Optimization of Distillation Processes.

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Abstract

In this work we present an overview of the main advances in column sequence optimization in zeotropic systems, ranging from systems using only conventional columns, each with a condenser and a reboiler, to fully thermally coupled systems with a single reboiler and a single condenser in the entire sequence. We also review the rigorous design of distillation columns, or column sequences. In all the cases we focus on mathematical programming approaches.

Keywords

Distillation. Optimization. Column sequencing. Thermally Coupled Distillation. Petlyuk Columns. Shortcut distillation. Heat Integration in Distillation. Distillation modeling. Rigorous distillation models.

Introduction

Distillation is the most important operation for separation and purification in process industries, and this situation is unlikely to change in the near future. In order to get an idea of the importance of distillation, Humphrey [1] estimated that in the United States there are 40,000 distillation columns in operation that handle more than 90% of separations and purifications. The capital investment for these distillation systems is estimated to be 8 billion US$. Using data by Mix et al [2], Soave & Feliu [3] estimated that distillation accounts about 3% of the total US energy consumption, which is equivalent to 2.87×10^{18} J (2.87 million TJ) per year, or to a power consumption of 91 GW, or 54 million tons of crude oil. Distillation columns use very large amounts of energy because of the evaporation steps that are involved. Typically more than half of the process heat distributed to a plant is dedicated to supply heat in the reboilers of distillation columns [4]. Unfortunately, this enormous amount of energy is introduced in the bottom of the column and approximately the same amount of energy is removed in the top, but at significantly lower temperature, which renders a very inefficient process, but also one of the most effective for the separation of mixtures.

The general separation problem was defined more than 40 years ago by Rudd and Watson [5] as the transformation of several source mixtures into several product mixtures. Interestingly in 1983 Westerberg [6] claimed that this problem was essentially unsolved. Nowadays we can say that this general problem has not been completely solved. We will focus on the more restricted, and much more studied problem of separating a single source mixture into several products using only distillation columns. In general, to separate a complex mixture a sequence of columns is necessary. However, before going into the details of column sequencing it is useful to provide some optimization background and the corresponding methods for the approximate and rigorous optimization of a single column.

Optimization Background

The economic optimization of a distillation column involves the selection of the number of trays and feed location, as well as the operating conditions to minimize the total investment and operating cost. Continuous decisions are related to the operating conditions and energy involved in the separation, while discrete decisions are related to the total number of trays and the tray positions of each feed and product streams. If we consider as well, the order in which the separation is performed –It is possible to find significant differences in total cost and energy consumption between a good sequence and a bad one [6]. As the number of components increases, the number of possible alternatives can be enormous and the selection of the correct sequence becomes a major challenge.

Using an equation based environment there are two major formulations for the mathematical representation of problems involving discrete and continuous variables: Mixed-Integer Non Linear Programming (MINLP) and Generalized Disjunctive Programming (GDP) [7]. Both approaches have been employed in literature to model distillation columns.

MINLP methods.

The most common form of MINLP problems is the special case in which 0-1 variables are linear while the continuous variables are nonlinear:

$$\begin{aligned} \min : & \; Z = \mathbf{c}^T \mathbf{y} + f(\mathbf{x}) \\ s.t. & \; \mathbf{Dy} + \mathbf{h}(\mathbf{x}) = \mathbf{0} \\ & \; \mathbf{By} + \mathbf{g}(\mathbf{x}) \le \mathbf{0} \\ & \; \mathbf{x} \in X, \quad \mathbf{y} \in \{0,1\}^m \end{aligned} \qquad \text{(MINLP)}$$

Major methods for solving MINLP problems include Branch and Bound [8-10] which is an extension of the linear case, except that NLP sub-problems are solved at each node. Generalized Benders Decomposition (GDB) [11, 12]. Outer Approximation (OA) [13-16] are iterative methods that solve a sequence of alternate NLP sub-problems and MILP master problems that predict lower bounds and new values for the 0-1 variables. The difference between GBD and OA methods lies in the definition of the MILP master problem. The OA method uses accumulated linearizations of the objective function and the constraints, while GBD uses accumulated Lagrangean functions parametric in 0-1 variables. The LP/NLP based branch and bound [17, 18] essentially integrates both sub-problems within one tree search. The Extended Cutting Plane method (ECP) [19, 20] does not solve NLP problems and relies only on successive linearizations. All these algorithms can be classified in terms of the following basic sub-problems [7] that are involved in each of these methods:

NLP Subproblems:

a) NLP relaxation

$$\begin{aligned} \min : & \; Z_{LB} = \mathbf{c}^T \mathbf{y} + f(\mathbf{x}) \\ s.t. & \; \mathbf{Dy} + \mathbf{h}(\mathbf{x}) = \mathbf{0} \\ & \; \mathbf{By} + \mathbf{g}(\mathbf{x}) \le \mathbf{0} \\ & \; \mathbf{x} \in X, \\ & \; 0 \le y_j \le 1 \quad j \in REL \\ & \; y_i \in \{0,1\}^{m-|REL|} \end{aligned} \qquad \text{(NLP-R)}$$

Where the subset of binary variables REL are relaxed to continuous bounded by their extreme values (0-1). When the dynamic subset REL includes all the binary variables NLP-R corresponds to the continuous relaxation and provides an absolute lower bound to the MINLP problem.

b) NLP subproblem for fixed y^k.

$$\begin{aligned} &\min : Z_{UB}^{k} = \mathbf{c}^T \mathbf{y}^k + f(\mathbf{x}) \\ &s.t.\ \mathbf{D}\mathbf{y}^k + \mathbf{h}(\mathbf{x}) = \mathbf{0} \\ &\quad \mathbf{B}\mathbf{y}^k + \mathbf{g}(\mathbf{x}) \le \mathbf{0} \\ &\quad \mathbf{x} \in X \end{aligned} \qquad \text{(NLP)}$$

Which yields an upper bound to the MINLP problem, provided that this NLP problem has a feasible solution. If this is not the case, the following feasibility sub-problem must be solved.

c) Feasibility problems for fixed yk.

$$\begin{aligned} &\min : \ \beta \\ &s.t.\ \beta \ge \mathbf{s}^1 \\ &\quad \beta \ge \mathbf{s}^2 \\ &\quad \beta \ge \mathbf{u} \\ &\quad \mathbf{D}\mathbf{y}^k + \mathbf{h}(\mathbf{x}) = \mathbf{s}^1 - \mathbf{s}^2 \\ &\quad \mathbf{B}\mathbf{y}^k + \mathbf{g}(\mathbf{x}) \le \mathbf{u} \\ &\quad \mathbf{s}^1 \ge 0,\ \ \mathbf{s}^2 \ge 0,\ \ \mathbf{u} \ge 0 \\ &\quad \mathbf{x} \in X;\ \ \beta \in \Re^1 \end{aligned} \qquad \text{(NLP-F)}$$

This can be interpreted as the minimization of the infinity norm as a measure of the infeasibility of the corresponding NLP sub-problem. It should be noted that for an infeasible sub-problem the solution of the NLP-F yields a positive value of the scalar beta.

Master (MILP) cutting plane:

The convexity of the nonlinear functions is exploited by replacing them with supporting hyperplanes, that are generally, but not necessarily, derived at the solution of the NLP sub-problem. In particular, the new binary values (y^{k+1}) are obtained from a MILP cutting plane problem that is based on K points (x^k) k= 1,2,… K generated at the K previous steps.

$$\left.\begin{array}{ll}\min:\ Z_L^k = \alpha & \\ s.t.\ \ \alpha \geq \mathbf{c}^T\mathbf{y} + f(\mathbf{x}^k) + \nabla f\left(\mathbf{x}^k\right)^T\left(\mathbf{x}-\mathbf{x}^k\right) & \\ \quad sign(\lambda_j)\left[\mathbf{d}_j^T\mathbf{y} + h_j(\mathbf{x}^k) + \nabla h_j\left(\mathbf{x}^k\right)^T\left(\mathbf{x}-\mathbf{x}^k\right)\right] \leq 0 & j \in J \\ \quad \mathbf{b}_i^T\mathbf{y} + g_i(\mathbf{x}^k) + \nabla g_i\left(\mathbf{x}^k\right)^T\left(\mathbf{x}-\mathbf{x}^k\right) \leq 0 & i \in I \end{array}\right\} k = 1, 2, 3....\ K$$

$$x \in X;\ y \in \{0,1\}^m \qquad \text{(M-MILP)}$$

where λ_j are the multipliers of the corresponding equation $j \in J$ in the NLP problem. The index j makes reference to the equations in J and the index i to the inequalities in I. The solution of M-MILP yields a valid lower bound to the original MINLP problem, which is non-decreasing with the number of linearization points K.

The different methods can be classified according to their use of the sub-problems (NLP-R; NLP, NLP-F) and the specific specialization of the M-MILP, as seen in Figure 1.

FIGURE 1

Generalized Disjunctive Programming

An alternative approach for representing discrete – continuous optimization problems is by using models consisting of algebraic constraints, logic disjunctions and logic propositions [21-25] This approach not only facilitates the development of the models by making the formulation intuitive, but it also keeps in the model the underlying logic structure of the problem that can be exploited to find the solution more efficiently. The general structure of a GDP can be represented as follows [26]:

$$\begin{array}{l} \min Z = f(x) + \sum_{k \in K} c_k \\ s.t.\ \ g(x) \leq 0 \\ \quad \bigvee_{i \in D_k} \begin{bmatrix} Y_{i,k} \\ r_{i,k}(x) \leq 0 \\ c_k = \gamma_{i,k} \end{bmatrix} \quad k \in K \\ \quad \Omega(Y) = True \\ \quad x^{Lo} \leq x \leq x^{Up} \\ \quad x \in \Re^n,\ c_k \in \Re^1,\ Y_{i,k} \in \{True, False\} \end{array} \qquad \text{(GDP)}$$

where $f : R^n \to R^1$ is a function of the continuous variables x in the objective function. $g : R^n \to R^1$ belongs to the set of global constraints, the disjunctions $k \in K$, are composed of a number or terms $i \in D_k$, that are connected by the OR operator. In each term there is a Boolean variable $Y_{i,k}$, a set of inequalities $r_{i,k}$: $R^n \to R^m$, and a cost variable c_k. If $Y_{i,k}$ is True then $r_{i,k} \le 0$ and $c_{i,k} = \gamma_{i,k}$ are enforced, otherwise they are ignored. The $\Omega(Y) = True$ are logic propositions for the Boolean variables expressed in the conjunctive normal form:

$$\Omega(Y) = \underset{t=1,2\ldots T}{\wedge} \left[\underset{Y_{i,k} \in R_t}{\vee} \left(Y_{i,k}\right) \underset{Y_{i,k} \in Q_t}{\vee} \left(\neg Y_{i,k}\right) \right] \qquad \text{(CNF)}$$

where for each clause t, $t = 1, 2, 3 \ldots T$, R_t is the subset of Boolean variables that are non-negated, and Q_t is the subset of Boolean variables that are negated. It is assumed that the logic constraints $\underset{i \in D_k}{\vee} Y_{i,k}$ are included in the general equation $\Omega(Y) = True$

In order to take advantage of the existing MINLP solvers, GDPs are often reformulated as an MINLP problem and solved using the standard solvers. In order to do so, two main transformations can be used in which the disjunctive constraints are expressed in terms of algebraic equations and the propositional logic is expressed in terms of linear equations.

The disjunctive constraints in (GDP) can be transformed by using either the big-M (BM) [27] or the convex hull reformulation (CH) [23].

The BM reformulation is as follows:

$$\begin{aligned} & r_{i,k}(x) \le M\left(1 - y_{i,k}\right) \; i \in D_k,\, k \in K \\ & \sum_{i \in D_k} y_{i,k} = 1 \qquad\qquad k \in K \\ & x \in R^n \\ & y_{i,k} \in \{0,1\} \qquad\quad i \in D_k,\, k \in K \end{aligned} \qquad \text{(BMR)}$$

Where the variable $y_{i,k}$ has a one to one correspondence with the Boolean variable $Y_{i,k}$. If the binary variable takes a value of one the inequality constraint is enforced; otherwise, if the parameter M is large enough the constraint becomes redundant.

The CH reformulation can be written as follows:

$$
\begin{array}{ll}
x = \sum_{i \in D_k} v^{i,k} & k \in K \\
y_{i,k} r\left(v^{i,k} / y_{i,k} \right) \le 0 & i \in D_k;\ k \in K \\
y_{i,k} x^{Lo} \le v^{i,k} \le y_{i,k} x^{Up} & i \in D_k;\ k \in K \\
\sum_{i \in D_k} y_{i,k} = 1 & k \in K \\
x \in R^n, \quad v^{i,k} \in R^n, \quad y_{i,k} \in \{0,1\} & i \in D_k;\ k \in K
\end{array} \qquad \text{(CHR)}
$$

There is also a one to one correspondence between disjunctions in GDP and CH. The size of the problem is increased by introducing a new set of disaggregated variables $v^{i,k}$ as well as new constraints. On the other hand, as proved in Grossmann and Lee [28] and extensively discussed by Vecchietti et al [29] the convex hull reformulation is at least as tight and generally tighter than the BM when the discrete domain is relaxed which can impact the efficiency of MINLP solvers since they rely heavily on the quality of those relaxations.

It is worth remarking that the term $y_{i,k} r\left(v^{i,k} / y_{i,k} \right) \le 0$ is convex if $r_{i,k}(x)$ is a convex function, but requires an adequate approximation to avoid singularities. Sawaya & Grossmann [30] proposed the following reformulation which yields an exact approximation for values of binaries equal to one or zero, for any value of $\varepsilon \in [0,1]$ in where the feasibility and convexity are maintained:

$$
y_{i,k} r\left(v^{i,k} / y_{i,k} \right) \approx \left[(1-\varepsilon) y_{i,k} + \varepsilon \right] r\left(v^{i,k} / \left[(1-\varepsilon) y_{i,k} + \varepsilon \right] \right) - \varepsilon r_{i,k}(0)(1 - y_{i,k}) \qquad (1)
$$

It should be note that the approximation in (1) assumes that $r_{i,k}(x)$ is defined in $x=0$ and that the inequality $y_{i,k} x^{Lo} \le v^{i,k} \le y_{i,k} x^{Up}$ is enforced.

The propositional logic in terms of Boolean variables, Conjunctions (AND operator) Disjunctions (OR operator), negations, implications, equivalences (double implications) and exclusive disjunctions (XOR operator) is transformed in a set of linear algebraic constraints in terms only of binary variables [24, 31, 32] (again there is a one to one relationship between binary and Boolean variables). This set of new linear equations is only feasible if the original set of logical propositions is true. This transformation can be done systematically through a set of three recursive steps to get the logic in its conjunctive normal form. Once the logic is expressed in its conjunctive normal form the transformation is straightforward. Details of the procedure can be found, for example in the text book by Biegler et al [32]. The final result is a set of linear equations than can be added either in the BMR or in the CHR problems:

$$\begin{aligned} &\mathbf{A\,y} \le \mathbf{b} \\ &\mathbf{y} \in \{0,1\}^m \end{aligned} \tag{2}$$

In order to fully exploit the logic structure of the GDP problems, two other solution methods have been proposed for the case of convex nonlinear GDP problems; the Disjunctive Branch and Bound (DBB) [23] and the Logic Based Outer Approximation (LBOA) method [33].

The basic idea of the disjunctive branch and bound is to directly branch on the constraints corresponding to particular terms in the disjunctions, while considering the convex hull of the remaining disjunctions. Although the tightness of the relaxation at each node is comparable with the obtained when solving the CH reformulation, the size of the problems solved are smaller and the numerical robustness improved.

For the case of Logic Based Outer Approximation methods, the idea is similar to the OA for MINLP problems. The main idea is to solve iteratively a Master problem given by a linear GDP problem, which will give a lower bound of the solution and a NLP sub-problem that will give an upper bound. The fixed values of the Boolean variables determine which equations must be included in each in each NLP sub-problem:

$$\begin{aligned} &\min:\ Z = f(x) + \sum_{k\in K} c_k \\ &s.t.\ \ g(x) \le 0 \\ &\qquad \left.\begin{aligned} r_{i,k}(x) &\le 0 \\ c_k &= \gamma_{i,k} \end{aligned}\right\} for\ \ Y_{i,k} = True;\ \ i \in D_k,\ k \in K \\ &\quad x^{Lo} \le x \le x^{Up} \\ &\quad x \in R^n,\ c_k \in R^1 \end{aligned} \tag{S-NLP}$$

As only the constraints that belong to the active terms in the disjunction are imposed the result is a reduced size S-NLP compared to the direct application of OA in the MINLP reformulation. The initialization requires that all the terms in the disjunctions appear at least once in any NLP, so it is initially necessary to solve a set of S-NLP subproblems to accomplish this requirement. The Master linear GDP can then be written as follows:

$$
\begin{aligned}
&\min Z = \alpha + \sum_{k \in K} c_k \\
&s.t.\ \left.\begin{aligned} &\alpha \geq f(x^l) + \nabla f(x^l)^T \left(x - x^l\right) \\ &g(x^l) + \nabla g(x^l)^T \left(x - x^l\right) \leq 0 \end{aligned}\right\} \ l = 1,\ 2,\ 3 \ldots L \\
&\bigvee_{i \in D_k} \left[\begin{gathered} Y_{i,k} \\ r_{i,k}(x^l) + \nabla r_{i,k}(x^l)^T \left(x - x^l\right) \leq 0 \quad l \in L_{i,k} \\ c_k = \gamma_{i,k} \end{gathered} \right] \ k \in K \\
&\Omega\left(Y\right) = True \\
&x^{Lo} \leq x \leq x^{Up} \\
&\alpha \in R^1;\ x \in R^n;\ c_k \in R^1;\ Y_{i,k} \in \left\{True,\ False\right\};\ i \in D_k,\ k \in K
\end{aligned}
\tag{M-LGDP}
$$

Optimization of a single distillation column.

The optimization of distillation columns involves the selection of the number of trays, the feed location and the operating conditions to minimize a performance function, usually the total investment and operating costs. Discrete decisions are related to the calculation of the number of trays and feed and products location, and continuous decisions are related to the operation conditions. Due to the discrete-continuous nature of the problem and to the complex equations involved, it is common use shortcut or aggregated models together with some rules of thumb that under some assumptions have proved to produce good results, at least in the first stages of design where a rigorous design is neither necessary nor convenient due to the large computational effort needed. Taking this fact into account, we first show an overview of the most used shortcut methods and then we will present the alternatives for rigorous optimization of a single column.

Shortcut methods.

Fenske – Underwood – Gilliland (FUG)

The most used and successful method for distillation design is the method of Fenske-Underwood – Gilliland [34-36] (FUG). The FUG method assumes a constant molar overflow and constant relative volatilities in all the trays of the distillation column. Although these conditions seem too restrictive they can be applied to a large class of mixtures (i.e. hydrocarbon separations, alcohols, etc). This method considers two extreme ideal situations. a) The distillation column operates at total reflux (no feed is entering or exiting from the column), which allows calculating the minimum number of trays for a given separation of two key components, and b) when the column operates at pinch conditions, (infinite number of trays), which allows calculating the minimum reflux. The optimal situation is in some point in between these two extreme cases.

If we assume a total reflux (see Figure 2) the equilibrium equations for the key components at the reboiler are:

$$\begin{aligned} (y_{LK})_R &= K_{LK}(x_{LK})_R \\ (y_{HK})_R &= K_{HK}(x_{HK})_R \end{aligned} \qquad (3)$$

Dividing those equations:

$$\left(\frac{y_{LK}}{y_{HK}}\right)_R = \alpha_R \left(\frac{x_{LK}}{x_{HK}}\right)_R \qquad (4)$$

where $\alpha_R = \frac{K_{LK}}{K_{HK}}$

FIGURE 2

In the total reflux conditions, the feed, distillate and bottoms are all zero. An overall mass balance in the reboiler yields:

$$V = L \qquad (5)$$

A mass balance including the reboiler and a tray N (envelope 1 in Figure 2) gives the following equations:

$$\left.\begin{aligned} V(y_{LK})_R &= L(x_{LK})_N \\ V(y_{HK})_R &= L(x_{HK})_N \end{aligned}\right\} \Rightarrow \begin{aligned} (y_{LK})_R &= (x_{LK})_N \\ (y_{HK})_R &= (x_{HK})_N \end{aligned} \qquad (6)$$

The liquid composition of the reboiler stage, which is a given specification, is correlated with the liquid composition of the previous stage N, which can be consequently calculated.

