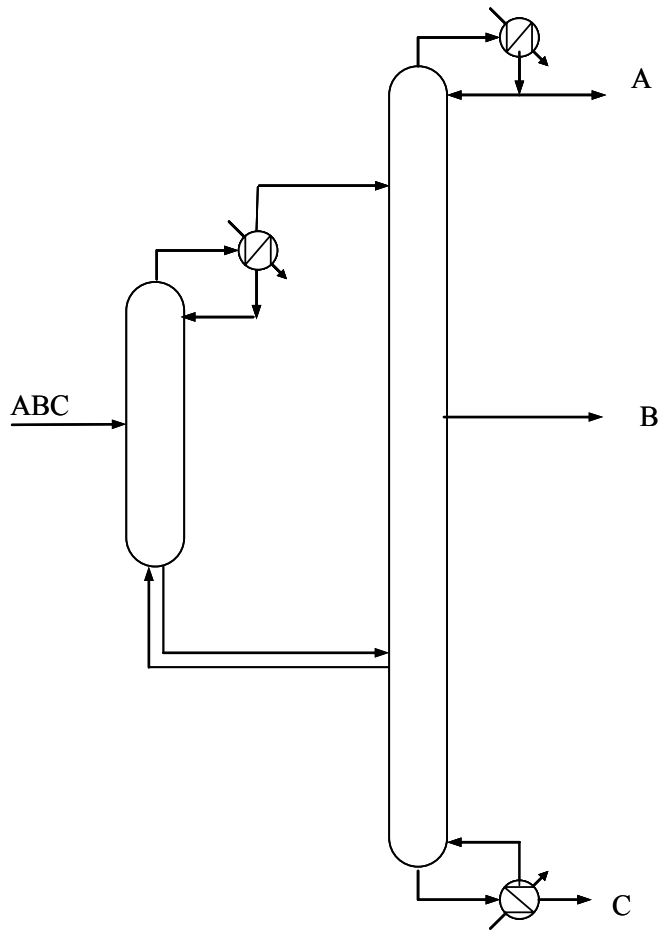


Figure 12a

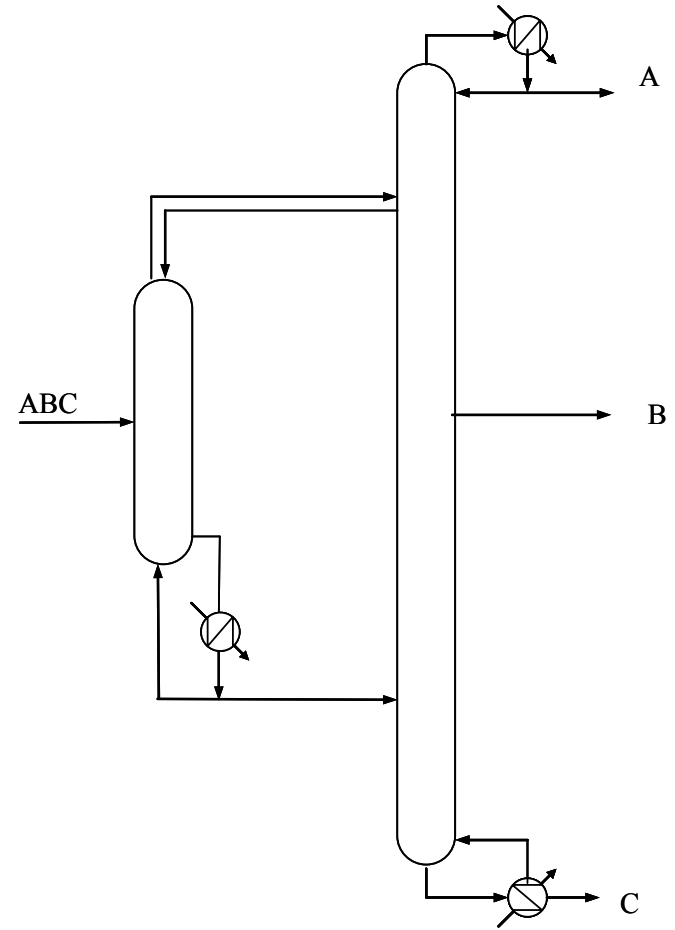
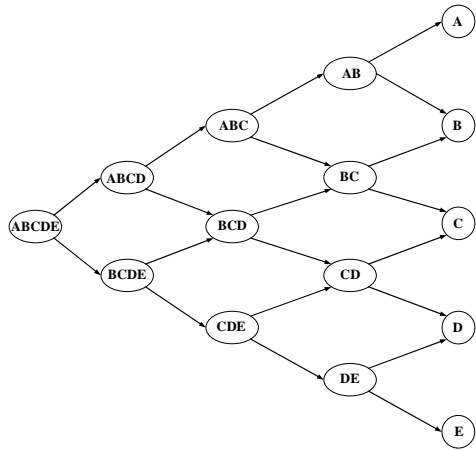
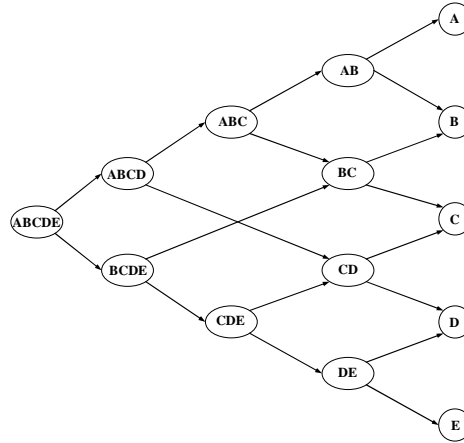


