J_ID: AIC Customer A_ID: AIC15204 Cadmus Art: AIC15204 Ed. Ref. No.: AICHE-15-17560.R1 Date: 20-February-16 Stage: Page: 1

AIChE

Global Optimization of Multicomponent Distillation Configurations: 2. Enumeration Based Global Minimization Algorithm

AQ4

Rakesh Agrawal
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

Ulaganathan Nallasivam, Vishesh H. Shah, Anirudh A. Shenvi, Joshua Huff, and Mohit Tawarmalani
Krannert School of Management, Purdue University, West Lafayette, IN 47907

DOI 10.1002/aic.15204
Published online in Wiley Online Library (wileyonlinelibrary.com)

We present a general Global Minimization Algorithm (GMA) to identify basic or thermally coupled distillation configurations that require the least vapor duty under minimum reflux conditions for separating any ideal or near-ideal multicomponent mixture into a desired number of product streams. In this algorithm, global optimality is guaranteed by modeling the system using Underwood equations and reformulating the resulting constraints to bilinear inequalities. The speed of convergence to the globally optimal solution is increased by using appropriate feasibility and optimality based variable-range reduction techniques and by developing valid inequalities. The GMA can be coupled with already developed techniques that enumerate basic and thermally coupled distillation configurations, to provide for the first time, a global optimization based rank-list of distillation configurations. © 2016 American Institute of Chemical Engineers *AIChE J*, 00: 000–000, 2016

Keywords: transition split, preferred split, multicomponent distillation, distillation configurations, global optimization

Introduction

Several alternative distillation configurations can be used for separating an ideal or near-ideal multicomponent mixture into a desired number of product streams. Many mathematical models have been proposed for systematically synthesizing all these possible distillation configurations.[1–5] In these models, the distillation configurations use the same number of distillation columns to separate a given feed mixture into the desired product streams. However, the distillation configurations may or may not have the same number of heat exchangers. As a result, these configurations can differ in installation costs. Moreover, even though they carry out the same separation task, these configurations have been found to differ significantly in their vapor duty requirements, leading to significantly different operating costs. It is thus important to identify a distillation configuration for which the total installation and operating costs are minimum.

Furthermore, distillation configurations for a given separation task can even have a different number of distillation columns. A distillation configuration to separate a mixture into n product streams can be classified as having less than $(n-1)$ distillation columns or at least $(n-1)$ distillation columns. The configurations with at least $(n-1)$ distillation columns can be further classified either as basic or non-basic distillation configurations.[6] Basic configurations have exactly $(n-1)$ distillation columns while non-basic distillation configurations use more than $(n-1)$ distillation columns for an n-component separation. Configurations with less than $(n-1)$ columns are typically attractive only for limited types of multicomponent separation problems as pointed out by Shenvi et al.[7], while non-basic distillation configurations (that use more than $(n-1)$ columns) have been shown, through extensive computations for four component separations, to have higher operating costs than optimal basic configurations, as presented by Giridhar and Agrawal[8]. Non-basic configurations are also expected to have higher capital costs than basic configurations due to additional distillation columns and associated heat exchangers. Therefore, in this work, we only include basic configurations in our search space.

The search space is defined as the set of all possible distillation configurations that are candidate solutions during the search for a globally optimal configuration. Structurally, a distillation configuration can be described by a unique set of discrete binary integer variables. The value of each integer variable would indicate the presence or absence of the corresponding unit in the configuration. For example, an integer variable can represent presence or absence of a heat exchanger at a specific location in a configuration. In addition to this structural description of a configuration, continuous variables are also needed to represent internal and external flow rates and compositions in a configuration. Therefore, each distillation configuration in a search space is mathematically associated with a unique set of integer and continuous variables, and the search for an optimal configuration involves optimization

AQ1 Correspondence concerning this article should be addressed to M. Tawarmalani and R. Agrawal at mtawarma@purdue.edu and agrawalr@purdue.edu.

ID: nagarajulum Time: 20:38 I Path: //chenas03/Cenpro/ApplicationFiles/Journals/Wiley/AIC#/Vol00000/160054/Comp/APPFile/JW-AIC#160054

over both continuous and discrete integer variables. The search for a globally optimal configuration can be carried out in two ways. The first approach is to formulate the problem as a single mixed-integer nonlinear programming (MINLP) problem[4,5] solved by a local optimization solver. In this approach, the distillation configuration search space is defined as a mathematical superstructure that contains all possible configurations. The MINLP approach attempts to find the globally optimal solution without enumerating all the configurations in the search space. As pointed out by Caballero and Grossmann[4], this approach faces three important challenges: unless globality can be assured, (1) in most cases, a feasible solution is not found because of singularities that arise with disappearing column sections, (2) Iterations are very time consuming, and (3) even if a solution is found, it often corresponds to a poor local optimum.