Dividing equations in (6) and substituting in equation (4) we get:

$$\left(\frac{x_{LK}}{x_{HK}}\right)_N = \alpha_R \left(\frac{x_{LK}}{x_{HK}}\right)_R \tag{7}$$

Proceeding backwards from tray N to tray N-1 to N-2, and until we reach the composition of distillate stage, which is known we get:

$$\left(\frac{x_{LK}}{x_{HK}}\right)_D = \alpha_1 \cdot \alpha_2 \cdot \alpha_3 \cdot \ldots \cdot \alpha_{N-1} \cdot \alpha_N \cdot \alpha_R \left(\frac{x_{LK}}{x_{HK}}\right)_R \tag{8}$$

Extending the procedure to all the stages in the distillation column and assuming an average relative volatility for all the stages, we finally get the well-known Fenske equation [34] that relates the minimum number of trays with the composition of key components in distillate and bottoms.

$$\left(\frac{x_{LK}}{x_{HK}}\right)_D = \alpha^{Nmin} \left(\frac{x_{LK}}{x_{HK}}\right)_R \tag{9}$$

The other extreme situation is when the column operates at minimum reflux conditions (infinite number of trays). In this situation the concentration profiles reach a ‘pinch point’ in which the concentrations do not change from one stage to another:

$$\begin{aligned} x_{j-1} &= x_j = x_{j+1} \\ y_{j-1} &= y_j = y_{j+1} \end{aligned} \tag{10}$$

A mass balance around the envelope 2 (Figure 2) in the rectifying section for all the i components yields:

$$V_{\min} y_{j+1,i} = L_{\min} x_{j,i} + D x_{D,i} \tag{11}$$

The equilibrium conditions for component i in tray (j+1) are given by:

$$y_{j+1.i} = K_i x_{j+1,i} \tag{12}$$

and because the pinch point conditions (equation (10)) it is equivalent to:

$$y_{j+1.i} = K_i x_{j,i} \tag{13}$$

The equilibrium constant of component i can be written in terms of relative volatility referred to component k:

$$K_i = \alpha_{i,k} K_k \tag{14}$$

Substituting equations (13) and (14) in (11) and taking the sum over all components:

$$\sum V_{min}\, y_{j+1,i} = \frac{\sum D\, x_{D,i}}{1 - \dfrac{L_{min}}{V_{min}\alpha_{i,k} K_k}} \tag{15}$$

Equation (15) is usually rewritten as follows:

$$V_{\min} = D \sum \frac{\alpha_{i,k}\ x_{D,i}}{\alpha_{i,k} - \dfrac{L_{\min}}{V_{\min} K_k}} \tag{16}$$

In the same way for the stripping section we reach:

$$-\overline{V}_{\min} = B \sum \frac{\alpha_{i,k}\ x_{B,i}}{\alpha_{i,k} - \dfrac{\overline{L}_{\min}}{\overline{V}_{\min} K_k}} \tag{17}$$

In conditions of minimum reflux, Underwood proved that

$$\phi = \frac{L_{min}}{V_{min} K_k} = \frac{\overline{L}_{min}}{\overline{V}_{min} K_k} = \overline{\phi} \tag{18}$$

Equations (17) and (18) allow solving the problem. However, because usually the feed to the system is completely specified it is convenient to substitute one of those equations by a linear combination of both as follows: Subtracting equations (17) and (18) and from an overall mass balance:

$$V_{\min} - \overline{V}_{\min} = \sum \frac{\alpha_{i,k}\left(D\, x_{D,i} + B\, x_{B,i}\right)}{\alpha_{i,k} - \phi} = \sum \frac{\alpha_{i,k}\ F\, z_{F,i}}{\alpha_{i,k} - \phi} = F(1-q) \tag{19}$$

where q is the liquid fraction in the feed. Values of q greater than 1 indicate a sub-cooled feed stream. Negative values indicate a superheated vapor.

Therefore, given the feed conditions, it is possible to use equation (19) to calculate the Underwood roots (ϕ). Equation (19) has N roots, but only N-1 correspond to values of ϕ with physical meaning and are bounded by the relative volatilities:

$$0 < \phi_1 < \alpha_N < \phi_2 < \alpha_{N-1} < \phi_3 < \ \ldots < \alpha_2 < \phi_N < \alpha_1 \tag{20}$$

Of those N-1 Underwood roots only those whose value is between the relative volatilities of the key components are active. Therefore, if the recovery of the key components is specified (i.e. > 95%) assuming that all the components lighter than the light key are obtained in the distillate and all the heavier than heavy key are obtained in the bottoms stream it is possible to use equation (19) to calculate the active Underwood roots and then equations (17) or (18) to determine the distribution of the intermediate non key components. i.e. if there are S intermediate non key components we have S+1 active underwood roots and from (17) we can write S+1 equations where the unknowns are the S molar fractions of the distributed components plus the minimum vapor flowrate.

The minimum number of theoretical trays and the minimum reflux are two extreme operating conditions; the actual operation must be some place in between. The optimum is usually located in values between 1.1 and 1.5 times the minimum reflux. To optimize the column a general shortcut method for determining the number of stages required for a multicomponent distillation at finite reflux ratios would be extremely useful. Unfortunately, such a method has not been developed. However, Gilliland [35] used empirical data to correlate the number of stages at finite reflux ratios with the number of stages and to the minimum reflux ratio. He presented his results in a graphical correlation using the following two parameters

$$Y = \frac{N - N_{\min}}{N+1} \qquad X = \frac{R - R_{\min}}{R+1} \tag{21}$$

Molokanov [37] fit the Gilliland correlation to the following equation

$$Y = 1 - \exp\left[\frac{1+54.4X}{11+117.2X}\left(\frac{X-1}{X^{0.5}}\right)\right] \tag{22}$$

Implicit in the application of the Gilliland correlation is that the theoretical stages must be optimally distributed between the rectifying and stripping sections. Again there is not an equation based on first principles that allow determining such a distribution, but according to Seader and Henley [38] a reasonably good approximation is given by Kirkbride equation [39].

$$\frac{N_R}{N_S} = \left[\frac{z_{HK}}{z_{LK}}\left(\frac{x_{LK,B}}{x_{HK,D}}\right)^2 \frac{B}{D}\right]^{0.206} \tag{23}$$

Application of the Kirkbride equation requires knowledge of the distillate and bottoms composition at the specified finite reflux ratio. Seader and Henley [39] suggest that the distribution of components at finite reflux is close to that estimated by the Fenske equation at total reflux conditions.

Due to the wide application of the FUG method it has been modified to deal with multiple feeds, side draws or complex column configurations [40-48]. Interestingly, the Underwood method can be extended to azeotropic systems [49]. The idea consists of treating azeotropes as pseudo-components. An N component system with A azeotropes is treated as an enlarged (N+A) component system. This enlarged system is divided into compartments, where each compartment behaves like a non-azeotropic distillation region formed by the singular points that appears in it.

Group Methods

Another approach that deserves especial attention is based on group methods. Group methods (GM) basically use approximate calculations to relate the outlet stream properties to the inlet stream specifications and number of equilibrium trays. These approximation procedures are called *group methods* because they provide only an overall treatment of the stages in the cascade without considering detailed changes in the temperature and composition of individual stages. However, they are much easier to solve because they involve fewer variables and constraints. They can be used to represent as cascade of trays in many countercurrent operations like absorption, stripping, distillation, leaching or extraction [50]. Although, due to its initial limitations. GM were used mainly in absorption, recent developments have reached excellent results in distillation [50].

Group methods were originally devised for simple hand calculations that were performed in an iterative manner. However, its equation based nature, allows its easy incorporation in a mathematical programming model. The specifications for the entering vapor V_{N+1} and the entering liquid L_0 are the inputs to the model. The method evaluates the properties of the outputs ($V_1; L_N$) in terms of the inputs and the characteristics of the cascade. In the following analysis we assume adiabatic operation and a known pressure drop in the cascade. The following presentation follows the lines of Kamath et al [50]

The fundamental equations for the group contribution methods are the mass and energy balance in the cascade:

$$\begin{aligned} &V_{N+1}\, y_{N+1,i} + L_0\, x_{0,i} = V_1 y_{1,i} + L_N\, x_{N,i} \quad i \in C \\ &V_{N+1}\, H_{N+1} + L_0 h_0 = V_1 H_1 + L_N h_N \end{aligned} \tag{24}$$

Where C refers to the set of components.

The performance equation of the cascade, derived initially by Kremser in 1930 [51] is:

$$V_1\, y_{1,i} = V_{N+1,}\, y_{N+1,i}\, \phi_{A,i} + L_0 x_{0,i}\left(1-\phi_{S,i}\right) \;\; i \in C \tag{25}$$

where $\phi_{A,i}$, $\phi_{S,i}$ denote the recovery factors for absorption and stripping sections.

There are $2\left(|C|+1\right)$ variables in the model given by (24) and (25). We have $\left(2|C|+1\right)$ independent equations – C mass balances, C performance equations and the energy balance-, therefore we have one degree of freedom.

The recovery factors in equation (25) are given by,

$$\phi_{A,i} = \frac{A_{e,i}-1}{A_{e,i}^{N+1}-1}; \quad \phi_{S,i} = \frac{S_{e,i}-1}{S_{e,i}^{N+1}-1} \quad i \in C \tag{26}$$

where $A_{e,i}$, $S_{e,i}$ are the effective absorption and stripping factors, and represent average values for all the trays contained in the cascade. Edmister [52] proposed the following average scheme:

$$\begin{aligned} A_{e,i} &= \left[A_{N,i}\left(A_{1,i}+1\right)+0.25\right]^{0.5} - 0.5 \\ S_{e,i} &= \left[S_{1,i}\left(S_{N,i}+1\right)+0.25\right]^{0.5} - 0.5 \end{aligned} \tag{27}$$

Equation (27) uses factors at the top and bottom of the cascade. These factors are in turn calculated using the following expressions,

$$\left.\begin{aligned} A_{1,i} &= \frac{L_1}{K_{1,i}V_1}; \quad A_{N,i} = \frac{L_N}{K_{N,i}V_N} \\ S_{1,i} &= \frac{1}{A_{1,i}}; \quad S_{N,i} = \frac{1}{A_{N,i}} \end{aligned}\right\} i \in C \tag{28}$$

Equation (28) introduces two new variables L_1 and V_N, that do not appear previously in the model. Therefore, the model has three degrees of freedom. Different approaches have been used with GM that differ on how these three degrees of freedom are satisfied.

Kresmer [51] proposed the following three approximations:

$$\begin{aligned} L_1 &= L_0 \\ V_N &= V_{N+1} \\ T_N &= \frac{T_0 + T_{N+1}}{2} \end{aligned} \tag{29}$$

Kremser did not included the energy balance and instead used the following approximation,

$$T_1 = \frac{T_0 + T_{N+1}}{2} \tag{30}$$

Kremser assumed that there was not too much change either in the liquid in the first stage or in the vapor in the last stage. Besides, he used identical approximations for temperatures of the vapor and liquid streams exiting the cascade and they are both considered to be equal to the arithmetic mean of the temperature of entering vapor and liquid streams. Although these seem crude approximations, it is necessary to take into account that Kremser developed the model for recovery the gasoline from natural gas where only a small fraction is absorbed.

Edmister [53], for the case of distillation systems proposed a different set of approximations to satisfy the three degrees of freedom. However, he proposed different equations depending on whether the cascade is an absorber or a stripper. For the absorber they are,

$$V_N = V_{N+1}\left(\frac{V_1}{V_{N+1}}\right)^{1/N} \tag{31}$$

$$\frac{T_N - T_1}{T_N - T_0} = \frac{V_{N+1} - V_2}{V_{N+1} - V_1} \tag{32}$$

$$L_1 = L_0 + V_2 - V_1 \tag{33}$$

Equation (31) gives an approximation for V_N assuming that the vapor contraction per stage is the same percentage of the vapor flow to that stage. Equation (32) assumes that the temperature change of the liquid is proportional to volume of gas absorbed. Finally, equation (33) is a rigorous mole balance for L1, but it contains the new variable V_2 that can be approximated by an analogous assumption to equation (31).

$$V_2 = V_1 \left(\frac{V_{N+1}}{V_1} \right)^{1/N} \tag{34}$$

For the stripping cascade the equations are similar to those for the absorber but the dependencies are in terms of the molar flow of liquid instead of vapor,

$$L_1 = L_0 \left(\frac{L_N}{L_0} \right)^{1/N} \tag{35}$$

$$\frac{T_0 - T_1}{T_0 - T_N} = \frac{L_0 - L_1}{L_0 - L_N} \tag{36}$$

$$V_N = V_{N+1} + L_{N-1} - L_N \tag{37}$$

$$L_{N-1} = L_N \left(\frac{L_0}{L_N} \right)^{1/N} \tag{38}$$

The major limitation of the Edmister approach is clearly that in complex cascades (i.e. multiple feeds and or side streams), for some of the sections is not clear whether such sections behave like a stripper or like an absorber. In order to overcome those limitations Kamath et al [50] proposed an alternate set of specifications for the degrees of freedom. The first two equations are based on the fact that since the outlet streams are coming out of first and last tray of the cascade, they must be under vapor-liquid equilibrium. Hence, for the outlet vapor they imposed that it should be at dew point conditions:

$$\sum_{i \in C} \frac{y_{1,i}}{K_{1,i}} = 1 \tag{39}$$

Besides, the outlet liquid must be saturated liquid,

$$\sum_{i \in C} K_{N,i}\, x_{N,i} = 1 \tag{40}$$

Note that these two equations are not approximations and try to capture the physical behavior of the system. To satisfy the third degree of freedom Kamath and coworkers proposed the following equation:

$$L_1 - L_N = V_1 - V_N \tag{41}$$

Equation (41) is based on an approximation of mole balance with an assumption that the decrease in vapor at the bottom is approximately equal to the increase in liquid at the top and vice versa.

Aggregated Models

Caballero & Grossmann [54] using as base the work on heat and mass transfer networks proposed by Bagajewicz & Manousiouthakis [55] proposed an aggregated model based on mass balances and equilibrium feasibility, expressed in terms of flows, inlet concentrations, and recoveries. The energy balance can then be decoupled from the mass balance and the utilities can be calculated for each separation task. The main assumptions for this model are:

Each single column is divided into two sections (two mass exchange zones). In each of the sections the molar flow rate of vapor and liquid are assumed to be constant.

The pinch point can be located only in the extreme points of the sections. If this is not the case, this behavior must be 'captured' a priori in order to correctly implement the model. Feasibility of mass exchange is established when both ends of a mass exchanger's operating line lie below the equilibrium curve (and above if the equilibrium curve is based on the heavier component). Since the liquid curve is concave, thermodynamic feasibility of mass exchange can be verified by examining the end points at each stream. In a multicomponent mixture the feasibility constraints will depend on the separation that the column performs. For example, in a column with three components, say A B and C, in which we want to perform the separation A/BC (A is the most volatile and C the least) the following constraints must hold at the ends of the streams:

$$y_A \le K_A x_A; \quad y_i \ge K_i x_i \quad i = B, C \tag{42}$$

The model for a column is as described below:

It is assumed that the pinch point can be in the extreme points of each section. Therefore for a conventional distillation column there are four pinch point candidates: S = [s ϵ(top, mt, mb, bot) | pinch point candidates] where mt is the bottom part of the top section, and mb is the top of the bottom section.

Overall mass balances for each section:

$$\left.\begin{array}{l} Vin_{i,mt} + Lin_{i,top} = Vin_{i,top} + Lin_{i,mt} \\ Vin_{i,bot} + Lin_{i,mb} = Vin_{i,mb} + Lin_{i,bot} \end{array}\right\} \quad i \in COM \qquad (43)$$

$$\left.\begin{array}{l} V_s = \sum_i Vin_{i,s} \\ L_s = \sum_i Lin_{i,s} \end{array}\right\} \quad i \in COM, \ s \in S \qquad (44)$$

$$V_{top} = V_{mt}; \ V_{mb} = V_{bot} \quad L_{top} = L_{mt}; \ L_{mb} = L_{bot} \qquad (45)$$

where V_{in}, L_{in} make reference to the flowrate of the individual components in the vapor and liquid respectively, and *L, V* are the overall liquid and vapor molar flow rate respectively.

Overall mass balance

$$F_i = pt_i + pb_i \qquad i \in COM \qquad (46)$$

where *F* is the individual flow rate of the component i in the feed, and *pt* and *pb* are the individual flow rates of the top and bottom products respectively.

Mass and Energy Balances in the feed section

It is assumed that the feed is introduced at its bubble point and it mixes with the liquid stream.

$$F_i + Lin_{i,mt} + Vin_{i,mb} = Lin_{i,mb} + Vin_{i,mt} \quad i \in COM \qquad (47)$$

$$\left.\begin{array}{l} \sum_i F_i h_i + \sum_i Lin_{i,mt} h_{i,mt} + \sum_i Vin_{i,mb} H_{i,mb} = \\ \sum_i Lin_{i,mb} h_{i,mb} + \sum_i Vin_{i,mt} H_{i,mt} \end{array}\right\} \quad i \in COM \qquad (48)$$

where *H, h* correspond to the specific enthalpies of the vapor and liquid respectively.

Mass balances in condenser and reboiler, that are treated as splitters:

$$\left.\begin{aligned} &Vin_{i,top} = pt_i + Lin_{i,top} \\ &pt_i = \eta_1\, Vin_{i,top} \\ &Lin_{i,top} = (1-\eta_1) Vin_{i,top} \end{aligned}\right\} \quad i \in COM \tag{49}$$

$$\left.\begin{aligned} &Lin_{i,bot} = pb_i + Vin_{i,bot} \\ &pb_i = \eta_2\, Lin_{i,bot} \\ &Vin_{i,bot} = (1-\eta_2) Lin_{i,bot} \end{aligned}\right\} \quad i \in COM \tag{50}$$

where η_1, η_2 are split fractions to be determined and COM is the set of components.

Equilibrium equations

The equations are not restricted to any particular equilibrium model. In general,

$$K_{i,s} = f(x_{1s}, x_{2s}, \ldots x_{ns},, P, T_s) \qquad i \in COM, \; s \in S \tag{51}$$

where *K* is the equilibrium constant,. $x_{j,s}$ ($j = 1, 2 \ldots n$) is the molar fraction of the component j in the liquid fraction at position s in the column, *P* is the pressure in the column and *T* the temperature in section s of the column.

It is assumed that a total condenser is used, and that the bottom product is extracted from the reboiler as liquid. Therefore, all products are saturated liquids. Of course these equations can be modified to deal with vapor products:

$$\left.\begin{aligned} &\sum_i pt_i\, K_{i,con} = \sum_i pt_i \\ &\sum_i pb_i\, K_{i,reb} = \sum_i pb_i \end{aligned}\right\} \quad i \in COM \tag{52}$$

where ‘reb’ and ‘con’ make reference to the reboiler and condenser, respectively.

The temperature increases from the top to the bottom of the column.

$$T_{con} \le T_{top} \le T_{mt} \le T_{mb} \le T_{bot} \le T_{reb} \tag{53}$$

The feasibility pinch constraints can be generalized as follows. These constraints have two functions. First, they represent the pinch constraints, and second they distribute the non-key components:

$$\frac{Vin_{i,s}}{V_s} \leq K_{i,s} \frac{Lin_{i,s}}{L_s} \qquad i \in COM, \ \ s \in S \tag{54}$$

if the product i is mostly present in the top of the column, or

$$\frac{Vin_{j,s}}{V_s} \geq K_{j,s} \frac{Lin_{j,s}}{L_s} \qquad j \in COM, \ \ s \in S \tag{55}$$

if the product j is mostly present in the bottom of the column.

A recovery factor (*f*) can be fixed for each component,

$$F_i \, f_i \leq pt_i \ \ or \ \ F_i \, f_i \leq pb_i \qquad i \in COM \tag{56}$$

depending on whether the product is obtained as a top or bottom product.

In the original work the authors used the vapor flow rate as objective function. Since the column has two sections they minimize the maximum of those two flows in the column.

$$Min \ \ Max(V_{top}, V_{bot}) \tag{57}$$

Defining a new variable α it is possible to transform the min-max problem to a regular minimization problem as follows:

$$\begin{aligned} & Min \ \alpha \\ & \ \ s.t. \ \ \alpha \geq V_{top} \\ & \qquad \ \ \alpha \geq V_{bot} \end{aligned} \tag{58}$$

Note that the previous model given by equations (43) to (58) only includes mass balances, and an energy balance in the feed section.

It is worth noting that equations (43) to (56) represent the aggregation of the equations of a tray by tray model. In particular, the mass balance equations (43,44,45, 46, 47, 49, 50) represent a linear combination of component mass balance in each tray with the assumption of equimolar flow. The enthalpy balances are relaxed since they are removed, except for the feed tray in equation (48). Finally the equilibrium equations are relaxed by two inequalities (54) and (55) which are imposed at the extremes of each section. Thus, if the same thermodynamic model is used, the aggregated model will yield a lower bound in the vapor flows with respect to a rigorous tray by tray model with equimolar flows. Furthermore, if the heat of vaporization decreases with relative volatility, the model also predicts a lower bound of the utilities (in this case energy balances are added to the reboiler and condenser). This is due to the relaxation of the equilibrium equations, which in turn will overpredict recoveries of lighter than key component.

Introducing heat balances in the reboiler and condenser allows calculating heat duties and temperatures that are useful for heat integration or to use another objective function including specific costs for utilities.