Figure 12b

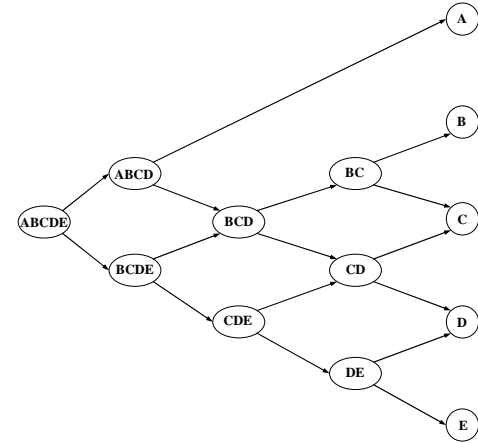
Figure 12



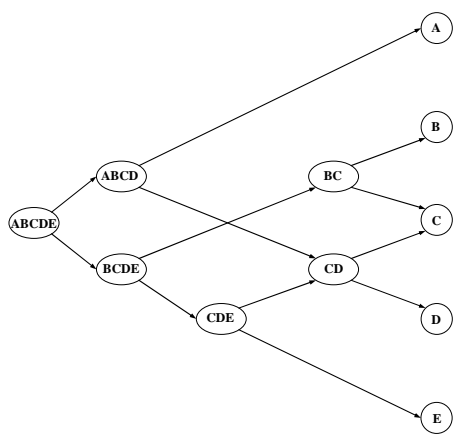
13a



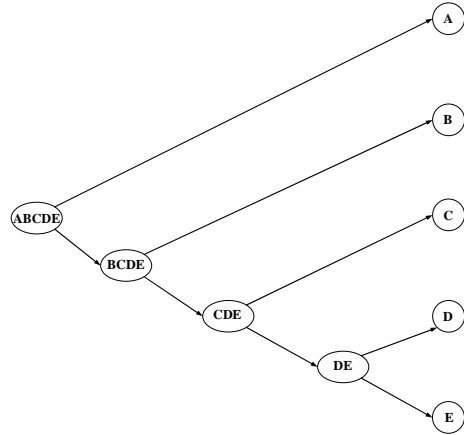
13b



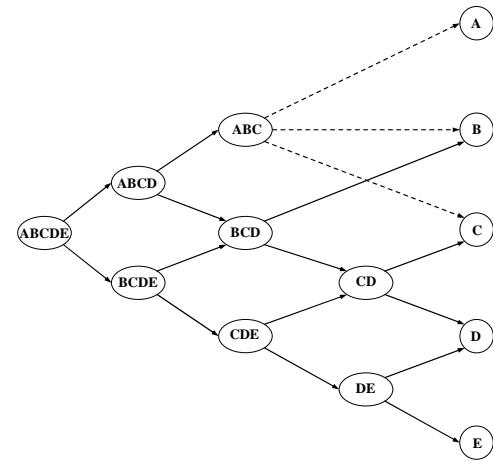
13c