To address these issues, Caballero and Grossmann[4] developed a super structure based model that could be solved through a modified version of a logic-based outer approximation algorithm.[9] In this approach the MINLP problem is decomposed into an MILP master problem and an nonlinear programming problem (NLP) sub-problem, with the master problem being formulated by replacing the nonlinear equations with their convex outer-approximations. This makes the master problem less sensitive to column sections that disappear in a particular solution, and also provides a better initial guess for the NLP sub-problem. The MILP master problem involves discrete optimization and is solved to generate a feasible configuration. The NLP sub-problem involves continuous optimization and is solved to optimize the feasible configuration generated by the MILP master problem. This process is repeated iteratively until the NLP solution starts worsening relative to a previous iteration. The configuration associated with current iteration is then selected as the optimal solution. Observe that this procedure does not guarantee the global optimality of the solution it identifies.

Subsequently, Caballero and Grossmann[5] presented a new iterative procedure to solve an MINLP problem that includes thermally coupled configurations in the search space. This procedure decomposes each problem into a master problem and sub-problem. In this procedure the integer variables associated with transfer-stream heat exchangers are assigned values of zero, that is, they are assumed to be absent during each iteration of the master problem. This approach thus identifies a completely thermally coupled (CTC) configuration during each iteration of the master problem. In the sub-problem, the heat exchangers are allowed to be present or absent while freezing the configuration structure to the solution generated by the master problem. These two steps are repeated iteratively until a stopping criterion is met in two consecutive iterations. This procedure also does not guarantee a globally optimal solution. The limitation of both these procedures lies in the decomposition of the original problem into subproblems. To guarantee global optimal solution is sought, such a decomposition cannot be performed.

The second approach for identifying an optimal distillation configuration is to synthesize the complete search space and to formulate individual NLP problems for each configuration in the search space. We refer to this approach as an enumeration based approach. Until now, the optimization of a distillation configuration was attempted either analytically or by solving a nonlinear programming problem (which may include integer variables as well) using state-of-art local optimization solvers. In the first part of this series of articles, we demonstrated that the analytical method, referred to as the Sequential Minimization Algorithm (SMA), is not a reliable global optimization tool.[10] Similarly, other researchers such as Giridhar and Agrawal[1] found that local optimization solvers were often unsuccessful in finding globally optimal solutions because of the nonlinear nature of the problem. To overcome this challenge, they recommended using multiple randomly generated initial guesses, but still could not guarantee global optimality while significantly increasing computational burden. Furthermore, in a few cases, no feasible solutions could be found for some NLP problems by this approach.

In this article, we present a general NLP-based formulation that can describe all basic and thermally coupled configurations, and can be solved to guaranteed global optimality. We refer to this formulation as a Global Minimization Algorithm (GMA), throughout this article. This algorithm is applied to each basic and thermally coupled distillation configuration to obtain its corresponding globally minimum vapor duty requirement. This algorithm uses a bilinear reformulation of the Underwood equations. To use this algorithm, we first generate all the configurations in the search space using the method of Shah and Agrawal[2,3]. Subsequently, GMA-based optimization of each configuration provides a global optimization based rank-list of distillation configurations. GMA is thus the first algorithm to guarantee that all globally optimal distillation configurations for any ideal or near-ideal multicomponent separation problem will be identified. Unlike the MINLP approach, this approach does involve the computational effort of evaluating each individual configuration in the search space, but is currently the only approach that is able to solve this problem to global optimality; further, this approach adds the capability exists to identify all configurations within a prespecified percent of the global optimum. A process flow chart illustrating the key steps of the GMA is shown in Figure 1. F1 Details about the GMA-based formulation will be described in the following sections. Strategies for reducing the computational time will also be discussed.

Search Space of Distillation Configurations

For general multicomponent distillation problems, the search space is limited to distillation configurations that use exactly $n-1$ distillation columns to separate an ideal or near-ideal multicomponent mixture into n product streams. This search space can be synthesized using the method of Shah and Agrawal[2,3], where every feasible distillation configuration for an n-component separation is represented as an $n \times n$ upper triangular matrix. The upper triangular elements correspond to streams in a configuration and can take values of either zero or one. A value of zero indicates that the corresponding stream is absent in the configuration, while a value of one indicates presence of the corresponding stream. For example, for a four component separation, all possible streams that may be present in a configuration are ABCD, ABC, BCD, AB, BC, CD, A, B, C, and D (see Figure 2a). The corresponding upper triangular F2 matrix with possible 0/1 values is shown in Figure 2b. Note that the main feed stream (element (1,1)) and the final product streams (elements in the final column) always have values of one in this matrix. The remaining streams are necessarily transferred between distillation columns and can take values of either zero or one. Figure 3 shows a feasible configuration F3 for a four-component separation. The streams ABC, BCD, and BC are absent in this particular configuration. The