One of the keys of the success of the FUG approach and to a lesser extent the GM and aggregated model is because it is possible to include all the equations in a mathematical programming model and determine the optimal operating conditions and investment costs. This approach is commonly used either for the preliminary design of a single column or for determining the best or more promising sequences of distillation columns in the separation of multicomponent mixtures, as will be shown in next sections.

Some other methods that had acquired importance are:

The Boundary Value Method. (BVM) Proposed by Levy et al [56] and extended with different works over the last 25 years [57-62], can be used to determine the minimum reflux ratio and feasible design parameters for a column separating a ternary homogeneous mixture. This BVM requires fully specified product compositions, the feed composition and the thermal condition of the feed. Once these specifications have been made, only one degree of freedom remains between the reflux and boil-up ratios. Specifying the reflux (or boil-up) ratio, the rectifying and stripping profiles can be calculated starting from the fully specified products. If these two profiles intersect the separation is feasible. The number of trays, composition profiles etc are then obtained. The optimal operating conditions can be obtained by iterative calculations. Julka and Doherty [60] extended the BVM to multicomponent mixtures. In this case, a split is feasible if two stages that lie on the composition profile of two different sections have the same liquid composition.

The Rectification Body Method (RBM). Proposed by Bausa et al [63] for the determination of minimum energy requirements of a specified split. For a given product, branches of the pinch point curves can be found. Rectification bodies can be constructed by joining points on the branches with straight lines. For either section of a column a rectification body can be constructed. The intersection of the rectification bodies of two sections of a column indicates its feasibility. The RBM can be used to calculate the minimum reflux ratio and minimum energy cost and to test the feasibility of a split. Because faces on rectification bodies are linearly approximated by joining branches of pinch point curves using straight lines, this method cannot guarantee accurate results. No information about column design (number of stages and operating reflux ratio) is obtained. The calculation of pinch point curves is, furthermore, computationally intensive [49].

Reversible distillation model (RDM). Developed by Koehler et al [64] This model assumes that heat can be transferred to and from a column at zero temperature difference and that no contact of non-equilibrium liquid and vapor streams is allowed. Reversible distillation path equations are derived by rearranging the column material balances as well as the equilibrium relationships for the most and least volatile components. The solution of this reduced set of equations requires that the flowrates of the most and least volatile components be specified at the feed plate. Numerical methods based on any reversible distillation model require knowledge of the products that can be achieved by the distillation before starting the computations for finding the minimum reflux.

The **driving force method** proposed by Gani & Bek-Pedersen [65]. It is a simple graphical method based on driving force for separation. Here the separation driving force is defined as $F_{Di}=|y_i-x_i|$, where the subscript i=LK denotes the light key component. Gani and Bek-Pedersen proved that the minimum or near minimum energy requirements generally correspond to a maximum in the driving force. The proposed method is quite simple and applies to two product distillations with N stages.

The **shortest stripping line** approach, developed by Lucia & Taylor [66] and extended by Lucia et al [67, 68]. The authors showed that exact separation boundaries for ternary mixtures are given by the set of locally longest residue curves (or distillation lines at infinite reflux) from any given unstable node to any reachable stable node. They also showed that the longest residue curve is related with the highest energy consumption for a given separation. Then the shortest curve should result should produce the minimum energy required for the same separation. The concept of shortest stripping lines can be extended to find minimum energy requirements in reactive distillation, hybrid separation processes, and reaction/separation/recycle systems regardless of the underlying thermodynamic models.

Although some of previous methods have been automated, not all of them can be easily included within a deterministic optimization algorithm. But in this context they are valuable tools for getting precise initial values and reliable bounds on the main variables for the rigorous design of distillation columns.

Rigorous tray by tray optimization models.

As commented above, the economic optimization of a distillation column involves the selection of the number of trays and feed location, as well as the operating conditions to minimize the total investment and operating cost. Continuous decisions are related to the operational conditions and energy involved in the separation, while discrete decisions are related to the total number of trays, and the tray positions of each feed and product streams. A major challenge is to perform the optimization using tray by tray models that assume phase equilibrium.

MINLP models

The simplest type of distillation design problem is the one where there is a fixed number of trays, and the goal is to select the optimal feed tray location [69]. Figure 3 shows that a superstructure that can be postulated is one where simply the feed is split into as many as there are trays, excluding condenser and reboiler. Of course the candidate trays can be constrained to a given set of trays according to the knowledge that the designer has about the physical behavior of the column. This is in essence the superstructure that was proposed by Sargent and Gaminibandara in 1976 [70]. The model can be easily written as a MINLP model by considering all the mass and enthalpy balances, phase equilibrium equations and that molar fraction summation equals 1 in each phase (MESH equations). In addition, the following mixed-integer constraints must be added:

Let $z_i : i \in FLOC$ denote the binary variable associated to the selection of 'i' as the feed tray. *FLOC* denote the set of trays in which the feed can enter the column, and $F_i \ i \in FLOC$ denote the amount of feed entering tray i.

$$\begin{aligned}
&\sum_{i \in FLOC} F_i = F \\
&\sum_{i \in FLOC} z_i = 1 \\
&F_i - F z_i \le 0 \qquad i \in FLOC \\
&z_i \in \{0,1\};\ F_i \ge 0 \quad i \in FLOC
\end{aligned} \tag{59}$$

The second and third constraints in (59) assure that the feed is entering in a single tray, this follows from the fact that only one tray can be selected (second constraint in (59)) and that if the tray $i \in FLOC$ is selected as the feed tray, the amount of feed entering other locations is zero because if $z_j = 0,\ j \ne i$ then the third equation in (59) forces the flow $F_j \le 0 \ j \ne i$.

FIGURE 3

An interesting property of the MINLP for fixed number of trays is that computational experience has shown that this problem is frequently solved as a relaxed NLP. The physical explanation is that one can expect the optimal distribution to be one where the feed is all directed into a single tray where the compositions matches closely the composition of the feed [69, 71-73].

Besides the MESH equations and the constraints in (59), specification on purity, recovery of some components is distillate or bottoms, etc. must be added to completely define the MINLP model.

When the objective is to optimize, not only the feed tray position but also the number of trays, the complexity of the model greatly increases as shown in the model by Viswanathan and Grossmann in 1993 [72] These authors proposed a superstructure that involves a variable reflux location as depicted in Figure 4. The basic idea was to consider a fixed feed tray with an upper bound of trays specified above and below the feed. The reflux is then returned to all trays above, and the reboil returned to all trays below the feed. Basically, this model determines which are the optimal tray locations for the reflux and reboil streams. The model relies on the MESH equations in each tray; specification on recoveries, purities, etc. The variable reflux / reboil return can be modeled as described bellow.

FIGURE 4

Defining the following sets:

$$
\begin{aligned}
&T = \{t \mid is\ a\ tray\ in\ the\ column\} \\
&RF_T = \{t \mid Candidate\ tray\ \ for\ reflux\ return\} \\
&RB_T = \{t \mid Candidate\ tray\ \ for\ reboil\ return\}
\end{aligned}
$$

Let Ld, Vr be the reflux and reboil flow rate returned to the column respectively, and let $r_t \quad t \in RF_t;\quad b_t \quad t \in RB_t$ be binaries that takes the value 1 if the reflux /reboil is returned to the tray t.

$$
\begin{aligned}
&Ld = \sum_{t \in RF_t} ref_t \\
&ref_t \le Ld^{Up}\, r_t \quad t \in RF_t \\
&Vr = \sum_{t \in RB_t} reb_t \\
&reb_t \le Vr^{Up}\, b_t \quad t \in RB_t \\
&Ld \ge 0,\ Vr \ge 0 \\
&ref_t \ge 0,\ r_t \in \{0,1\} \quad \forall t \in RF_t \\
&reb_t \ge 0,\ b_t \in \{0,1\} \ \forall t \in RB_t
\end{aligned}
\qquad (60)
$$

Viswanathan and Grossmann [72] also extended the model to include more than a single feed. The model is a combination of the two presented above; the different feeds are able to go to any tray in the column (or a subset of trays previously selected) and the reflux and reboil streams are postulated to return to a subset of different trays.

While in principle this model is suitable for optimizing the feed tray location and the number of trays, a major difficulty is related to the non-existing trays. In these trays, there is a zero liquid flow (rectifying section) or a zero vapor flow (stripping section), which can produce numerical problems due to the convergence of equilibrium equations with a zero value in the flow of one of the phases. In other words, the vapor-liquid equilibrium equations must be satisfied in trays where no mass transfer takes place.

Despite the increase of the computational time of the model and convergence problems, the model of Viswanathan and Grossmann has been successfully applied by different research groups. For example, Ciric and Gu [74] used the MINLP approach for the synthesis of ethylene glycol via ethylene oxide in a kinetic controlled reactive distillation column. Bauer and Stichlmair [75] applied the MINLP approach to the synthesis of sequences of azeotropic columns. Dünnebier and Pantelides [76] used the model to generate sequences of thermally coupled distillation columns.

The superstructure presented by Viswanathan and Grossmann (See Figure 4) is not the only possible alternative for the simultaneous determination of the feed tray position and the total number of trays. Barttfeld et al [71] studied the impact of different representations and models that can be used for the optimization of a single distillation column. Figure 5 shows three representations that are different to the original by Viswanathan and Grossmann that achieve the same objective. First, in Figure 5a a condenser and a reboiler are placed in all candidate trays for exchanging energy. This means that a variable reflux /reboil stream is considered by moving the condenser /reboiler. Otherwise, in the representation of variable reflux location Figure 4 the condenser and reboiler are fixed equipment. These two alternatives are the same if one fixed equipment is considered at each column ends. However, when variable heat exchange locations are modeled as a part of the optimization procedure some differences arise. In one case the problem consists of finding the optimal location for the energy exchanged, while in the other the optimal location for a secondary feed stream (reflux /reboil) is considered. The variable heat exchange has an important advantage; the energy can be exchanged at intermediate trays temperatures, possibly leading to more energy efficient designs [77]. The results have shown that the most energy efficient MINLP representation involves variable reboiler and feed tray location Figure 5b.

FIGURE 5

GDP Models

Yeomans and Grossmann [78] proposed a Generalized Disjunctive Programming model that overcomes the numerical difficulties of the MINLP models. The basic idea consist of dividing the trays in the distillation column in permanent trays (they exist in all the cases) and conditional trays (they can exist or not, depending on the optimal solution). For each existing tray the mass and energy transfers are taking into account and modeled using the MESH equations: component mass balances, tray energy balance, equilibrium equations and the summation of liquid and vapor mole fractions equal to 1. For a non-existing or inactive tray the model considers a simple bypass of liquid and vapor streams without mass or energy transfer, which give rise to trivial mass and energy balance equations (inlet and outlet flows and enthalpies are equal for both liquid and vapor phases). Because the MESH equations include the solution for trivial mass and energy balances, the only difference between existing and non-existing trays is the application of the equilibrium equations. As for the permanent trays, all the equations for an existing tray apply. Figure 6 shows a superstructure for this approach.

FIGURE 6

Conceptually the GDP model for the design of a single distillation column can be written as follows:

$$\begin{aligned}
&\min: \ Z = Total\ \ Annual\ \ Cost \\
&s.t. \\
&\quad MESH\,equations\ \ for\ \ permanent\ \ trays \\
&\quad Mass\,/\ Energy\ \ balances\ \ for\ conditional\ trays \\
&\quad purity,\ recovery...\ constraints \\
&\quad \begin{bmatrix} Y_t \\ Equilibrium\ \ equations \end{bmatrix} \vee \begin{bmatrix} \neg Y_t \\ Bypass\ \ equations \\ (Input - Output\ \ relationships) \end{bmatrix} \quad t \in CondTrays \\
&\quad \Omega(Y) = True
\end{aligned} \tag{61}$$

The logical relationships in equation (61) are necessary to avoid the degeneracy due to equivalent solutions, i.e. in a given distillation section two solutions with the same number of trays but different distribution. This problem can be solved forcing all existing trays to be consecutive. For example, assuming that the trays are numbered from the top to the bottom of the column:

$$\begin{aligned} &Y_t \Rightarrow Y_{t+1} \quad t \in REC \\ &Y_t \Rightarrow Y_{t-1} \quad t \in STR \end{aligned} \tag{62}$$

where REC, STR make reference to the set of conditional trays in the rectifying and stripping sections respectively. In that way all the existing trays will be around the permanent feed tray.

As in the case of MINLP models, Barttfeld et al. [71] considered different representations for the GDP model with fixed and variable feeds as shown in Figure 7. The computational results showed that the most effective structure is the one with fixed feed, which was the original representation used by Yeomans and Grossmann [78]

FIGURE 7

As mentioned above, GDP formulations provide better numerical behavior than MINLP models, but because of the nonlinearities and non-convexities inherent to the distillation models, both MINLP and GDP formulations require good initial values and bounds to converge. Getting good initial values is not straightforward. Barttfeld et al [79] proposed a preprocessing phase to generate good initial estimates. The column topology in this phase corresponds to the one used for the economic optimization, except that the number of trays is fixed to the maximum specified. This means that the same upper bound on the number of trays has to be employed as well as the potential feed and product location. The initial design considered is the one that involves the minimum reflux conditions as well as minimum entropy production. This reversible separation provides a feasible design, and hence a good initial guess to the economic optimization. For the case of zeotropic columns, overall mass and energy balances are formulated as an NLP problem to compute the reversible products. This formulation is a well behaved problem that provides initial values and bounds for the rigorous tray-by-tray optimization problem.

Another options is to start with a simpler representation of the column through some shortcut method, and successively increase the complexity of the model using the results of previous steps to initialize the following, both at the level of model or even in the solution algorithm. For example, Harwardt and Marquardt [80] for the design of Internally Heat Integrated Distillation Columns (HIDiC) and vapor recompression (VRC) used a multistep approach. The results of a shortcut step, such us the minimum energy demand and the concentration profile estimated based on pinch points, were used to initialize the optimization. Based on these results a simplified model that comprises only component mole balances and equilibrium relations, but no energy balances, is solved. In subsequent solution steps the energy balance was included again and the model resolved. Two extra interesting modifications were added to the model. First, the vapor-liquid equilibrium calculations were performed as an external user defined function, in other words they were dropped from the equation based environment and solved as an implicit external function. This approach reduces the size of the optimization problem and enhances the flexibility to choose more complex thermodynamic models. Second, to solve the problem they use the so called successive relaxed MINLP (SR-MINLP) proposed by Kraemer et al [81]. They proposed to reformulate the MINLP or GDP problems as pure continuous problems with tailored big-M constraints, where all discrete decisions are represented by continuous variables. The discrete decisions are enforced by non-convex constraints that force the continuous variables to take discrete values. In this form the GDP problem is reformulated as

$$
\begin{aligned}
&\min Z = f(x) + \sum_{k \in K} c_k \\
&s.t.\ \ g(x) \le 0 \\
&\quad r_{i,k}(x) \le M_{i,k}\left(\sum_{j \in D_k \setminus \{i\}} y_{j,k}\right) \\
&\quad -M_{i,k}\left(\sum_{j \in D_k \setminus \{i\}} y_{j,k}\right) \le c_k - \gamma_{i,k} \le M_{i,k}\left(\sum_{j \in D_k \setminus \{i\}} y_{j,k}\right) \\
&\quad Ay \le b \\
&\quad \varphi_{FB}\left(y_{i,k}, \sum_{j \in D_k \setminus \{i\}} y_{j,k}\right) = 0 \quad i \in D_k, k \in K
\end{aligned}
\tag{R-GDP}
$$

Equation φ_{FB} is the so called Fischer-Burmeister function that constitutes the special constraints which force the integer decisions, in which at most one $y_{i,k}$ must be one.

$$y_{i,k} + \sum_{j \in D_k \setminus \{i\}} y_{j,k} - \sqrt{y_{i,k}^2 + \left(\sum_{j \in D_k \setminus \{i\}} y_{j,k} \right)^2} = 0 \qquad (63)$$

Due to the non-convex nature of (63), this continuous reformulation suffers from the drawback that the quality of the local optimal solution is highly dependable on the specific initial values to start the solution procedure. To counter this drawback of the continuous reformulation these authors relax the Fischer – Burmeinsteir according to:

$$y_{i,k} + \sum_{j \in D_k \setminus \{i\}} y_{j,k} - \sqrt{y_{i,k}^2 + \left(\sum_{j \in D_k \setminus \{i\}} y_{j,k} \right)^2} - M_{FB} \leq 0$$

The resulting SR-MINLP is solved in a sequential solving procedure where the problem is tightened with each step by reducing the value of the Big-M parameters.

Even with all these difficulties, complex problems have been successfully solved, including reactive distillation [74, 82]; azeotropic sequences [75, 83, 84] or hybrid membrane/distillation systems [85] among others.

While the results reported in this work have shown that there has been significant progress in the optimal design of complex distillation columns, it is clear that significant research is still needed in this area. For instance, the generation of a superstructure to azeotropic systems of more than three components remains an open question. The integration of these rigorous synthesis models as a part of a flowsheet superstructure has not been accomplished. At this point this has only been performed with short cut models. Finally, a major challenge that remains is the rigorous global optimization.

Synthesis of Distillation Sequences

As commented in the introduction, the general separation problem was defined more than 40 years ago by Rudd and Watson [5] as the transformation of several source mixtures into several product mixtures. In this chapter we will focus on the more restricted, and much more studied, problem of separating a single source mixture into several products using only distillation columns. Focusing even more, we look in particular at two kinds of problems: when the product sets contain non overlapping species with each other –sharp separations- or when there are overlapping species –nonsharp separations-. The nature of these two problems requires different solution approaches. In the case of sharp separations we can differentiate two cases; when each distillation column performs a sharp separation between consecutive keys, and when non-sharp separations are allowed in some columns –nonconsecutive keys-. Historically, sharp separation sequences were assumed to be performed by conventional columns that are columns having one feed and producing two products, and including a reboiler and a condenser. Here, we will follow this approach. Later we will show that this case arises naturally as a particular case of the more general thermally coupled distillation.

Sharp separation. Only conventional columns

The problem receiving the most and earliest attention has been the sharp separation of a single source mixture using conventional columns. The problem of enumerating the sequences without heat integration is straightforward [6]. However, the selection of the best alternative in terms of total cost or/and energy consumption is not so easy due to the large number of feasible alternatives when the number of components to be separated increases. The earliest attempts were based on case studies in order to develop heuristics with the objective of selecting the preferred structure [86-88]. Sets of heuristics are due to Rudd, Powers & Siirola [89] and Seader & Westerberg [90].

The first approaches using optimization algorithms used the tree search of alternatives. Thomson and King [91] used a heuristic, pseudo algorithm search that was almost a branch and bound search. It could fail by cycling but, when it worked it was very fast [6]. Hendry and Hughes [92] proposed a dynamic programming algorithm. Other important papers of these first works are in references [93-95]

Superstructures

According to Grossmann et al [96] in the application of mathematical programming techniques to design and synthesis problems it is always necessary to postulate a superstructure of alternatives. This is true whether one uses a high level aggregated model, or a fairly detailed model. While in some cases this is more or less straightforward, this in not true in the general case. The alternative representations of MINLP or GDP structures for a single column presented above shows that even in simple cases the representation is not unique. There are two major issues that arise in postulating a superstructure. The first is, given a set of alternatives that are to be analyzed, what are the major types of representations that can be used, and what are the implications for the modeling. The second, is for a given representation that is selected, what are all the feasible alternatives that must be included to guarantee that the global optimum is not overlooked.

As for types of superstructures, Yeomans and Grosmann [97] have characterized two major types of representation using the concepts of Tasks, States and Equipment. A State is the minimum set of physical and chemical properties needed to characterize a stream in a given context. They can be quantitative like pressure or temperature, or qualitative, i.e. mixture of BCD indicating that we have a stream formed by the compounds BCD inside some specifications which does not exclude the presence or other compounds. A Task is the chemical or physical transformation that relates two or more states. The Equipment is the physical device in which a task is performed.

The first major representation is the State-Task-Network which is motivated by the work in scheduling by Kondili, Pantelides and Sargent [98]. The basic idea here is to use only a representation that uses only two types of nodes: States and Tasks. See Figure 8. The assignment of equipment is dealt implicitly through the model. Both the case of one-task one-equipment (OTOE) in which a given task is assigned a single equipment or the variable task equipment assigned (VTE), in which a given task can be performed by different equipment were considered. The second representation is the State Equipment Network (SEN) that was motivated by the work of Smith [99]. In this case the superstructure uses two nodes; states and equipment, which assumes an a priori assignment of the different tasks to equipment based on the knowledge of the designer about the process. See Figure 9

FIGURE 8

FIGURE 9

Linear models for sharp split columns

One of the first approaches to synthesize distillation sequences using MILP methods is due to Andrecovich and Westerberg [100], The following presentation, although with some modifications is based on their work.