13d



13e



13f

Figure 13

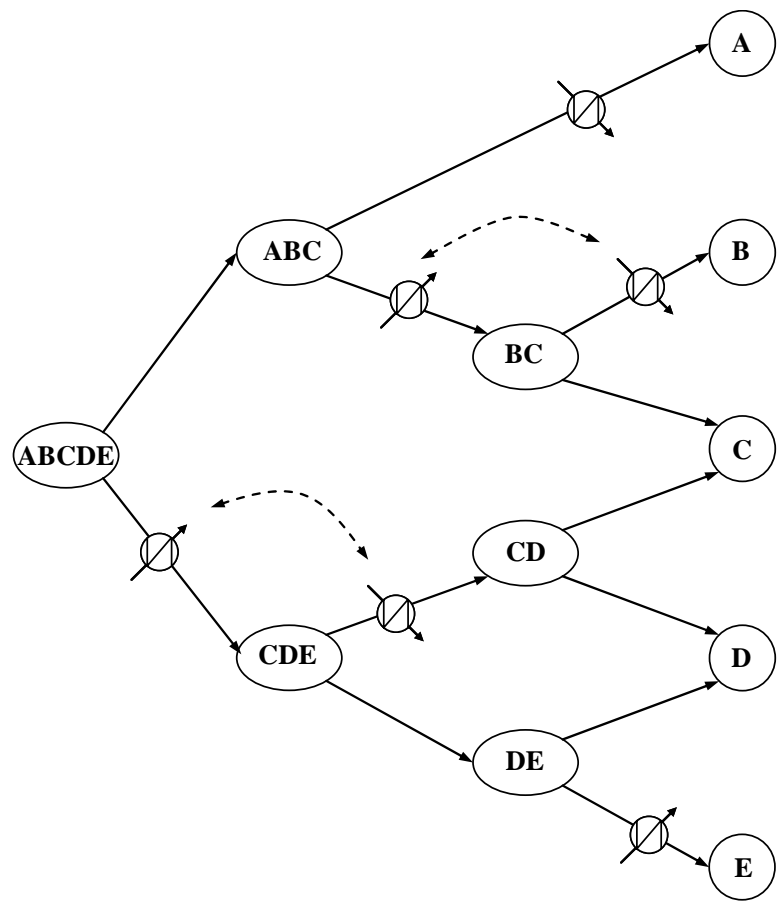
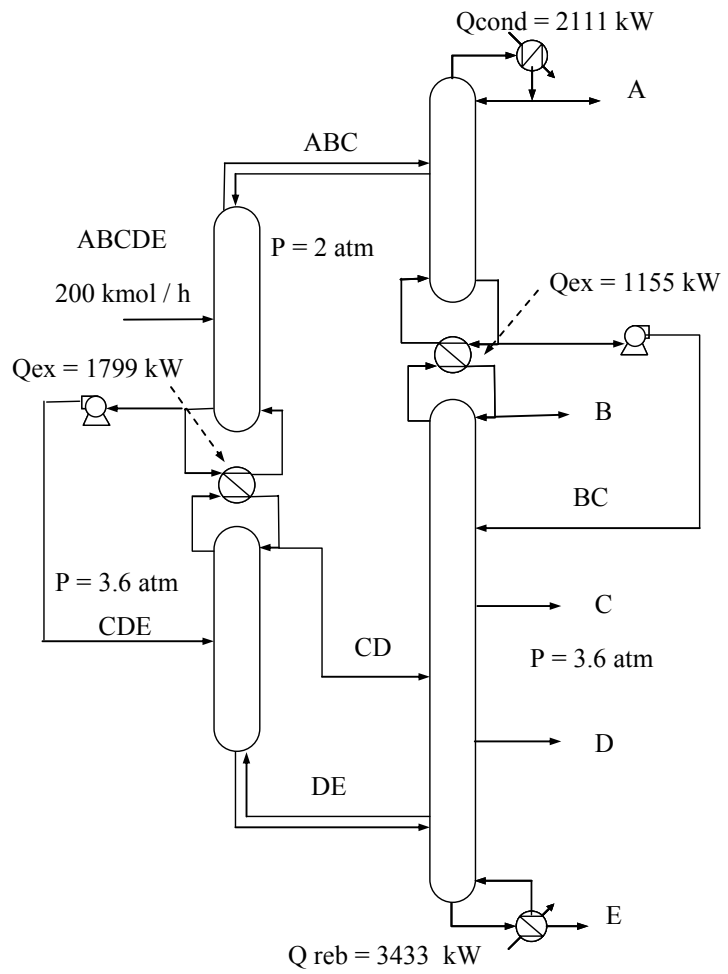


Figure 14

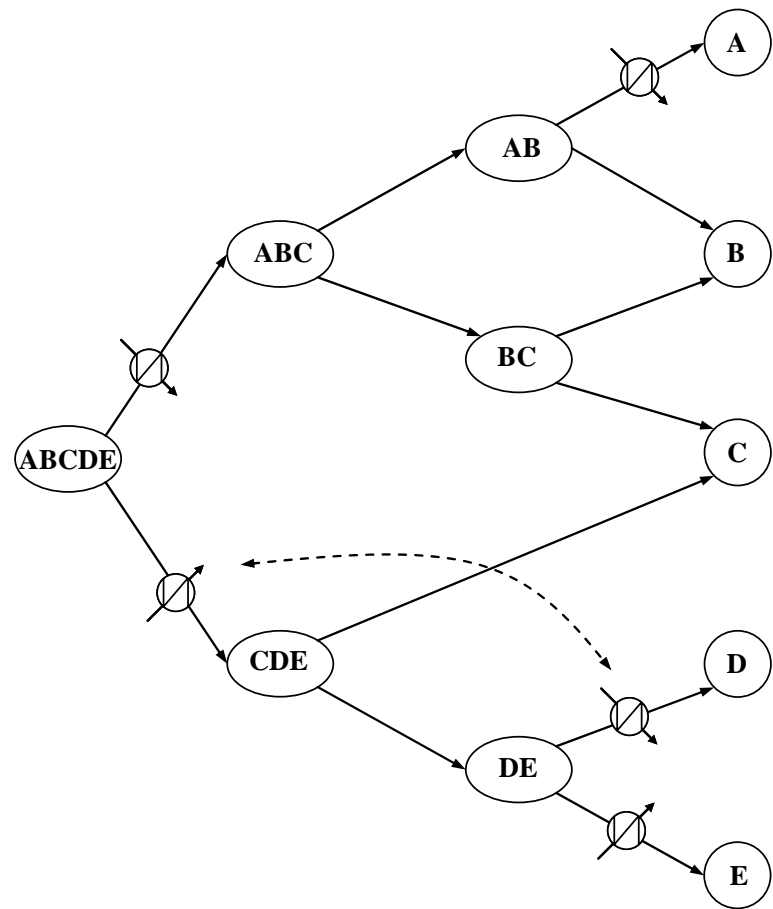
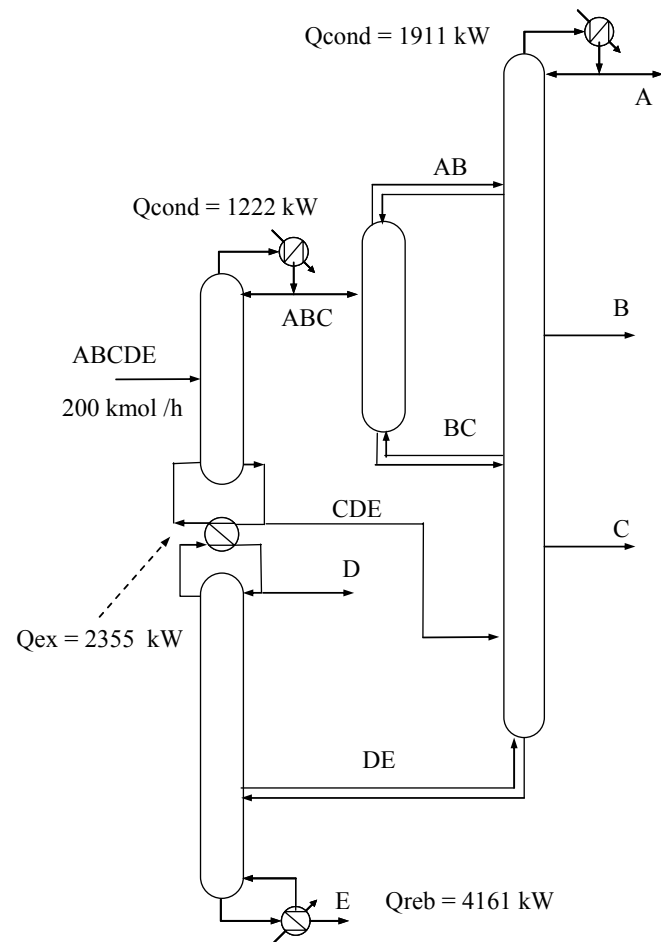