If it is consider that a fixed pressure and reflux ratio, then by performing short-cut calculations with any of the methods previously presented, it is possible to obtain linear mass balance relationships in terms of the feed flow rates as given by the following equation:

$$\begin{aligned} d_i &= \gamma_i f_i \\ b_i &= (1-\gamma_i) f_i \end{aligned} \tag{64}$$

where d_i, b_i represent the mass flowrates of components in the distillate and bottoms, and γ_i are the corresponding recovery fractions that are typically obtained from the mass balance in the short-cut model for a selected feed composition. By assuming the fractions γ_i to be constant, it is clear that equation (64) reduces to a linear expression. It is possible to consider a further simplification without significantly increasing the error that consists of assuming 100% recoveries of key components in each column. It is possible to determine a priori for each column the composition and total flow (or the component molar flow) entering the column.

From the above assumptions, in 1985 Andrecovich and Westerberg [100] proposed to model the heat duties of the condenser and reboiler and the capital cost in terms of the total flow rate entering each column. Assuming the same loads in condenser and reboiler, the heat duties for column k can be expressed as the linear functions:

$$Q_k = K_k F_k \tag{65}$$

where K_k is a constant derived from a shortcut calculation. Finally, the annualized cost of the column, that includes the fixed charge cost model for investment and the utility cost will be given by:

$$C_k = \alpha_k y_k + \beta_k F_k + (c_H + c_C) Q_k \tag{66}$$

where α_k is the annualized fixed charge cost in terms of the 0-1 binary variable y_k, β_k is the size factor for the column in terms of the total flow entering that column, and

c_H, c_C are the unit costs for the heating and cooling in the reboiler and condenser respectively.

It is worth noting that instead of using the K_k factors, or assuming the same loads in condenser and reboiler, or even assuming a linear size factor with the flow, it is possible to perform a rigorous optimization of each separation and exactly obtain the heat loads and optimal sizes of each possible distillation column, and therefore obtain the optimal separation sequence with the only approximation of 100% recovery.

Based on previous considerations, Andrecovich and Westerberg postulated the superstructure shown in Figure 10. Note that this superstructure corresponds to a State Task Network (STN) with an a priori assignment of tasks to equipment (One Task One Equipment –OTOE-) according to the Yeomans & Grossmann classification [97].

FIGURE 10

The model, a modification of the original proposed by Andrecovich & Westerberg can be written as follows:

Index sets

COL	[k | k is a column]
S	[m| m is a mixture] (i.e. ABCD, ABC, AB, BC, A, …)
COMP	[i| i is a component]
IP(m)	[m| m is an intermediate mixture] (i.e. AB, ABC, BCD, …)
TN(m)	[m | m is a terminal mixture] (i.e. A. B, C, D…)
SD(m,k)	[Distillate of column k goes to mixture m]
SB(m,k)	[Bottoms of column k goes to mixture m]
SF(m,k)	[mixture m is the feed of column k]
Init(k)	[columns k that have as feed the initial mixture]

Variables

$F_{k,i}, D_{k,i}, B_{k,i}$ Individual molar flow rates of Feed. Distillate and Bottoms of column k

Q_k Heat load in column k

$$
\begin{aligned}
&\min : Total\ \ Cost = \sum_{k \in COL} \alpha_k y_k + \beta_k F_k + \left(C_H + C_C\right) Q_k \\
&s.t. \\
&\quad F_0 z_i = \sum_{k \in Init} F_{k,i} \quad \forall i \in COMP \\
&\quad \sum_{k \in SD(m,k)} D_{k,i} + \sum_{k \in SB(m,k)} B_{k,i} = \sum_{k \in SF(m,k)} F_{k,i} \quad i \in COMP\ m \in IP \\
&\quad \sum_{k \in SD(m,k)} D_{k,i} + \sum_{k \in SB(m,k)} B_{k,i} = F_0 z_i \quad i \in COMP\ m \in TN \qquad \text{(A-W)} \\
&\quad Q_k - K_k \sum_{i \in COMP} F_{k,i} = 0 \quad k \in COL \\
&\quad F_{k,i} = D_{k.i} + B_{k,i} \qquad k \in COL;\ i \in COMP \\
&\quad D_{k,i} = F_{k,i} \qquad k \in COL;\ i \in COMP\ /\ i \le light\ key \\
&\quad F_{k,i} \le U y_k \qquad k \in COL;\ i \in COMP
\end{aligned}
$$

The first three constraints in the (A-W) model correspond to the mass balance in the initial node, in intermediate nodes and in terminal nodes, respectively. The fourth constraint represents the relation between the total flow and the heat load for a given column, equivalent to equation (65). The fifth and sixth constraints are the mass balances in a given column including the total sharp separation of keys (that must be consecutive). Finally, the last constraints force the variables to be zero if the column is not selected.

Nonlinear models for sharp split columns

In some situations the assumptions made for linear models can introduce significant errors. For instance, the feed entering at each possible column cannot be calculated a priori because the assumption of 100% recoveries of key components does not holds true. In this case, the calculation of a given column in the sequence and the determination of the optimal column sequence must be performed simultaneously.

Due to the mathematical complexity associated with a rigorous distillation column, the optimal determination of column sequences has been generally carried out using shortcut methods. But even with those shortcut methods, there is an intrinsic relationship between the superstructure, the model complexity and its associated numerical performance. Although there are other alternatives that will be briefly commented at the end of this section, we will focus here in the models related to the two superstructures commented above: STN and SEN.

Although the general problem consists of separating an N component mixture in M groups of compounds ($M \le N$) in such a way that any of this groups contains a key component that must be sharp separated from the rest (i.e. separate C3-C4-C5-C6 hydrocarbons), for the sake of simplicity and without loss of generality, we can assume that we want to sharp separate an N component mixture in its N pure constituents using conventional columns and consecutive keys. Under these conditions, generating an STN superstructure is straightforward: we only need to identify the states, the possible tasks and simply join the task with the states. For example, in a zeotropic four component mixture (ABCD) ordered by decreasing volatilities the states correspond to each of the possible mixtures. ABCD, ABC, BCD, AB, BC, CD. The possible tasks are the following:

From ABCD:	A/BCD	AB/CD	ABC/D
From ABC:	A/BC	AB/C	
From BCD:	B/CD	BC/D	
From AB	A/B		
From BC:	B/C		
From CD:	C/D		

Then the resulting superstructure is the one shown in Figure 8. It is possible to go a step further and assign a distillation column to each of the tasks. Then the STN approach reduces to the superstructure proposed by Andrecovich and Westerberg [100], see Figure 10.

Using the Underwood shortcut model the STN formulation can be written as follows:

Let define the following index sets

IP	m | m is an intermediate state (i.e. ABC; BCD; AB …)
IF	m | m is a final state (i.e. A, B, C…)
COL	k | k is a column (task) in the superstructure

FS_F	Columns k whose feed is the initial mixture
FS_m	Columns k whose feed is an intermediate state m
DS_m	Columns k that produce state m as a distillate
BS_m	Columns k that produce state m as a bottom stream
DP_m	Columns k that produce final product m as a distillate
BP_m	Columns k that produce final product m as a bottom stream
COM	i | i is a component in the mixture

The variables of the problem are

FT_k; $F_{i,k}$	Molar flow, total and of component i, entering the column k
DT_k; $D_{i,k}$	Distillate molar flows in column k
BT_k; $B_{i,k}$	Bottoms molar flows in column k
$V1_k, L1_k$	Molar flows of vapor and liquid in rectifying section of column k
$V2_k, L2_k$	Molar flows of vapor and liquid in stripping section of column k
Y_k	Boolean variable. True if the column k is selected

Data:

F_{0i}	Component molar flow entering the system
rec_i	Component recoveries.

The GDP model can be written as follows:

$$
\begin{array}{l}
\min: \sum_{k\in COL} (Total\ cost)_k \\
s.t. \\
\quad \sum_{k\in FS_F} FT_k = F_o \ ; \quad \sum_{k\in FS_F} F_{i,k} = F_{oi} \\
\quad \sum_{k\in DS_m} D_{i,k} + \sum_{k\in BS_m} B_{i,k} = \sum_{k\in FS_m} F_{i,k} \quad \forall i\in COM;\ m\in IP \\
\quad \sum_{k\in DP_m} D_{i,k} + \sum_{k\in BP_m} B_{i,k} \geq rec_i\ Fo_i \quad i\in COM \\
\quad \left[\begin{array}{c}
Y_k \\
F_{i,k} = D_{i,k} + B_{i,k} \quad i\in COM \\
V1_k = DT_k + L1_k \\
L2_k = BT_k + V2_k \\
FT_k + V2_k + L1_k = V1_k + L2_k \\
FT_k = \sum_{i\in COL} F_{i,k} \\
DT_k = \sum_{i\in COL} D_{i,k} \\
BT_k = \sum_{i\in COL} B_{i,k} \\
\sum_{i\in COM} \dfrac{\alpha_i F_{i,k}}{\alpha_i - \varphi_r} = V1_k - V2_k \\
\sum_{i\in COM} \dfrac{\alpha_i F_{i,k}}{\alpha_i - \varphi_r} = V1_k \\
Total\,cost_k = f\left(V1, V2, L1, L2\ldots\right)
\end{array}\right]
\vee
\left[\begin{array}{c}
\neg\, Y_k \\
F_{i,k} = 0 \\
D_{i,k} = 0 \\
B_{i,k} = 0 \\
V1_k = 0 \\
V2_k = 0 \\
L1_k = 0 \\
L2_k = 0 \\
FT_k = 0 \\
DT_k = 0 \\
BT_k = 0
\end{array}\right] \quad k\in COL \\
\quad \Omega(Y) = True
\end{array}
\qquad \text{(M-STN)}
$$

The first three constraints are mass balances in the initial feed node, in the intermediate states and in the final states (products), respectively. The disjunctions include all the equations to be solved if a given column is selected. The logical relationships are basically connectivity equations that can be obtained from the superstructure. For a 4 component mixture the logical relationships are the following:

$$
\begin{array}{l}
Y_{A/BCD} \underline{\vee} Y_{AB/CD} \underline{\vee} Y_{ABC/D} \\
Y_{A/BCD} \Rightarrow Y_{B/CD} \vee Y_{BC/D} \\
Y_{ABC/D} \Rightarrow Y_{A/BC} \vee Y_{AB/C} \\
Y_{AB/CD} \Rightarrow Y_{A/B} \wedge Y_{C/D} \\
Y_{A/BC} \Rightarrow Y_{ABC/D} \wedge Y_{B/C} \\
Y_{AB/C} \Rightarrow Y_{ABC/D} \wedge Y_{A/B} \\
Y_{BC/D} \Rightarrow Y_{A/BCD} \wedge Y_{B/C} \\
Y_{B/CD} \Rightarrow Y_{A/BCD} \wedge Y_{C/D} \\
Y_{A/B} \Rightarrow Y_{AB/CD} \vee Y_{AB/C} \\
Y_{B/C} \Rightarrow Y_{BC/D} \vee Y_{A/BC} \\
Y_{C/D} \Rightarrow Y_{AB/CD} \vee Y_{B/CD}
\end{array}
\qquad (67)
$$

In general, generating a SEN superstructure is not so straightforward, because the designer has to decide a priori which equipment to use. However, in this particular case, we know that we need exactly N-1 distillation columns (N is the number of components). The problem is then to assign a possible set of tasks to each distillation column in such a way that all the feasible alternatives are included. Figure 9 shows one possibility for a 4 component mixture, although the assignment of tasks to columns is not unique. It is interesting to note that Novak et al [101] used this suprestructure before the formalization by Yeomans and Grossmann [97]

In the SEN superstructure the logic of the problem is transferred to the selection of the particular task that a given column must perform and then to the streams connecting the different columns, but all the particular equations for a given column becomes in permanent equations. Like in the STN approach, using the Underwood equations, the model can be written as follows:

Let define the following index sets

COL	k | k is a column
Task	t | t is a separation task
CT_{kt}	t | task t is assigned to column k
ST	s| s is a stream
DF_{kk}	Indicates that there is a distillate stream from column k to column kk
BF_{kk}	Indicates that there is a bottoms stream from column k to column kk
$PD_{i,k}$	Pure product i is produced as distillate in column k
$PB_{i,k}$	Pure product i is produced as a bottom stream in column k
SZ_t	Stream s that does not exist (zero flow) if task t is selected.

The variables of the problem are

FT_k; $F_{i,k}$	Molar flow, total and of component i, entering the column k
DT_k; $D_{i,k}$	Distillate molar flows in column k

$BT_k;\ B_{i,k}$	Bottoms molar flows in column k
$V1_k, L1_k$	Molar flows of vapor and liquid in rectifying section of column k
$V2_k, L2_k$	Molar flows of vapor and liquid in stripping section of column k
$ST_k;\ S_{i,k}$	Molar flow, total and of component i, of external feed flow that goes to the mixer at the inlet of column k

$$
\begin{aligned}
&\min: \sum_{k\in COL} \left(Total\ Cost\right)_k \\
&s.t.\quad F_{0,i} = \sum_{k\in COL} S_{i,k} \\
&\qquad S_{i,k} + \sum_{kk\in DF_k} D_{i,kk} + \sum_{kk\in BF_k} B_{i,kk} = F_{i,k} \quad i\in COMP;\ k\in COL \\
&\qquad \sum_{k\in PD_i} D_{i,k} + \sum_{k\in PB_i} B_{i,k} \ge rec_i\, F_{0,i} \qquad i\in COMP \\
&\qquad F_{i,k} = D_{i,k} + B_{i,k} \quad i\in COM \\
&\qquad V1_k = DT_k + L1_k \\
&\qquad L2_k = BT_k + V2_k \\
&\qquad FT_k + V2_k + L1_k = V1_k + L2_k \\
&\qquad FT_k = \sum_{i\in COL} F_{i,k} \\
&\qquad DT_k = \sum_{i\in COL} D_{i,k} \\
&\qquad BT_k = \sum_{i\in COL} B_{i,k} \\
&\qquad \sum_{i\in COM} \frac{\alpha_i\, F_{i,k}}{\alpha_i - \varphi_{r,k}} = V1_k - V2_k \\
&\qquad \sum_{i\in COM} \frac{\alpha_i\, F_{i,k}}{\alpha_i - \varphi_{r,k}} = V1_k \\
&\qquad Total\,cost_k = f\left(V1, V2, L1, L2 \ldots\right) \\
&\bigvee_{t\in CT_k} \begin{bmatrix} Y_{t,k} \\ \alpha_i \le \varphi_{r,k} \le \alpha_j \quad i=HK;\ j=LK \\ \left.\begin{array}{r} D_{i,k}=0 \\ B_{i,k}=0 \end{array}\right\} k\in SZ_t \end{bmatrix} \qquad\qquad (\text{M-SEN}) \\
&\qquad \Omega(Y) = True
\end{aligned}
$$

The first constraint is the mass balance in the node for the external feed. The second one represents mass balances in the mixers entering the column. The third one are recovery constraints. The rest before the disjunctions are the equations that define each distillation column. Inside the disjunctions only the specific equations that define the task assigned to each column are included. The logical relationships are the same that in the STN model.

When both models are re-formulated as MINLPs the SEN produce models with fewer number of equations, and in general more robust from a numerical point of view [54, 102]. However, the reformulation to MINLP is usually easier with a STN model.

Finally, It is worth noting that the SEN or STN approaches are not the only options for superstructure optimization. Between these two extreme alternatives there are a large number of superstructures with intermediate characteristics that can be generated by aggregation of some tasks or by an initial partial assignment of equipment; see reference [54] for an example. Other alternatives include the work by Bagajewicz and Manousiouthakis [55]. These authors developed a model in which a distillation column was considered as a composite heat and mass exchanger operation. Assuming constant countercurrent molar flow rate, the mass exchange inside the distillation columns, can be treated as a pure mass transfer operation. Therefore, in this case a distillation network could be treated as a separable heat/mass exchange network. Papalexandri and Pistikopoulos [103] introduced a multipurpose mass/heat transfer module as a building block of a systematic representation of conventional and non-conventional process units and process structures.

Heat integrated distillation sequences

In this section we will assume that the heat integration will only be considered between different separation tasks. Thus the possibility of synthesizing multi-effect columns will be excluded. The interested reader can find information about for example in the works by Andrecovich and Westerberg [100, 104]. In the rest of the section, for the sake of simplicity, we assume a single hot and a single cold utility (e.g. steam and cooling water), although the extension to multiple utilities is straightforward. The following model is based on the works by Paules and Floudas [105, 106] and Raman and Grossmann [107]. The starting point is a model that allows calculating a sequence of columns (shortcut, aggregated, rigorous) including specifically the heat loads and temperatures in condenser and reboiler, and their dependence with the column pressure. The model assumes that a given condenser could eventually exchange heat with any reboiler (and viceversa). See Figure 11.

FIGURE 11

If T_c^{reb} and T_c^{con} are the reboiler and condenser temperatures of column c, EMAT is the minimum exchanger approach temperature, and TS and TC are the temperatures of steam and cooling utility, the two following constraints apply:

$$\left.\begin{array}{l} T_c^{reb} \le TS - EMAT \\ T_c^{con} \ge TC + EMAT \end{array}\right\} c \in COL \qquad (68)$$

To consider the potential exchanges of heat, the variable QEX_{kj} is introduced, that is the amount of heat exchanged between the condenser of column *k* and the reboiler of column *j*. We also define the binary variable w_{kj} which is equal to 1 if the condenser of column *k* supplies heat to reboiler of column *j* and zero otherwise. Thus, the following conditional constraints apply:

$$\left.\begin{array}{l} QEX_{k,j} \le U_k w_{k,j} \\ T_k^{con} \ge T_j^{reb} + EMAT - U_{k,j}\left(1 - w_{k,j}\right) \end{array}\right\} k, j \in COL \;\; k \ne j \qquad (69)$$

If $w_{k,j}$ =1 the temperature of the condenser in column *k* must be larger than the temperature in the reboiler of column *j*. If $w_{k,j}$=0, the heat exchanged between the condenser of column *k* and the reboiler of column *j* is forced to be zero.

Heat balances must hold for cooling and heating utilities:

$$\left.\begin{array}{l} \sum\limits_{j \in COL} QEX_{c,j} + QC_c = Q_c^{reb} \\ \sum\limits_{j \in COL} QEX_{j,c} + QH_c = Q_c^{con} \end{array}\right\} c \in COL \qquad (70)$$

Finally, the logic constraints can be added that relate the existence of columns with the selection of matches:

If a column is not selected, the corresponding matches to that column cannot take place:

$$\left.\begin{array}{l} w_{j,k} \le y_k \\ w_{k,j} \le y_k \end{array}\right\} k, j \in COL;\; k \ne j. \qquad (71)$$

Either column j supplies heat to column k, or vice versa:

$$w_{j,k} + w_{k,j} \leq 1 \quad k, j \in COL; \quad k \neq j \qquad (72)$$

One interesting characteristic of the model in equations (68) to (72) is that can be 'added' to any existing process model. The only modification will be in the objective function to take into account the reduction in utilities consumption.

Synthesis of complex distillation sequences (Thermally coupled distillation).

From the point of view of energy requirements, separation sequences using conventional columns (a single feed with two product streams, a condenser, and a reboiler) suffer from an inherent inefficiency produced by the thermodynamic irreversibility during the mixing of streams at the feed, top, and bottom of the column [108]. 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 Petluyk and co-workers [108] showed that this inefficiency can be improved by removing some heat exchangers and introducing thermal coupling between columns, see Figure 12. 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, and under some circumstances, also the capital costs. A fully thermally coupled (FTC) configuration is reached when the entire vapor load is provided by a single reboiler and all the reflux by a single condenser, see Figure 13. Different researchers have shown that thermally coupled configurations are capable of typically achieving 30% energy reduction, when compared to conventional systems [109-111]. Halvorsen and Skogestad [112-114] proved that the minimum energy consumption for an N-component mixture is always obtained for the FTC configuration.

FIGURE 12

FIGURE 13

The first known thermally coupled system dates from 1949, due to Wright [115], now known as a divided wall column. While the final detailed theoretical study was developed by Petlyuk et al [108], the lack of reliable design methods and concerns about the operation and control of these columns have prevented their application. The discovery of the concept of “thermodynamically equivalent configuration” [116, 117], the further development of this new concept [118, 119] together with improved control strategies [120-124], have made complex columns a realistic alternative to conventional designs.

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

1) The energy must be supplied under the worst conditions, at the highest temperature in the reboiler and removed at the lowest temperature in the condenser, preventing, in some cases, the use of utilities such as medium or low pressure steam.
2) When using conventional columns, it is common to constrain the alternatives to sharp separations. For example, in a three-component mixture (ABC), sorted by volatilities, we postulate initially separations A from BC (A/BC) and AB from C (AB/C). However, in FTC distillation, we could introduce sloppy separations -an intermediate product is allowed to distribute along the column- and, therefore, we increase the number of column sections. This increase does not imply an increase in the number of columns, but usually an increase in the total number of trays. A detailed discussion on the number of column sections needed for a given separation can be found in Agrawal [125] and Caballero & Grossmann [126-129].
3) In FTC systems, the minimum vapor flow is that of the most difficult separation, and therefore some column sections will have larger 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 to sequences of simple columns. Instead, the

optimum configuration will be dependent on the specific mixture and feed conditions.

Therefore, the objective should be to find the optimal a sequence of columns in a search space that includes all the alternatives: from systems with only conventional columns and sharp split of consecutive keys to fully thermally coupled systems in which the vapor load for the entire system is supplied by a single reboiler and the reflux provided by a single reboiler going through all the intermediate alternatives.

Therefore, the first task consists of determining which are the characteristics that a feasible, eventually optimal, sequence must have. Depending on the number of distillation columns used to separate an N component mixture into N product streams, the sequence can be classified as more than N-1 column configurations, as exactly N-1 columns and less than N-1 column configurations.

The case of zeotropic mixtures, sequences with exactly N-1 columns, named basic configurations by Agrawal [130], are characterized by the following three features:

1. Mixtures (or states) with the same components are transferred only once from one distillation column to another.
2. A final product is obtained in a single location of the sequence.
3. The feed stream and all the intermediate mixtures are split into exactly two product streams by two columns sections.

Configurations that violate the first two features and obey the third produce sequences with more than N-1 columns. These configurations, also referred as non-basic, have higher operating cost than the best basic configuration [129, 131, 132]. Non basic configurations also tend to have higher capital cost due to the additional distillation columns, and therefore non-basic configurations can be removed from the search space.

Configurations that violate the third feature have higher operating cost than the best basic configuration due to increased heat duty, especially for getting high purity products. However, the reduced number of columns in some situations could compensate the extra energy consumption. In the literature some of these cases can be found, for example those due to Brugma,[133] or Kaibel [117], Kim et al [134] or Errico & Rong [135]. However in this work, we will focus only on basic configurations.

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

1. Sequences obeying the three distinguish features can always be arranged in N-1 columns although the total number of separation tasks can be larger. Consider the following example. We want to separate a four component mixture ABCD where the components are sorted by decreasing volatilities (A is the most volatile component, D the less). Say we perform the following separation tasks (AB/BCD that means separate A from CD letting the B component to be optimally distributed between distillate and bottoms; A/B; BC/CD; B/C and C/D). In this example we can identify 5 separation tasks, and this sequence can be performed using 5 distillation columns, but this sequence can be easily arranged in three distillation columns (See Figure 14). In fact it can be rearranged in 16 thermodynamically equivalent configurations using three distillation columns [119] (see next point)

FIGURE 14

2. When a thermal couple appears, the arrangement of separation tasks in the actual columns is not unique. Using the two flows of the thermal couple it is possible to move a column section from an actual column to another and obtain different arrangement of tasks in actual columns. Figure 15 shows an example. All the configurations obtained moving column sections using a thermal coupled are said to be thermodynamically equivalent. From the point of view of simulation all the temperatures, flows, concentrations etc. are the same. From a practical point of view there are some differences due to different pressure losses and some practical considerations in transfer, mainly of vapor streams. But at the preliminary design we can consider these configurations to be equivalent. A detailed discussion on thermodynamically equivalent configurations can be found in references [116, 118, 119, 136].

FIGURE 15

3. The total number of thermodynamically equivalent configurations can be very large. For example, in a five component mixture there are 203 basic configurations but more than 8000 arrangements in actual columns –most of them with very similar performance in terms of total cost-. To avoid this degeneracy it is convenient to represent a sequence in terms of the separation tasks involved instead of the particular equipment used to perform the separation. In other words, all the thermodynamically equivalent configurations perform the same sequence of separation tasks.

From the previous paragraphs some major considerations must be taken into account in order to develop a MINLP or GDP model to select the best column sequence:

1. A superstructure based on equipment (i.e. SEN) is not possible neither convenient if we want to avoid the degeneracy due to thermodynamically equivalent configurations.
2. A procedure is needed for estimating the cost of the tasks without assuming a specific column configuration.
3. A practical set of logical relationships is needed that allows constraining the search to basic configurations.

Related to superstructure representations the STN approach can be easily adapted to any complex zeotropic system. The procedure is equivalent to generating an STN superstructure for sharp split and consecutive keys but now including all the possible sharp splits between two non - necessarily consecutive keys. Figure 16 shows this superstructure for a 4 component mixture.

FIGURE 16

In the STN superstructure the number of tasks rapidly grows with the number of components. In order to use a more compact representation a superstructure obtained by the aggregation in a single ‘super-task’ of some task is used. See Figure 17. This superstructure is similar to that proposed by Sargent and Gaminibandara [70] in 1976, although here the bypasses are explicitly included to account for all the alternatives, and it is a task based approach instead of a column based approach.

FIGURE 17

Even though no particular configuration in actual columns is assumed, a given separation task is formed by two column sections: a rectifying and a stripping section (although maybe in the final arrangement of tasks in actual columns these two sections are placed in different columns). In this sense it is possible to consider a separation task like a pseudo-column which conceptually facilitates the modeling; i.e. it is possible to use any of the shortcut, aggregated or even rigorous models presented before to any of these pseudo-columns. With this approach it is also possible to calculate the cost of each column section. It is possible that the final cost of each column section slightly increases in the final arrangement in columns (i.e. by increasing the diameter of some sections in order to build a single diameter column). Taking also into account that the total number of actual columns is always N-1 and that operating costs do not depend on the particular arrangement in columns of a set of tasks, it is possible to accurately estimate the total annual cost of a sequence or at least to get a tight lower bound to the final cost.

As discussed in previous paragraphs a sequence of distillation columns that includes from conventional to fully thermally coupled columns must include the space of all the basic configurations

The first rule based algorithm for generating the full set of basic configurations was proposed by Agrawal [130]. Following this line, Ivakpour & Kasiri [137] later proposed a formulation in which distillation configurations are represented mathematically as upper triangular matrices. Independently Shah & Agrawal [138] presented an alternate matrix formulation in which distillation configurations are generated by exploring all possible instances of the presence or absence of transfer streams. Particularly, this last approach is very efficient for generating the full set of basic configurations. All these rule based approaches have proved to be effective when generating alternatives, but the enumeration of all the alternatives is, except in the case of a reduced number of alternatives, an inefficient strategy. These approaches can be easily adapted to metaheuristic optimization methods (i.e. genetic algorithms, Particle Swarm Optimization, etc.). However, formulating them within a deterministic mathematical programming framework is not obvious.

Based mainly on the observations in the seminal paper by Agrawal [125], Caballero & Grossmann [126, 128, 129] proposed a complete set of logical rules in terms of Boolean variables that implicitly include all the basic column configurations. These logical equations can be transformed into algebraic linear equations in terms of binary variables and integrated within a mathematical programming environment. The objective in those works was not to generate explicitly all the basic configurations, but to develop a set of logic equations that ensure a strong relaxation when solving the resulting MINLPs that include all the performance equations of the distillation columns, and trying to extract the best configuration without an explicit enumeration of all the alternatives. It is interesting to point out that Shah & Agrawal [138] proposed a valid alternative set of equations in terms also of binary variables that could also be integrated in a mathematical programming environment. However, their focus was on checking quickly if a given alternative is a basic one (with excellent performance). It was not in the performance when those equations are integrated with the model of the columns in a mathematical programming environment. In fact some of their equations can be obtained from the aggregation of some of the logic relations presented by Caballero & Grossmann [128, 129], and therefore a worse relaxation can be expected.

For the model and logical relationships it is necessary first to define the following index sets:

TASK = [t | t is a given task]

e.g. TASK= [(ABC/BCD), (AB/BCD), (ABC/CD), (AB/BC), (AB/C)
(B/CD), (BC/CD), (A/B), (B/C), (C/D)]

STATES = [s | s is a state]

e.g. STATES= [(ABCD), (ABC), (BCD), (AB), (BC), (CD),
(A), (B), (C), (D)]

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

e.g. IMS= [(ABC), (BCD), (AB), (BC), (CD)]

COMP = [i | i is a component to be separated in the mixture]

e.g. COMP = [A, B, C, D]

FS_T = [t | t is a possible initial task; Task that receives the external feed]

e.g. TASK [(A/BCD), (AB/BCD), (AB/CD), (ABC/BCD), (ABC/CD), (ABC/D)]

TS_s= [tasks t that the state s is able to produce]

e.g. TS_{ABCD}.= [(AB/BCD), (ABC/BCD) ,(ABC/CD)]
TS_{ABC} = [(AB/BC), (AB/C)]
TS_{BCD}= [(B/CD), (BC/CD)]

ST_s= [tasks t that are able to produce state s]

e.g ST_{ABC} = [(ABC/CD), (ABC/BCD)]
ST_{BCD} = [(AB/BCD), (ABC/BCD)]
ST_{AB} = [(AB/BCD), (AB/BC), (AB/C)]
ST_{BC} = [(AB/BC), (BC/CD)]
ST_{CD} = [(ABC/CD), (B/CD), (BC/CD)]

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

e.g. $RECT_{ABC}$ = [(ABC/CD), (ABC/BCD)]

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

$RECT_{BC}$ = [(BC/CD)]

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

e.g. $STRIP_{BCD}$ = [(AB/BCD), (ABC/BCD)]

$STRIP_{BC}$ = [(AB/BC)]

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

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

e.g. FP = [(A), (B), (C), (D)] do not confuse with components, although the name is the same.

P_REC_s = [tasks t that produce final product s through a rectifying section]

e.g. PRE_A = [(A/B)]
PRE_B = [(B/CD), (B/C)]
PRE_C = [(C/D)]

P_STR_s = [tasks t that produce final product s through a stripping section]

e.g. PST_B = [(A/B)]
PST_C = [(AB/C), (B/C)]
PST_D = [(C/D)]

and the following Boolean variables.

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

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

$$\bigvee_{t \in TS_t} Y_t \veebar R \quad ; \quad s \in COL \tag{L1}$$

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

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

$$\left.\begin{array}{l} \bigvee_{t \in RECT_S} Y_t \veebar R \\ \bigvee_{t \in STRIP_S} Y_t \veebar R \end{array}\right\} s \in STATES \tag{L2}$$

where R has the same meaning than in equation (L1). Note that if we want only systems with the minimum number of column sections at a given state, except products, it should be produced at most by one contribution. Note also that when at least a state is produced by two contributions, the number of separation tasks is not the minimum.

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

$$\bigvee_{t\in(P\_REC_s \cup P\_STR_s)} Y_t \ ; \quad s \in FP \tag{L3}$$

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. A given final product must always exist, produced by a rectifying section, by a stripping section or by both. Therefore an equivalent form of express this logical relationship is that if a final product is not produced by any rectifying (stripping) section the heat exchanger related to that product must exist.*

$$\left.\begin{array}{l} \neg\left(\bigvee_{t\in P\_REC_s} Y_t\right) \Rightarrow W_s \\ \neg\left(\bigvee_{t\in P\_STR_s} Y_t\right) \Rightarrow W_s \end{array}\right\} \ s \in FP \tag{L4}$$

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).*

$$\left(Y_t \wedge Y_k\right) \Rightarrow \neg W_s \quad \left\{\begin{array}{l} t \in RECT_s \\ k \in STRIP_s \\ s \in STATES \end{array}\right. \tag{L5}$$

6. *Connectivity relationships between tasks in the superstructure*

$$\left.\begin{array}{l} Y_t \Rightarrow \bigvee_{k\in TS_s} Y_k ; \quad t \in ST_s \\ Y_t \Rightarrow \bigvee_{k\in ST_s} Y_k \ ; \quad t \in TS_s \end{array}\right\} \ s \in STATES \tag{L6}$$

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

$$W_s \Rightarrow \bigvee_{ST_s} Y_t ; \quad s \in STATES \tag{L7}$$

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

$$\begin{array}{ll} Y_t \wedge W_s \Rightarrow WC_s & t \in RECT_s \\ Y_t \wedge W_s \Rightarrow WR_s & t \in STRIP_s \end{array} \tag{L8}$$

It is convenient to complete the pervious rule adding that:

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

$$\neg W_S \Rightarrow \neg WC_S \wedge \neg WR_S \quad s \in STATES \tag{L9}$$

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. Equations (L8,L9) force wc and wr to take integer values when y and w are integer. Therefore, the variables wr and wc do not increase the combinatorial complexity of the problem.

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

$$Y_t \Rightarrow Z_s ; \quad t \in ST_S \tag{L10}$$

$$Z_s \Rightarrow \bigvee_{t \in TS_s} Y_t \tag{L11}$$

Equation (L10) can 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 (L11) 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 to declare as binary either yt or zs , but not both. Whether yt is declared as binary zs can be declared as continuous between zero and one and vice-versa.

The previous equations ensure that any sequence of tasks and the selected heat exchangers is a feasible separation that can be arranged in N-1 distillation columns.

A detailed description of the model is too large for being included here. The interested reader is referred to the original works, references [126, 128, 129]. However, a conceptual model showing the most important points in the model is presented here. The following is referred to a pure STN superstructure:

The objective function is any performance measure of the system, i.e. total annualized cost:

$$\min : \mathrm{TAC} = \frac{r(1+r)^L}{(1+r)^L - 1}\left[Capital\ costs \right] + Operating\ costs \qquad (73)$$

where the capital cost are annualized assuming a depreciation interval of L and an interest rate r (typical values are r = 0.1; L = 10 year).

The disjunctions related with the existence of a given task:

$$\begin{bmatrix} Y_t \\ Equations\ of\ the\ task \\ (shortcut,\ aggregated,\ rigorous...) \\ Task\ \mathrm{cost}_t = f(V1, V2, L1, L2, ...) \end{bmatrix} \underline{\vee} \begin{bmatrix} \neg Y_t \\ x_t = 0 \\ Task\ cost_t = 0 \end{bmatrix} \qquad \text{(D-1)}$$

A graphical conceptual representation of this disjunction is shown in Figure 18

FIGURE 18

If an intermediate state (Zs) exists, this state could have associated a heat exchanger (Ws) or form a thermal couple. If there is a heat exchanger this can be a condenser or a reboiler. If the state does not exist then all flows related to that state must be zero. The conceptual graphical representation in Figure 19 illustrated this situation.

FIGURE 19

In the conceptual representation of Figure 19 the variable Z_S takes the value true if the state s exists and false, otherwise. It is important to recall that there is a one to one relationship between a sequence of tasks and a sequence of states. Therefore, the introduction of the new boolean variables Zs do not increase the combinatorial complexity of the model. Even more, if the problem is solved using a MINLP reformulation, it is necessary to define as binary variables those that are either related to tasks, Yt, or those that are related to states, Zs (the other can be defined as a continuous variables bounded between 0 and 1). The logical relationships will force the other set of variables to take the correct integer values.

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

The disjunction inside the first term in Figure 19 is related to the existence or not of a heat exchanger in a state (if Ws is True heat exchanger is selected). Again, it is worth noting that there is a one to one relationship between assigning heat exchangers to states or to tasks. The logical relationships force that if one is selected (i.e. tasks), the corresponding correct state is selected and vice versa. If the heat exchanger is selected, the equations are different depending if the heat exchanger is a condenser or a reboiler. The inner most disjunction (those related to WCs -True if heat exchanger is a condenser- or WRs -True if heat exchanger is a reboiler-) includes the energy balance in the condenser or reboiler and the cost equations.

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

A final state is a state related with a pure product, or in general with a stream that leaves the system (the sequence of columns), and then these states must always exist. The most volatile product will always have a condenser and the heaviest a reboiler. However, the rest could have a condenser or a reboiler if it is produced by a single contribution, or no heat exchanger at all if produced by two contributions. In this last case the internal liquid and vapor flows of at least one of the tasks that generate the state must be adjusted to satisfy the mass balances. The following conceptual disjunction shows this situation. Figure 20.

FIGURE 20

The only remaining equations are mass balances in the initial mixture and desired recoveries of each final product.

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Figure Captions

Figure 1. *Major steps involved in the MINLP algorithms*

Figure 2. *Column operating at total reflux*

Figure 3. *Superstructure for the feed tray location model.*

Figure 4. *Superstructure of Viswanathan and Grossmann.*

Figure 5. *MINLP distillation column representations. (a) Variable reboiler and condenser location. (b) Variable reboiler location. (c) Variable condenser location*

Figure 6. *Superstructure for GDP optimization.*

Figure 7. *Two alternative superstructures for GDP column optimization.*

Figure 8. *STN superstructure for the sharp separation of a 4 component zeotropic mixture.*

Figure 9. *SEN superstructure for the sharp separation of a 4 component zeotropic mixture.*

Figure 10. *Superstructure proposed by Andrecovich and Westerberg for the sharp separation of a four component mixture using sharp split and consecutive key components.*

Figure 11. *Superstructure for heat integration. All possible matches between condensers and reboilers are considered.*

Figure 12. *Introduction of a thermal couple by removing the intermediate condenser.*

Figure 13. *Fully thermally coupled configuration (Petluyk configuration) for a three component mixture. Only one condenser and one reboiler for the entire system.*

Figure 14. *The basic sequence with 5 separation tasks (see text) can be arranged in just three columns.*

Figure 15. *State task representation –center- and its eight thermodynamic equivalent configurations in actual columns.*

Figure 16. *STN superstructure for a 4 component mixture. Sharp split of no - necessarily consecutive key components.*

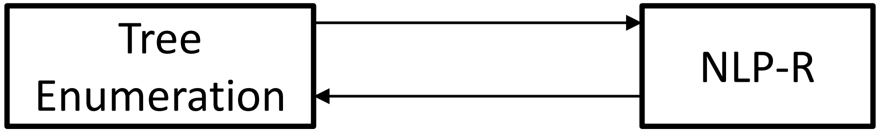
Figure 17. *STN-Aggregated superstructure.*

Figure 18. *Conceptual representation of disjunction (D-1).*

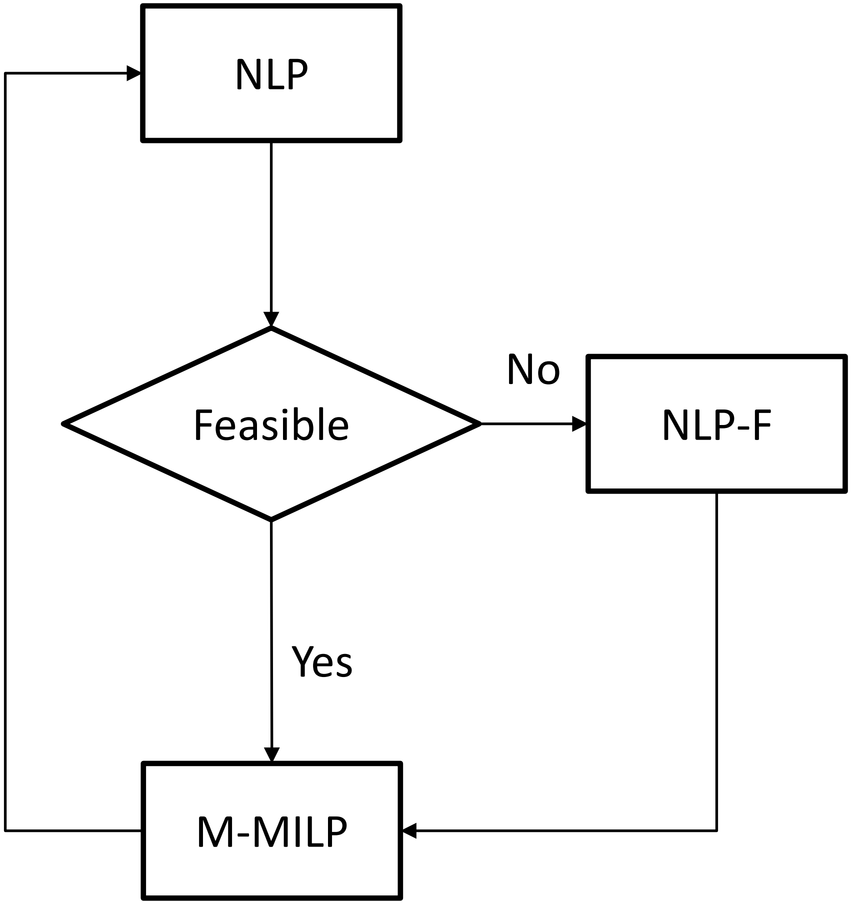
Figure 19. *Disjunctive representation of alternatives if state s exists.*

Figure 20. *Conceptual representation of the disjunction associated to final states (pure products)*