Figure 15

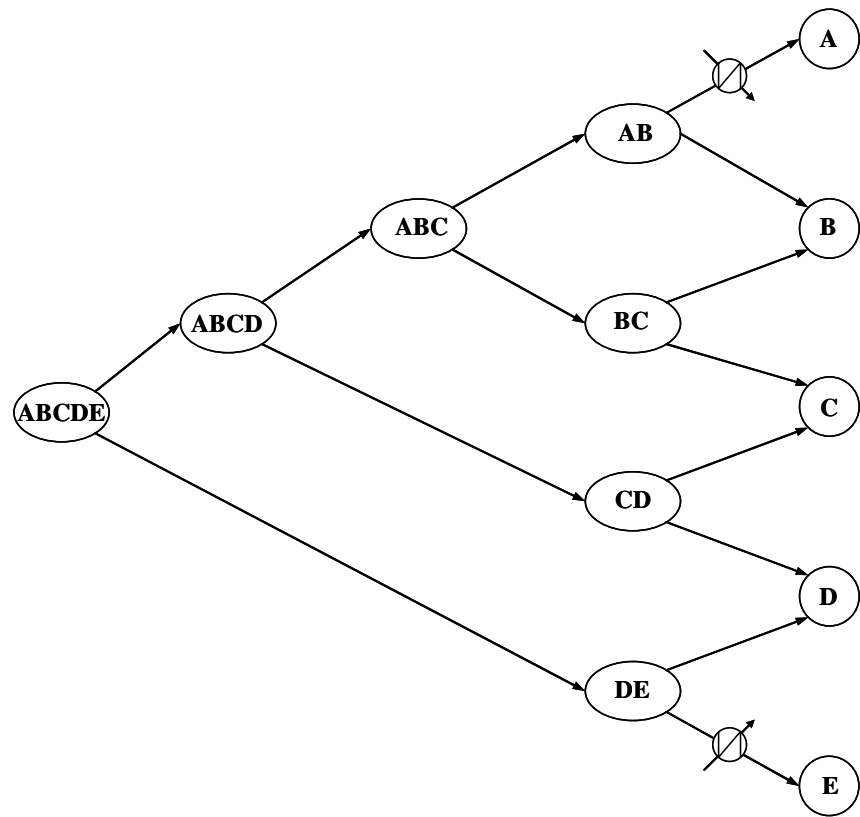
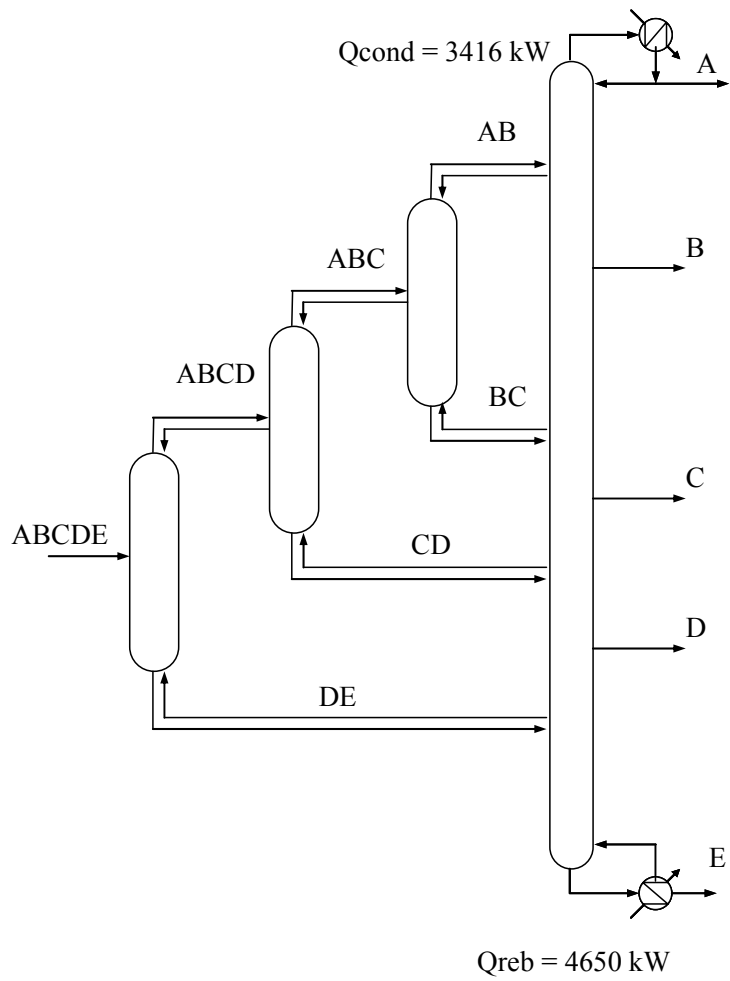