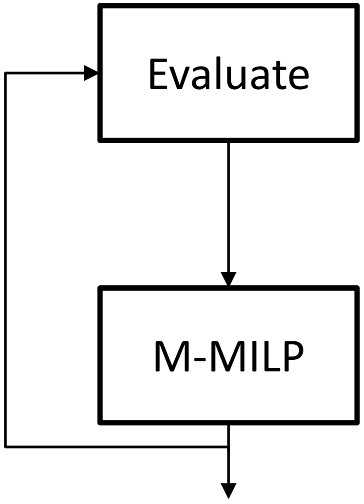
Figure 1



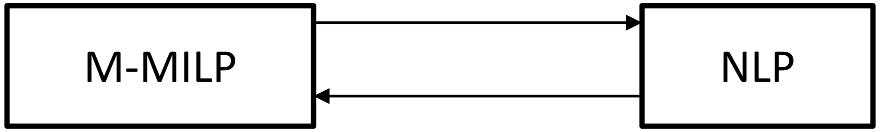
(a) Branch and Bound



(b) GDB, OA

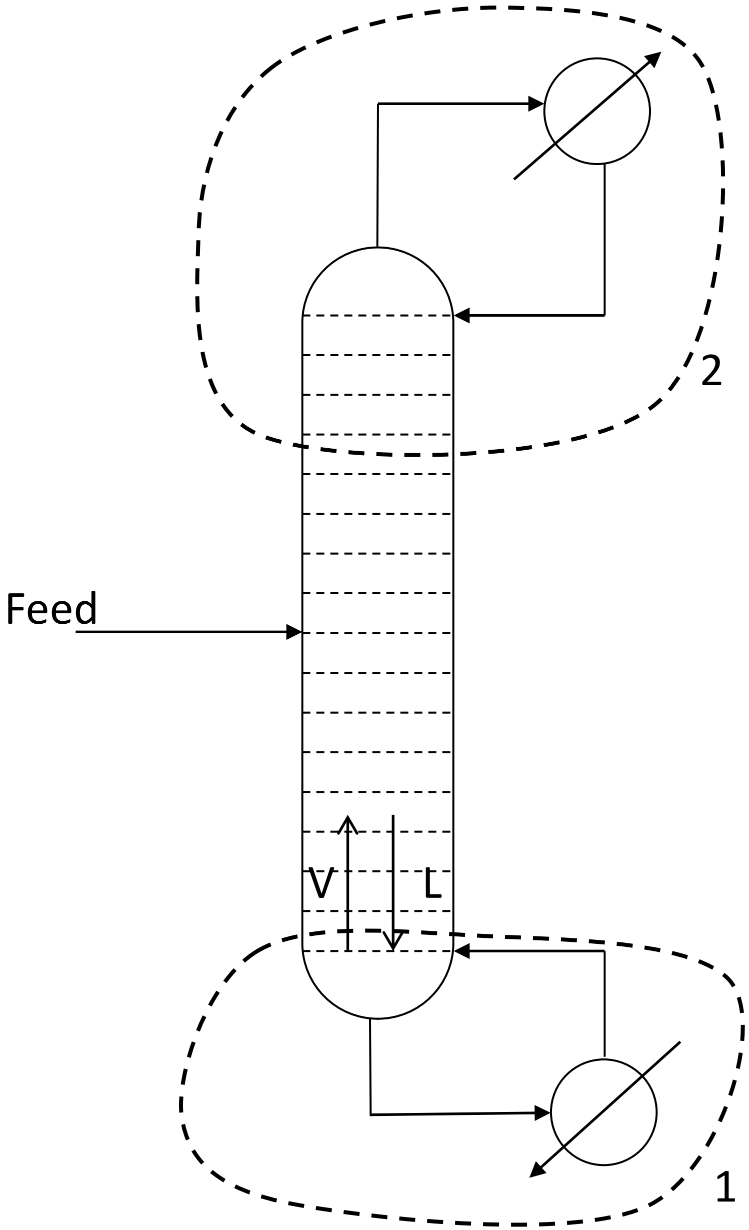


(c) ECP



(d) LP/NLP Based Branch and Bound

Figure 2



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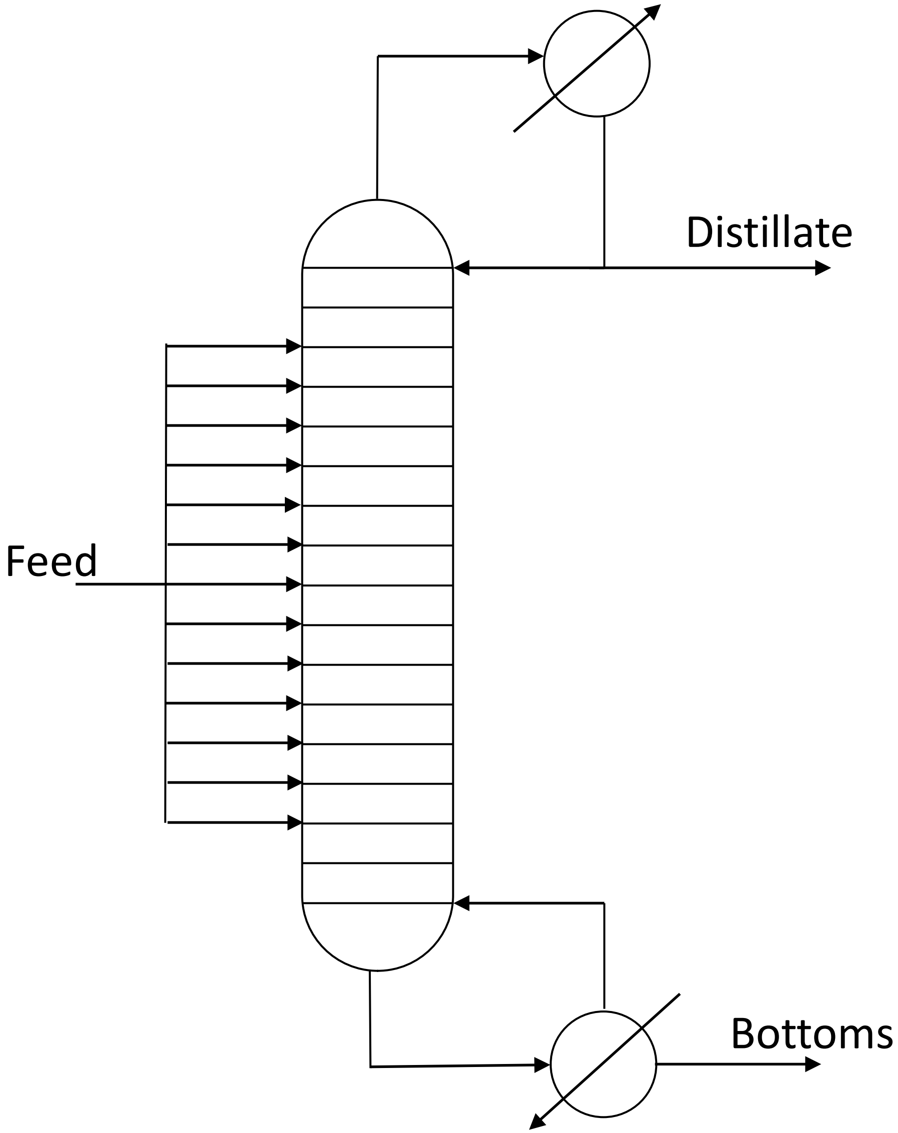

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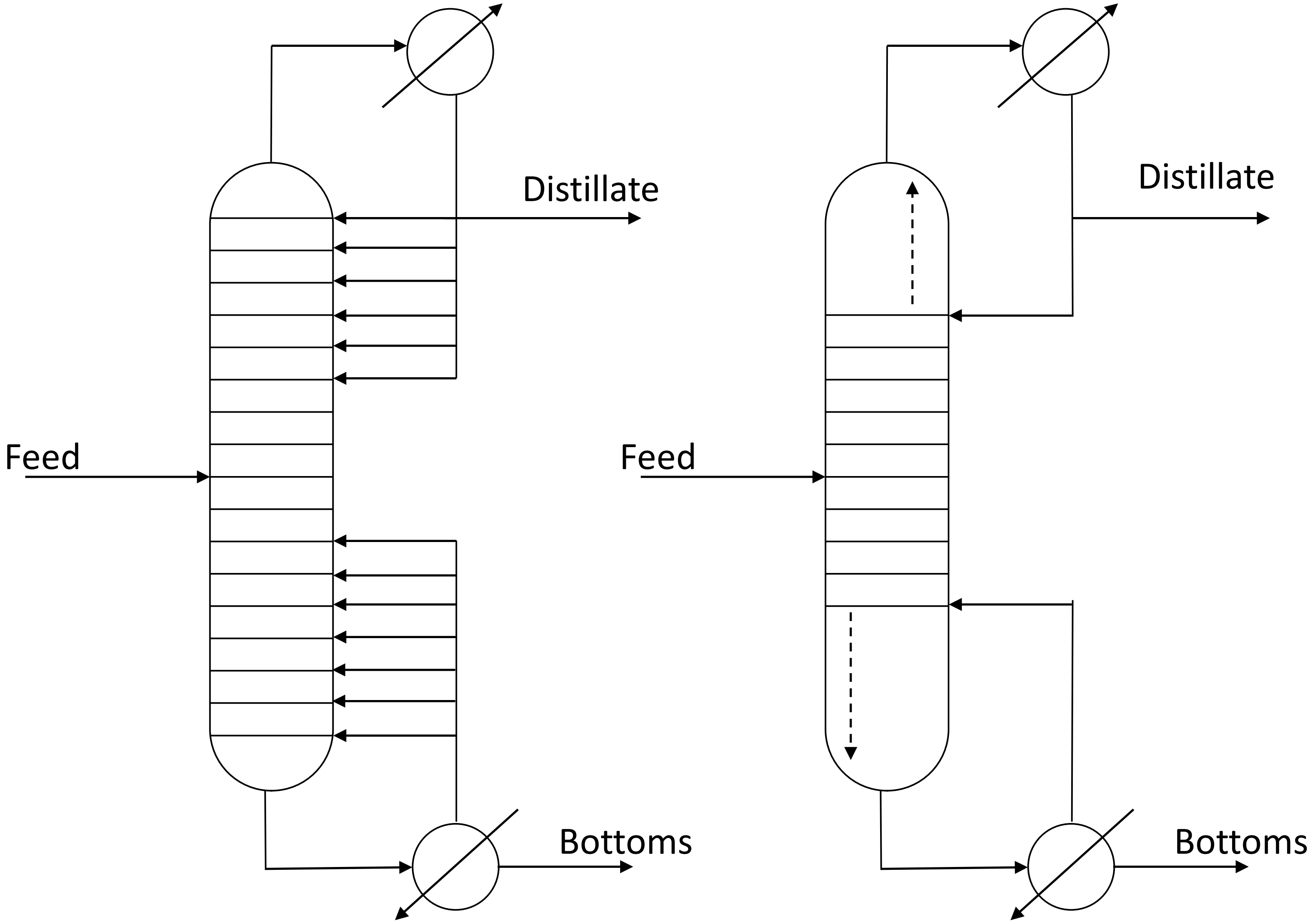

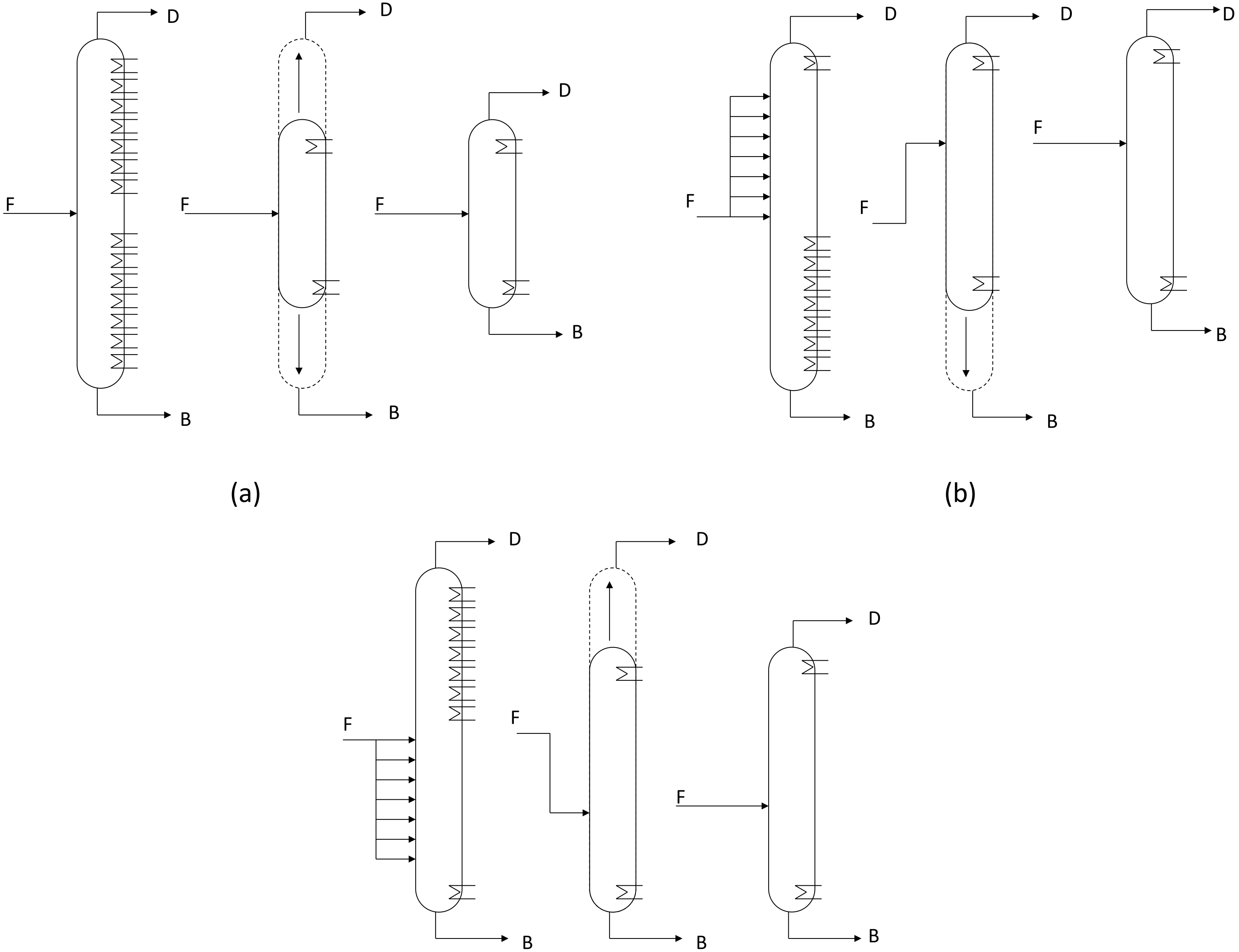

(a)

(b)

(c)

Figure 5

Figure 6

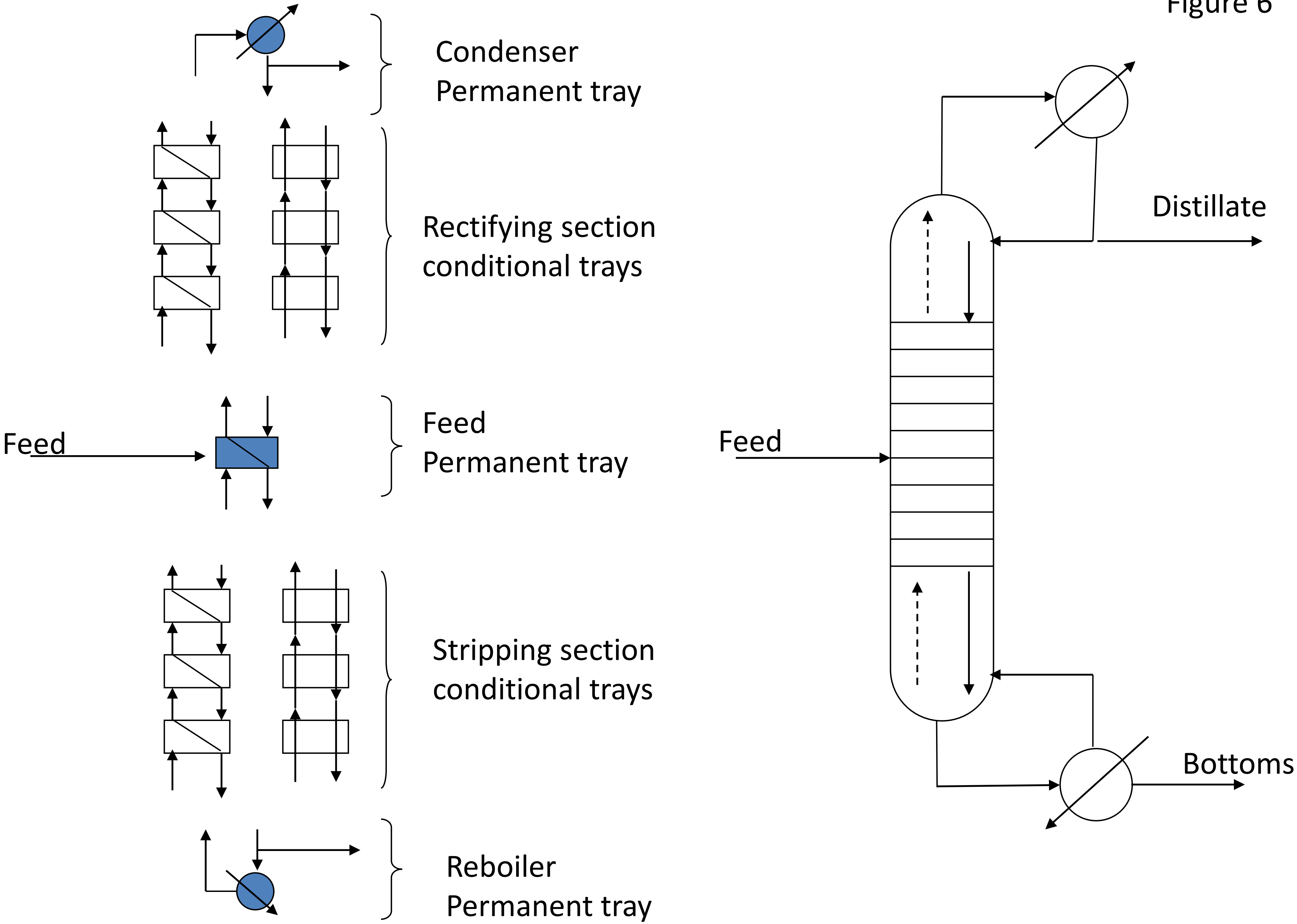
Condenser
Permanent tray
Rectifying section
conditional trays
Feed
Feed
Permanent tray
Stripping section
conditional trays
Reboiler
Permanent tray
Distillate
Feed
Bottoms

Figure 7

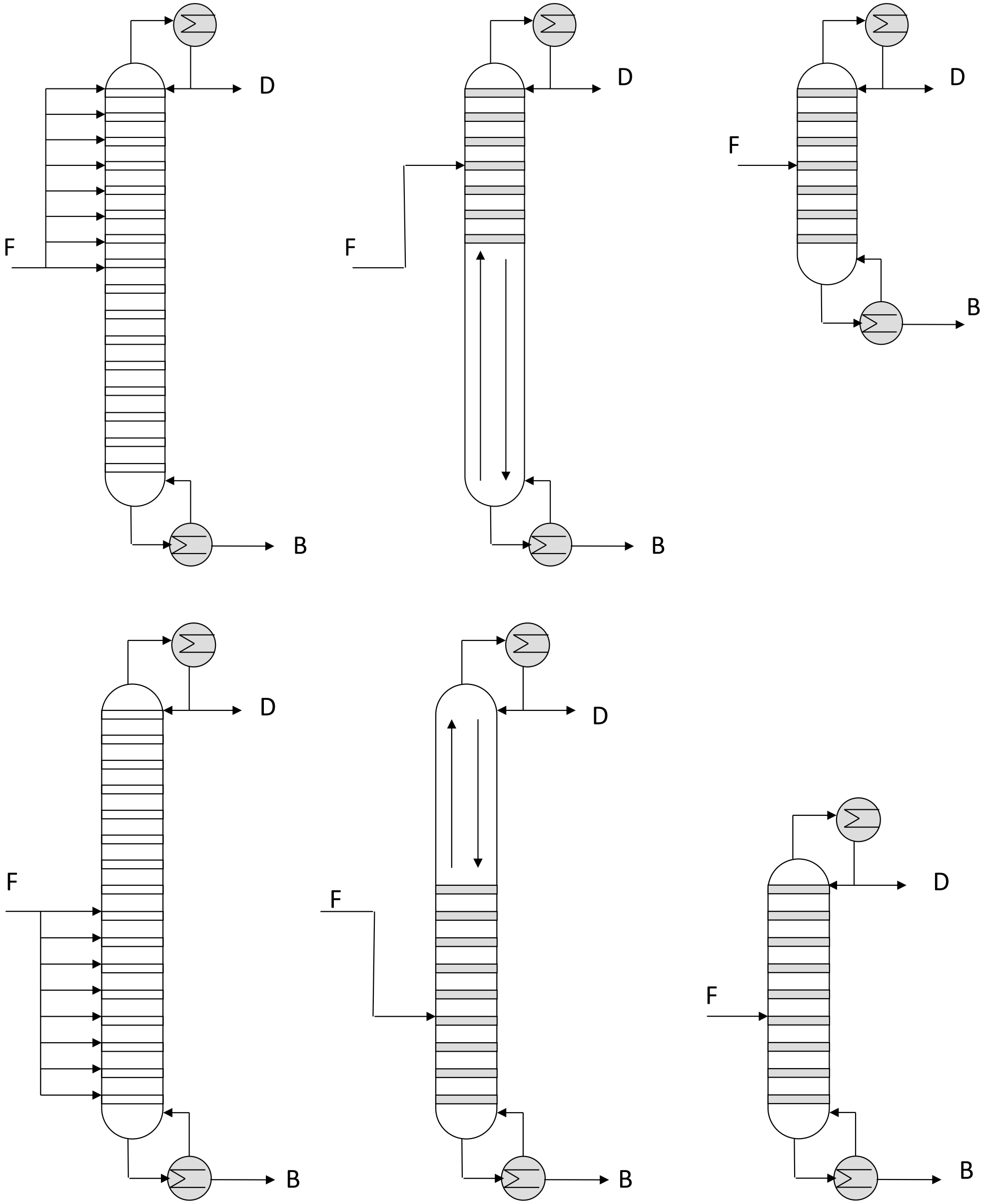

Figure 8

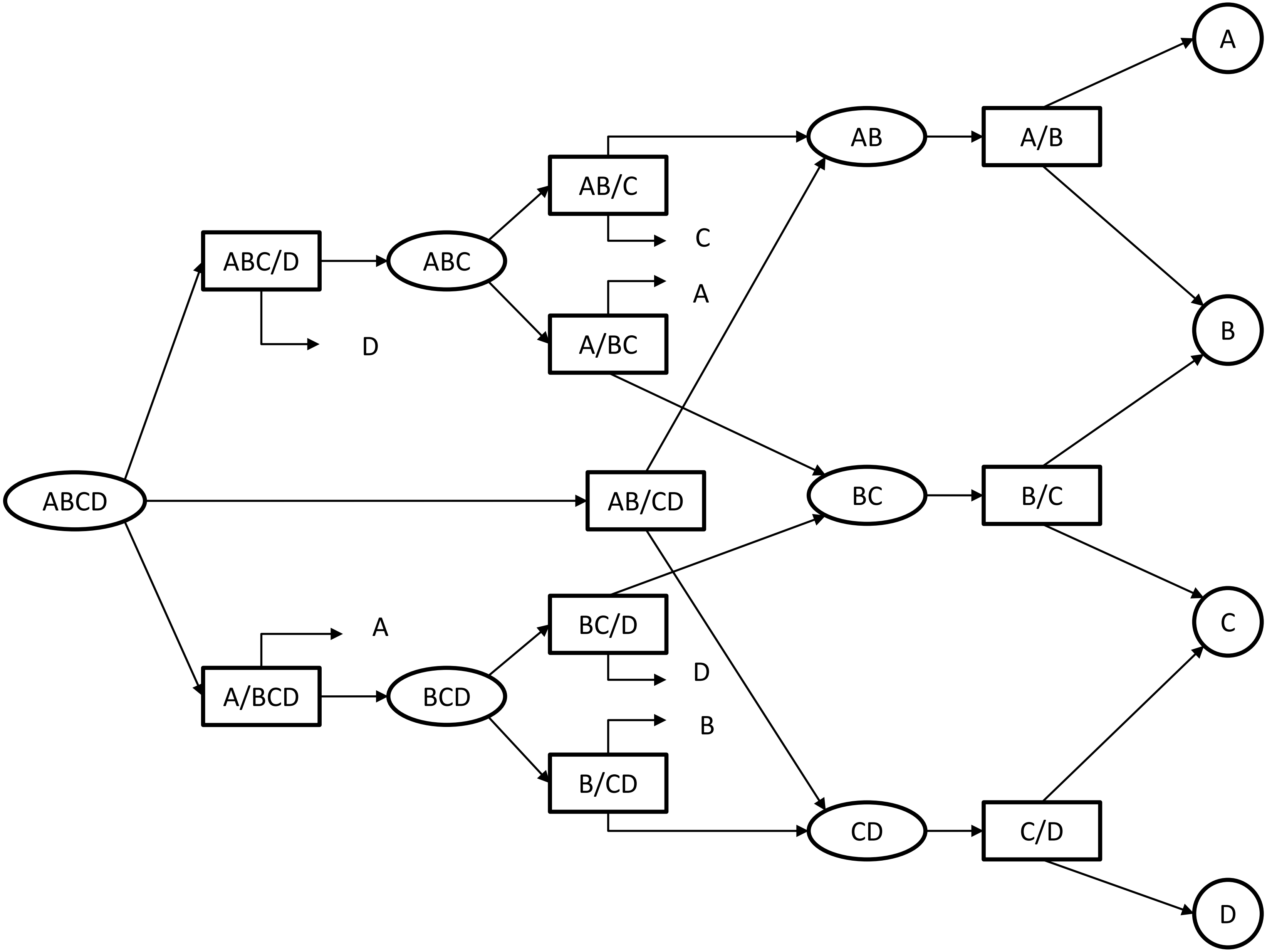
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Figure 9

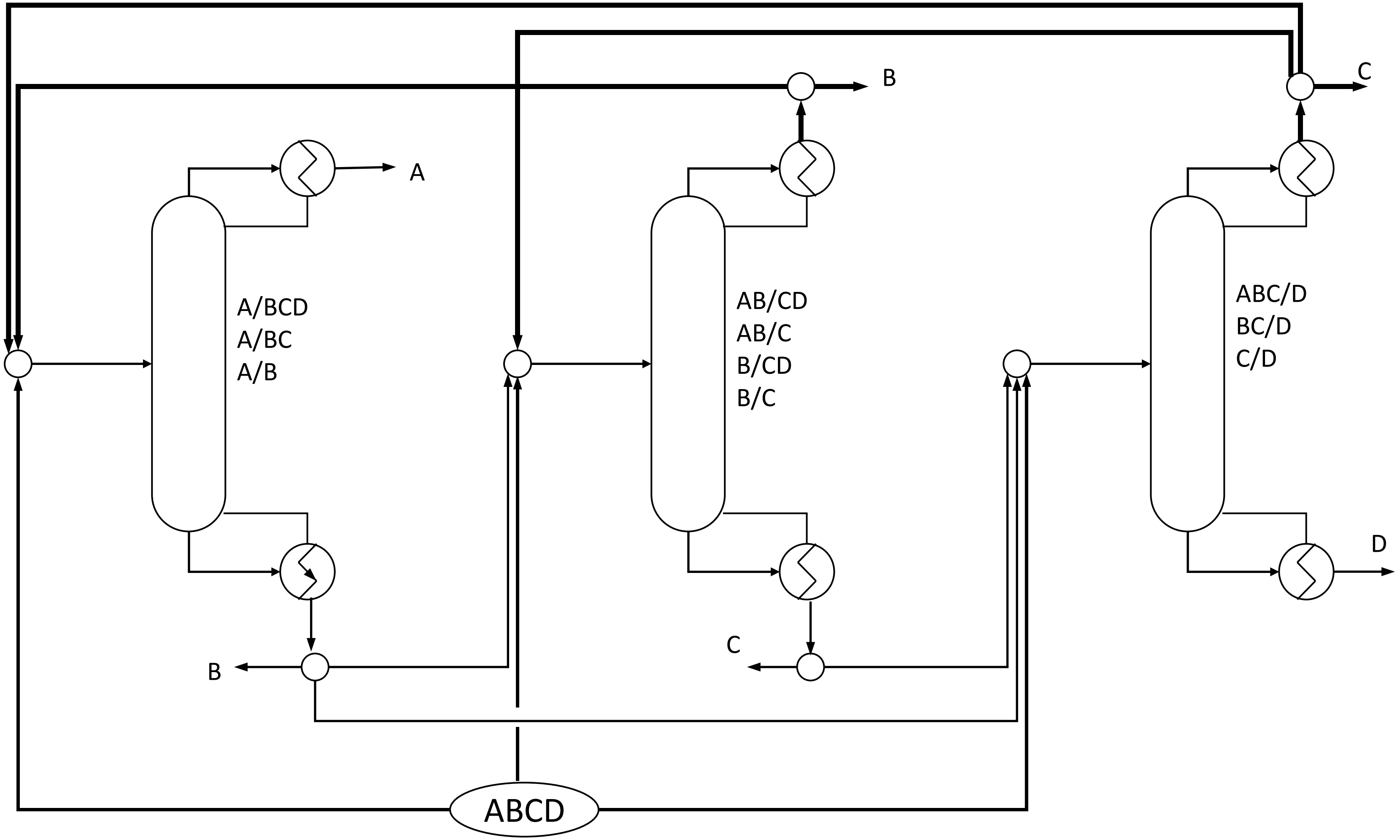


Figure 10

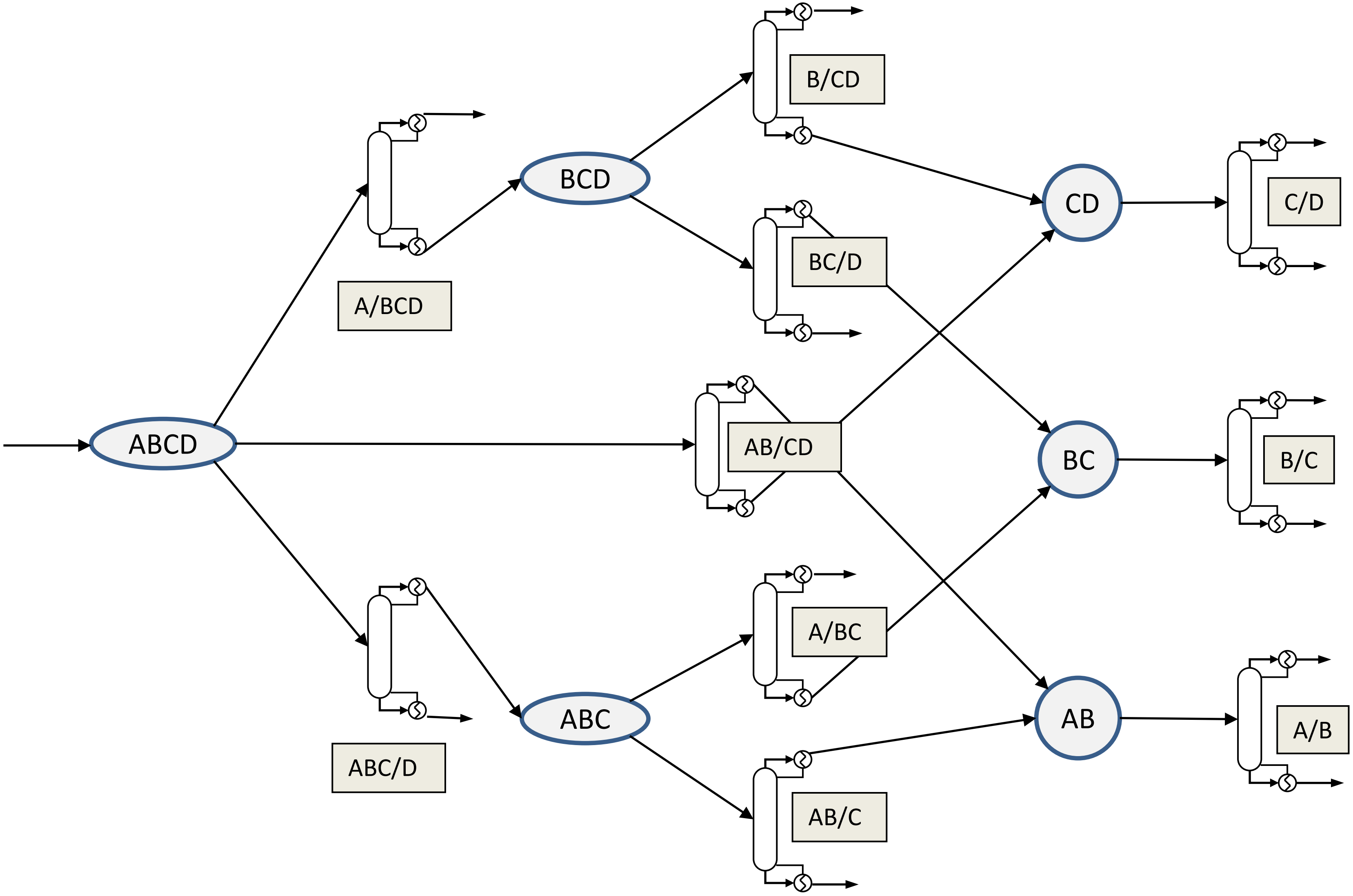
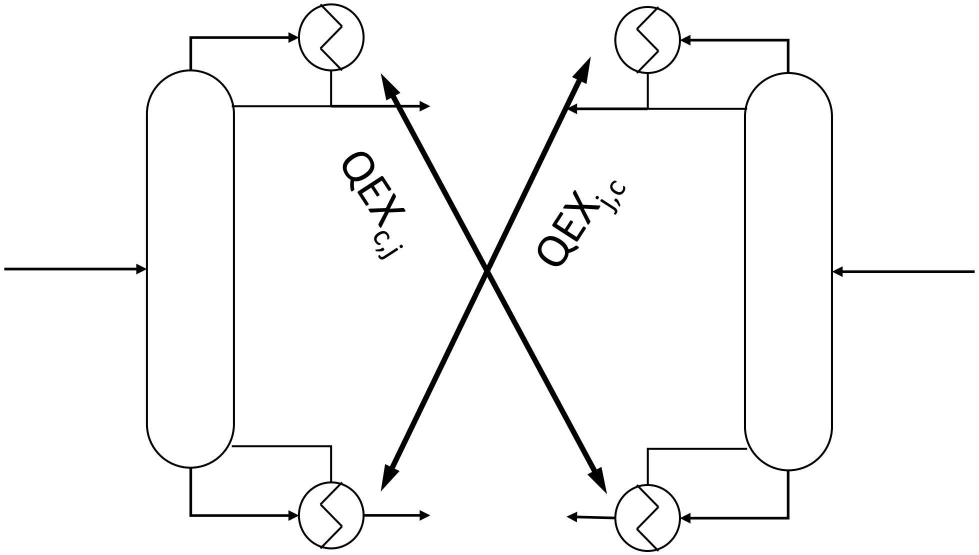


Figure 11



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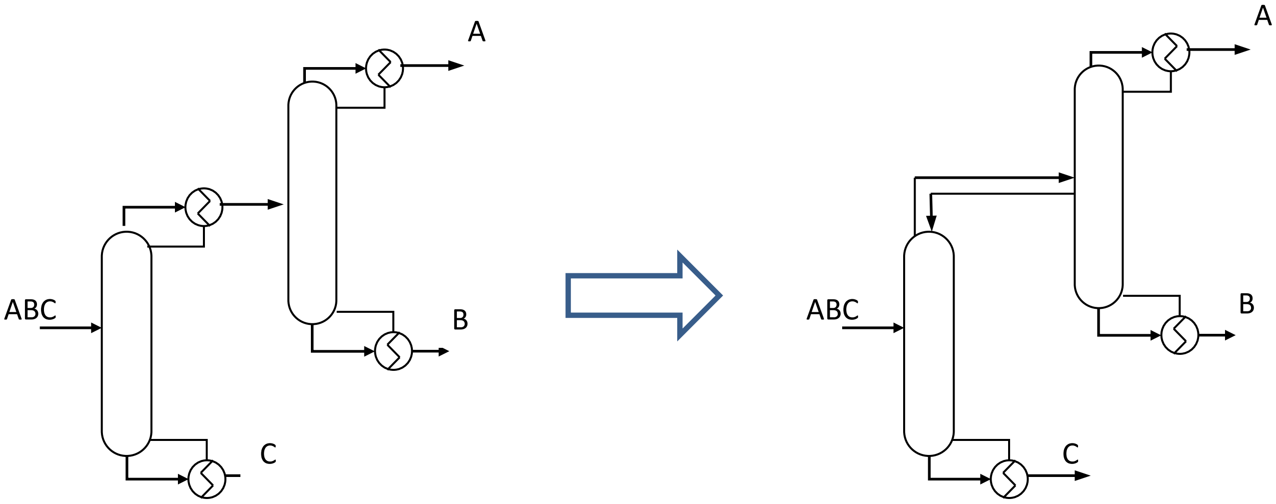

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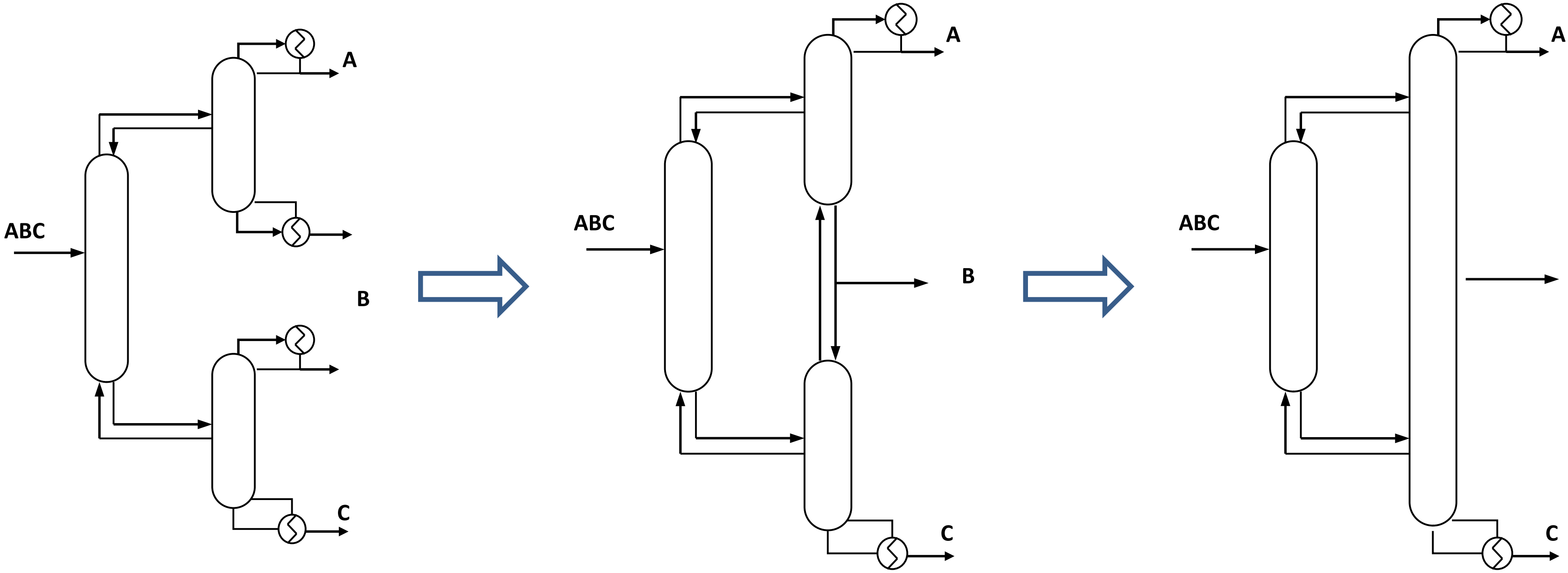
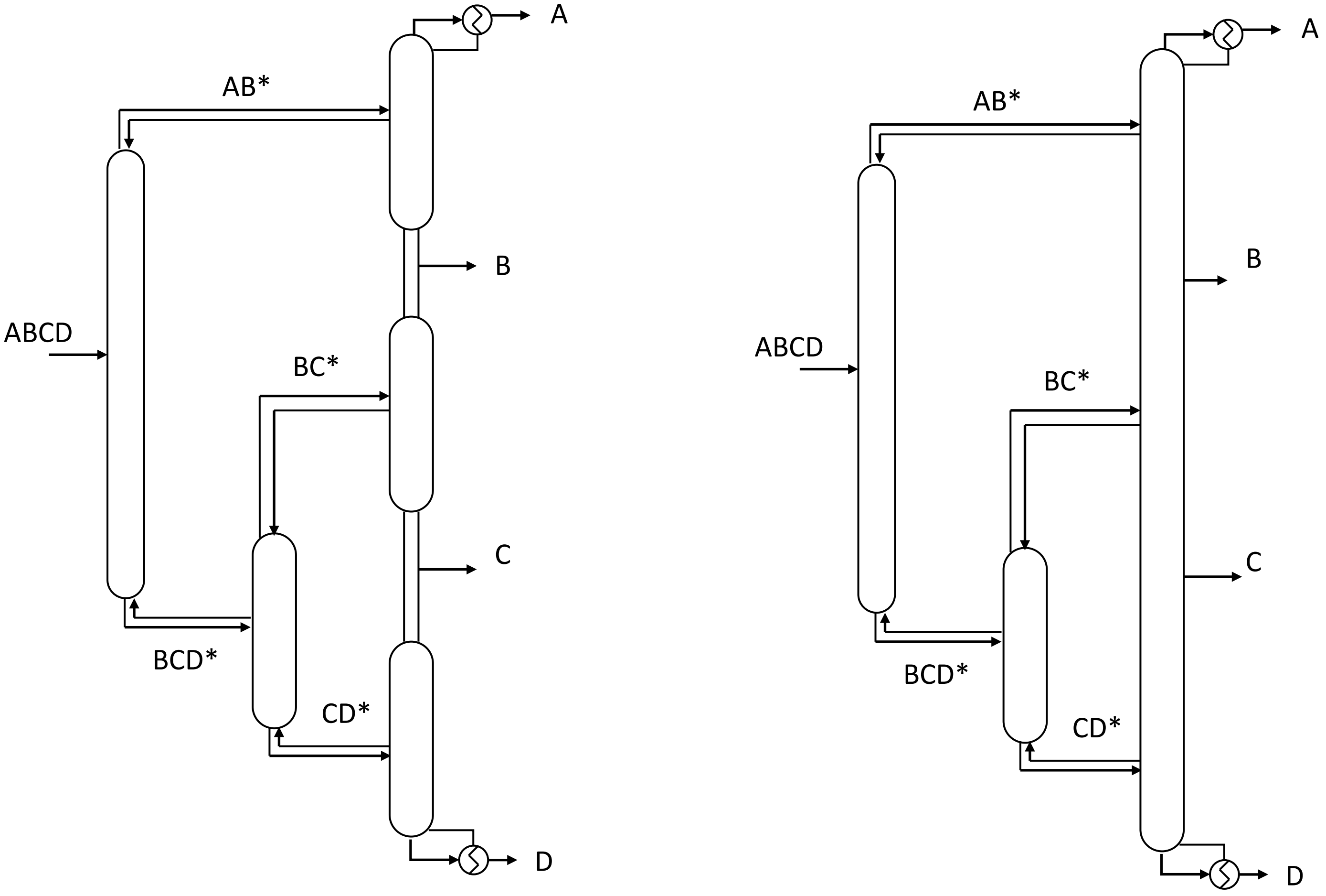