Figure 16

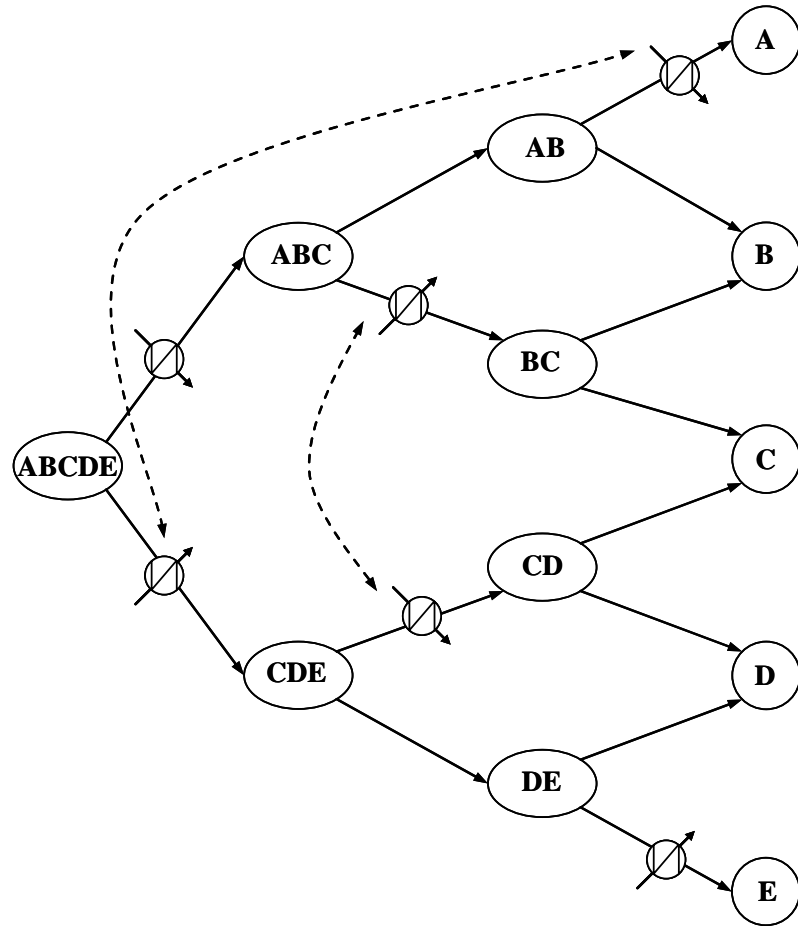
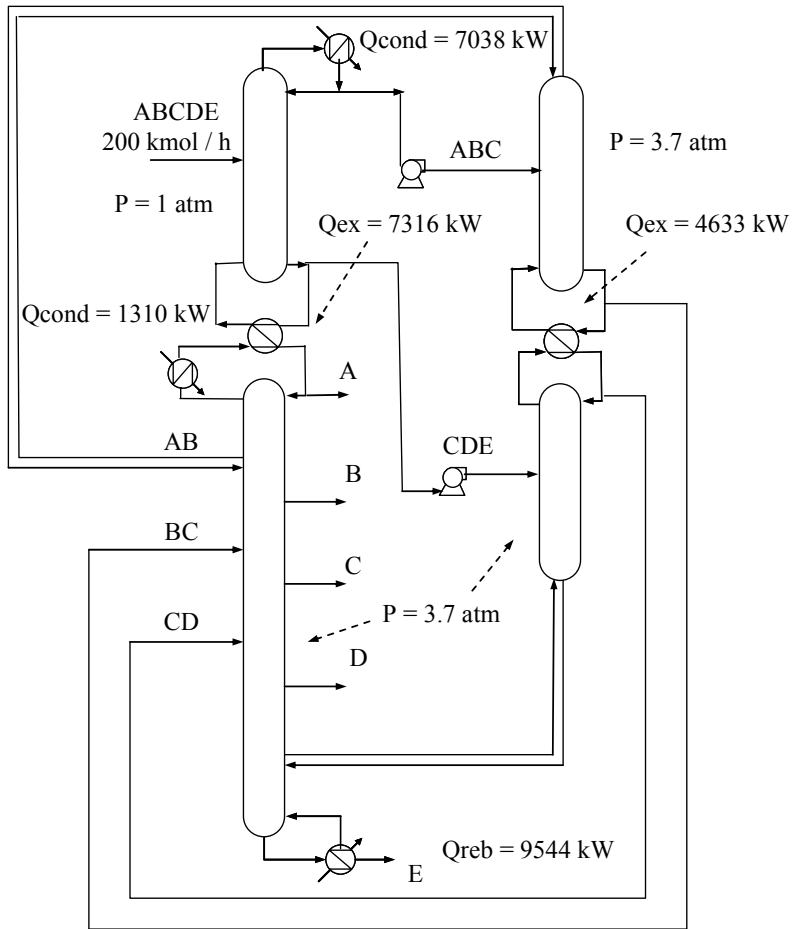


Figure 17

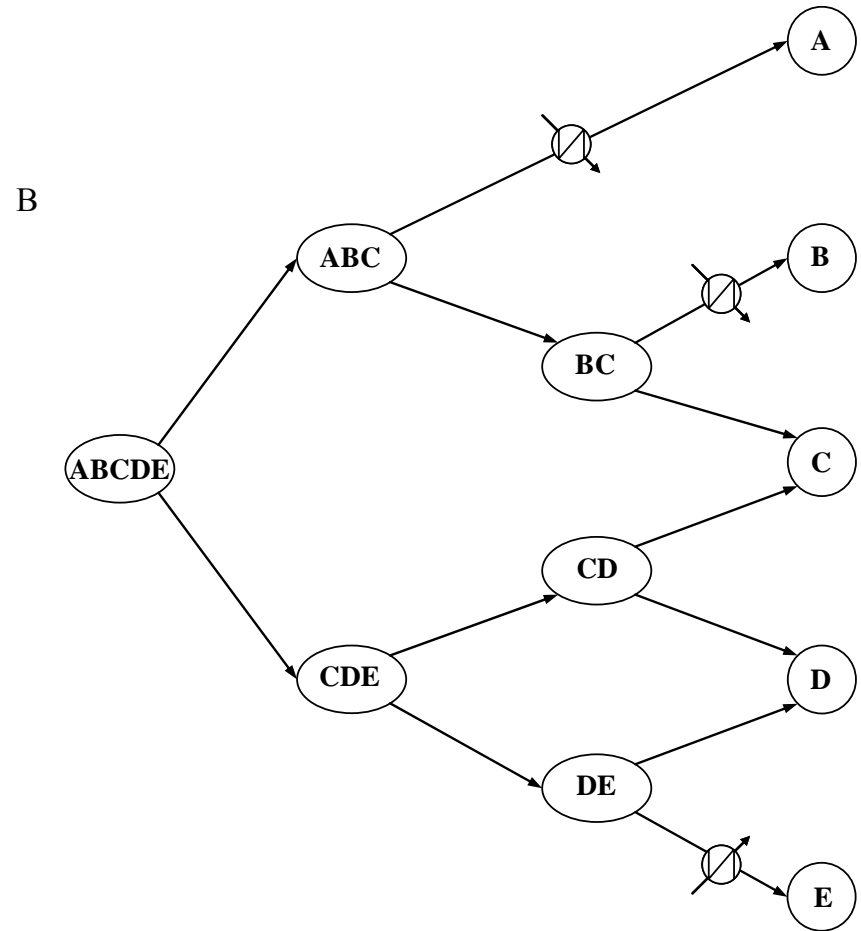
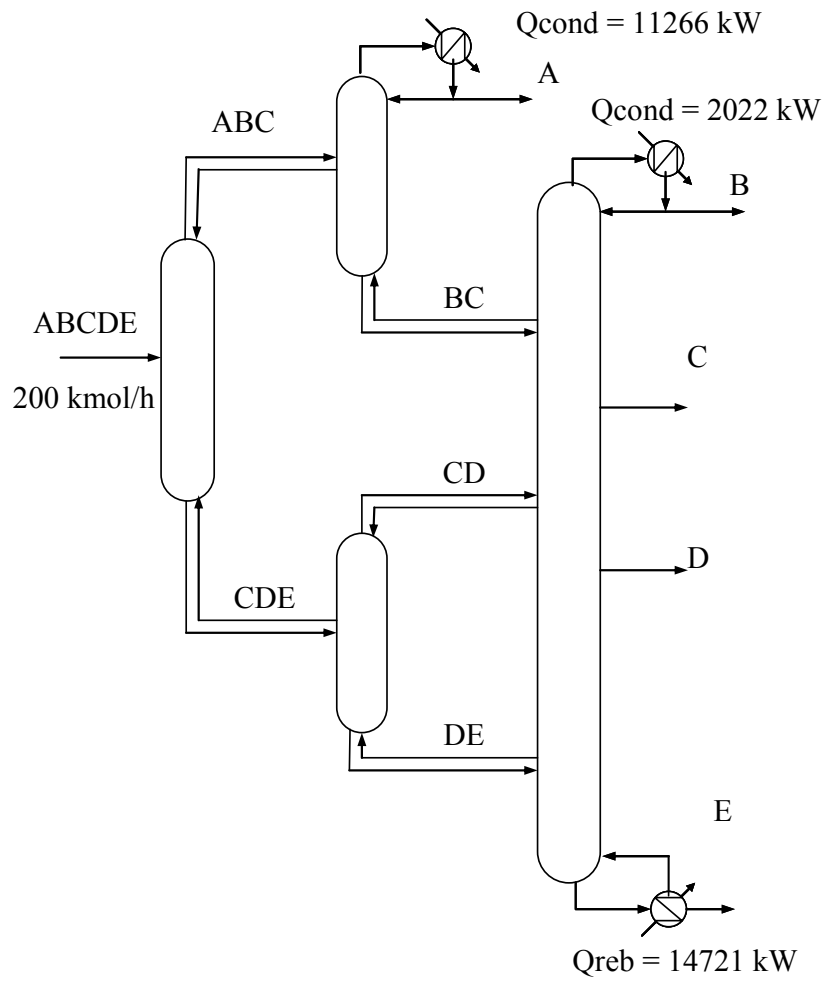