Figure 14



(a) (b)

Figure 15

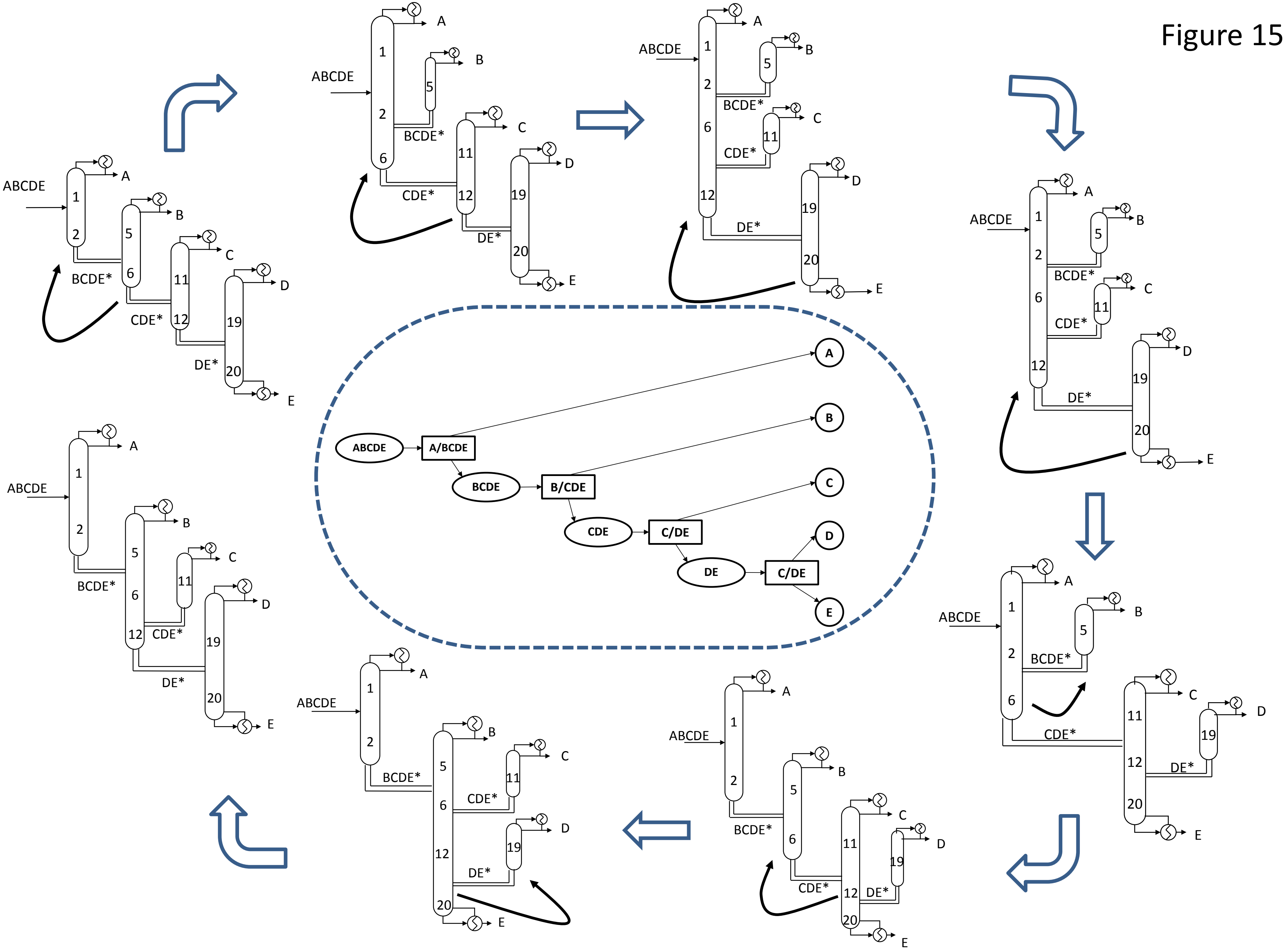

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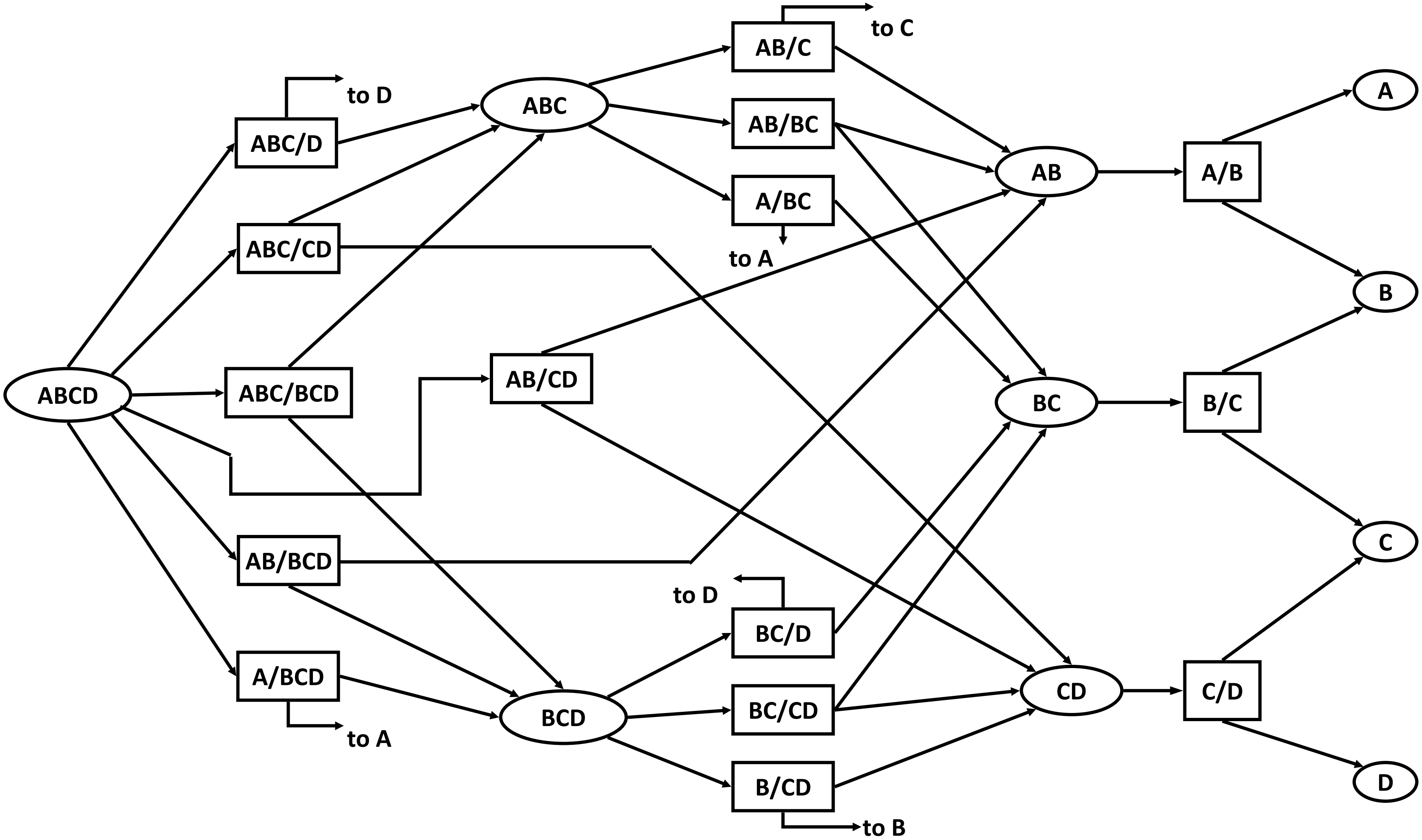
Figure 16



to C
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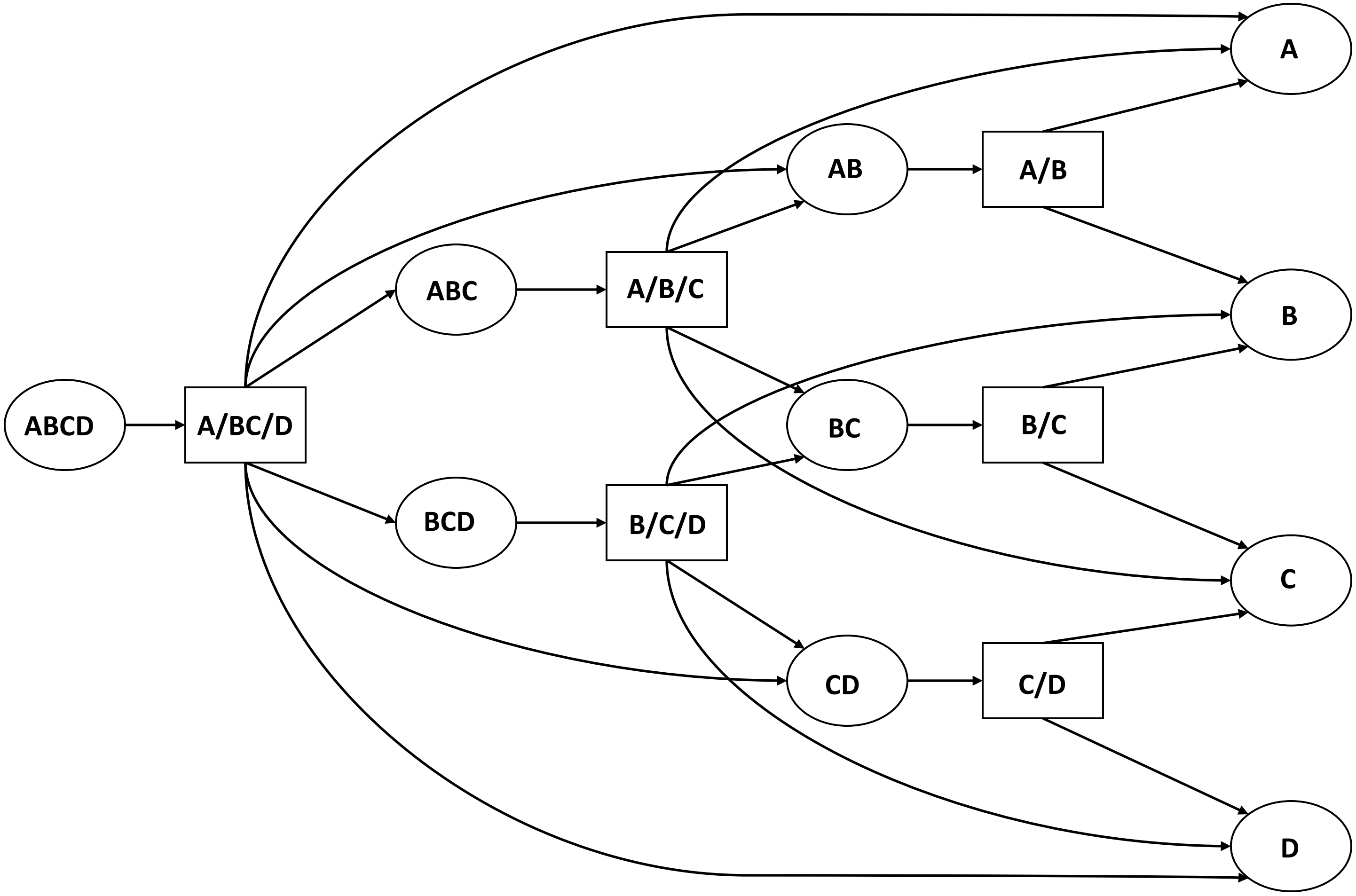
Figure 17



A/BC/D:	A/BCD AB/BCD AB/CD ABC/BCD ABC/CD ABC/D
A/B/C:	A/BC AB/BC AB/C
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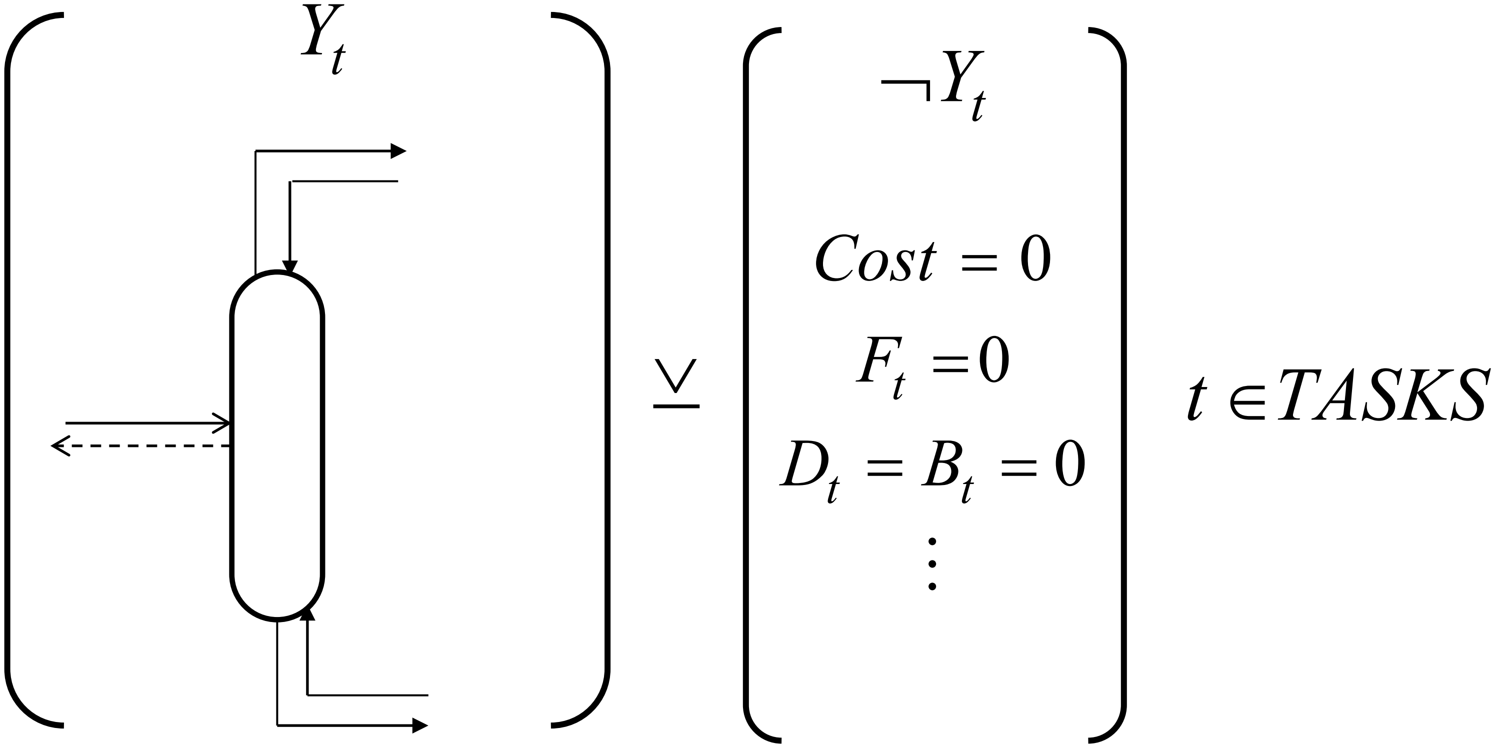
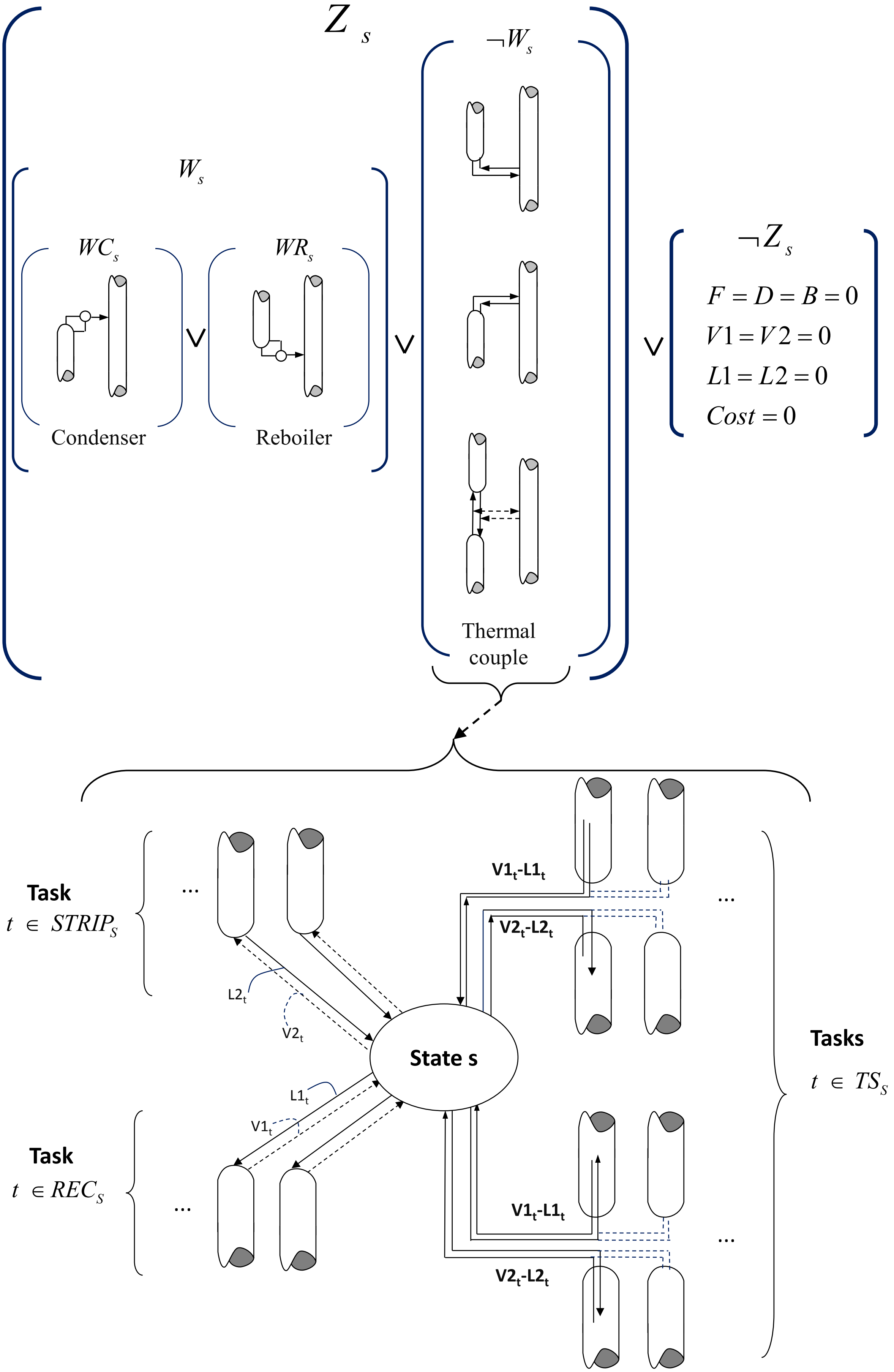
B/C:	B/C
C/D:	C/D

Figure 18



$$\begin{bmatrix} Y_t \\ \\ \\ \end{bmatrix} \veebar \begin{bmatrix} \neg Y_t \\ Cost = 0 \\ F_t = 0 \\ D_t = B_t = 0 \\ \vdots \end{bmatrix} \quad t \in TASKS$$


Z_s
$\neg W_s$
W_s
WC_s
WR_s
Condenser
Reboiler
$\vee$
$\vee$
$\vee$
$\neg Z_s$
$F = D = B = 0$
$V1 = V2 = 0$
$L1 = L2 = 0$
$Cost = 0$
Thermal couple
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L1$_t$
V1$_t$
Task
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V2$_t$-L2$_t$
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Figure 20