Figure 18

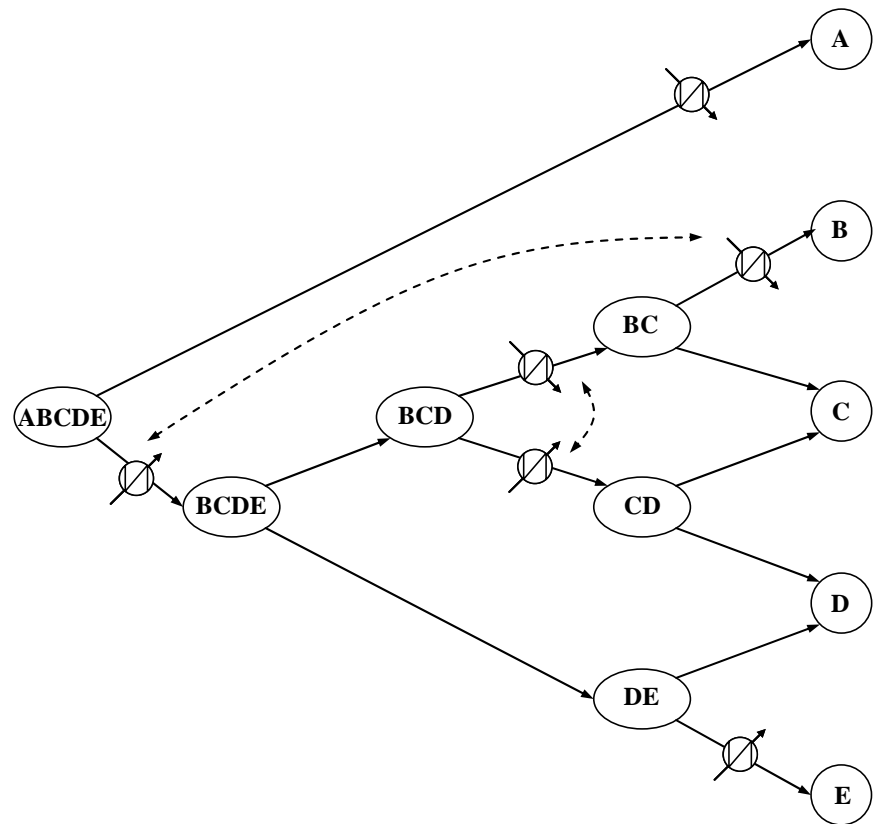
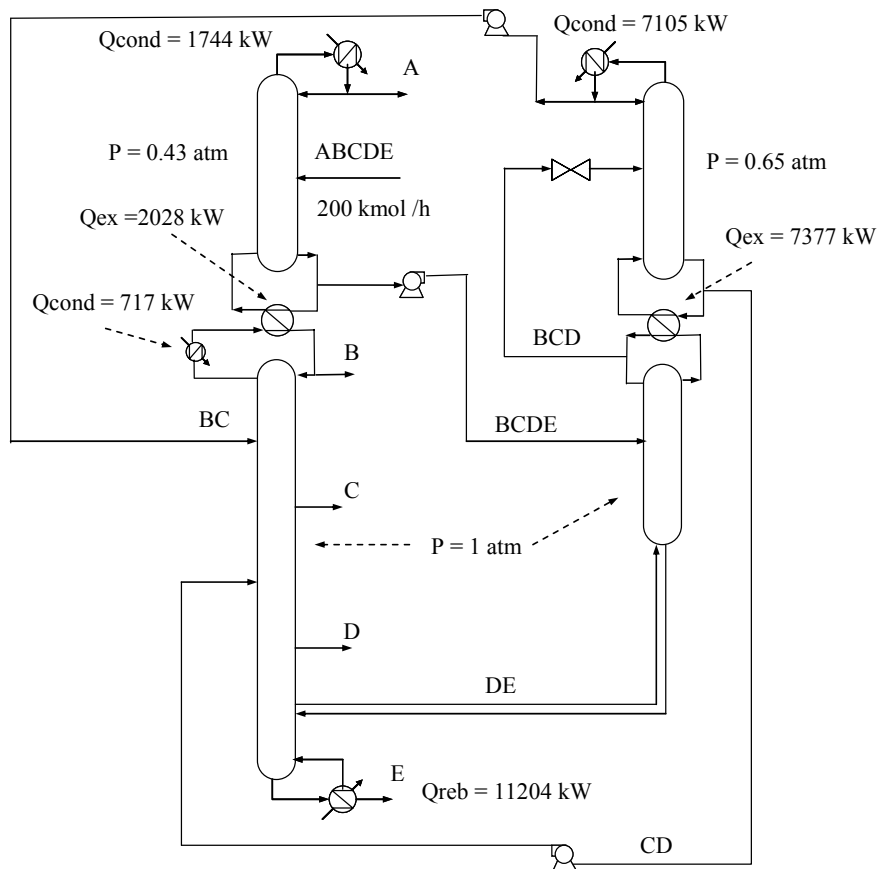


Figure 19

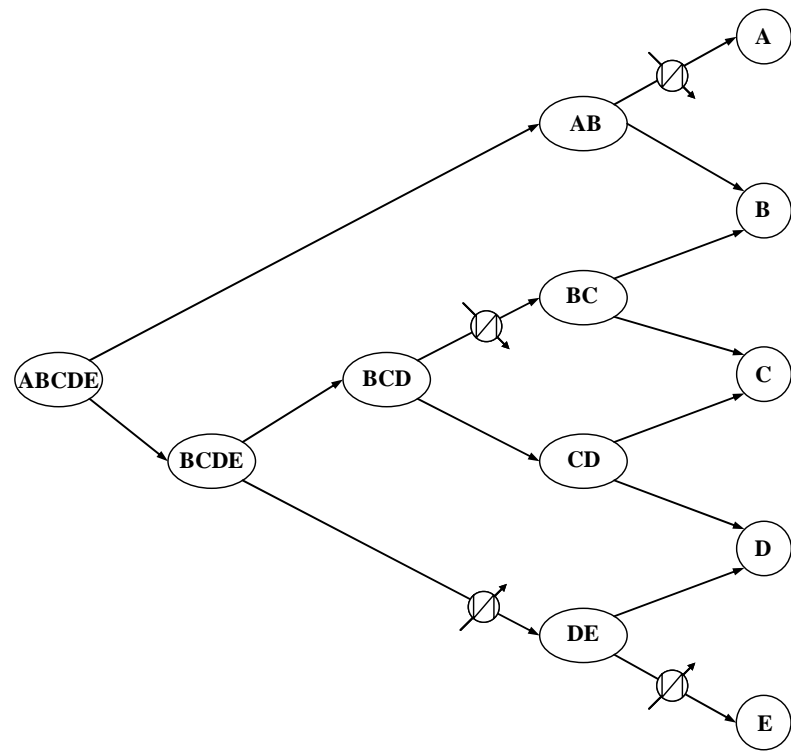
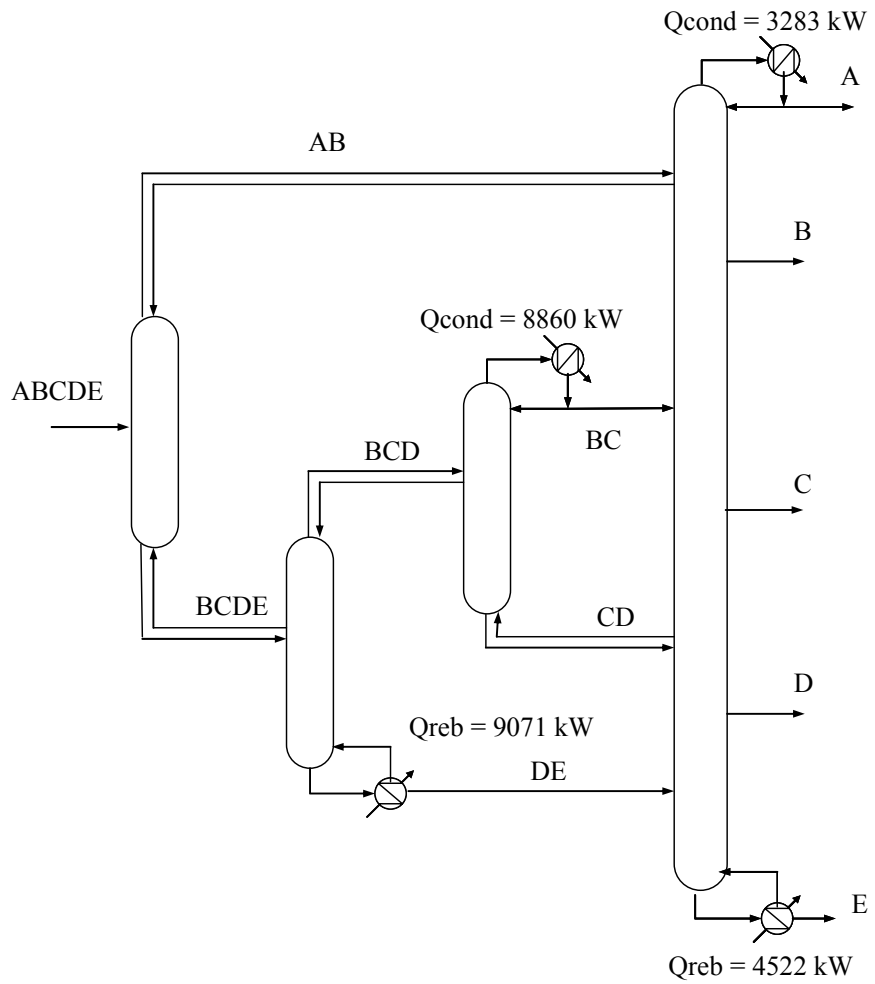


Figure 20