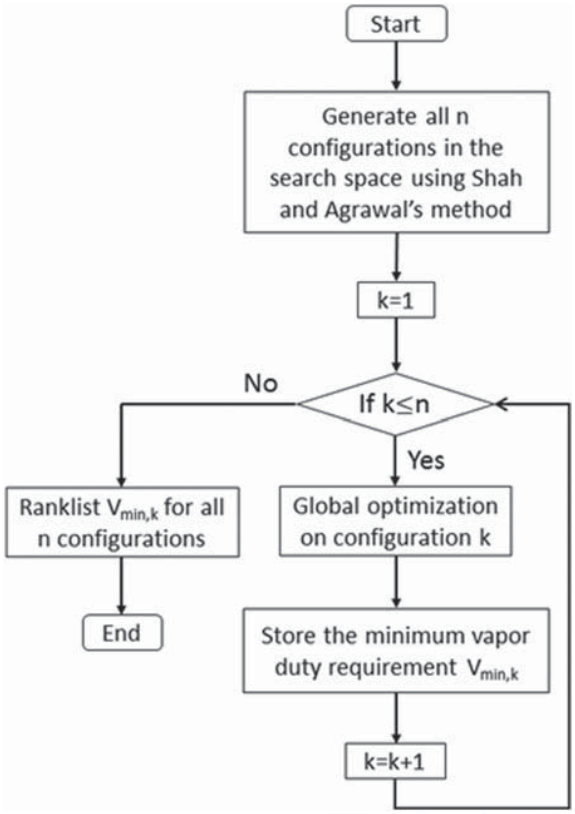

Figure 1. Process flow chart of GMA method.

corresponding stream matrix and 0–1 upper triangular matrix is shown in Figure 4. Any feasible basic distillation configuration is thus represented by a unique 0–1 upper triangular matrix in the matrix method.

Shah and Agrawal[2,3] provide mathematical constraints to ensure that only matrices corresponding to feasible basic distillation configurations are included in the search space. A procedure is also given to convert a feasible 0–1 upper triangular matrix into a distillation configuration as shown in Figures 5a–c. A feasible configuration for a five-component separation is represented by the 0–1 upper triangular matrix shown in Figure 5a. The corresponding stream matrix is shown in Figure 5b. This stream matrix is used to enumerate the splits by starting with the main feed stream followed by each of the transfer streams present in the matrix. For any stream in the matrix, horizontal movement to its right identifies its top product and diagonal movement to its right identifies its bottom product. Therefore, the splits for the matrix shown in Figure 5b are ABCDE to ABC/BCDE, ABC to A/BC, BCDE to BC/CDE, BC to B/C, CDE to CD/E, and CD to C/D. Next each split is assigned to a distillation column, with splits producing the same streams being assigned to the same distillation column. Therefore, split

$$\begin{bmatrix} ABCD & ABC & AB & A \\ 0 & BCD & BC & B \\ 0 & 0 & CD & C \\ 0 & 0 & 0 & D \end{bmatrix} \quad \begin{bmatrix} 1 & 0/1 & 0/1 & 1 \\ 0 & 0/1 & 0/1 & 1 \\ 0 & 0 & 0/1 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

(a) (b)

Figure 2. Stream and 0–1 upper triangular matrices for a four component separation.

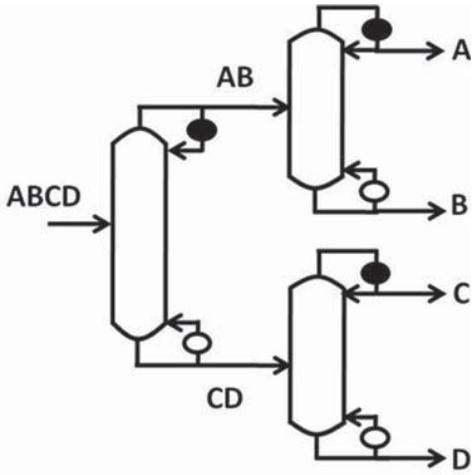

Figure 3. A feasible configuration for a four component separation.

ABCDE → ABC/BCDE is assigned to distillation column 1, splits ABC to A/BC and BCDE to BC/CDE are assigned to distillation column 2 from which the common product stream BC is obtained as a sidedraw, split CDE to CD/E is assigned to distillation column 3 and splits BC to B/C and CD to C/D are assigned to distillation column 4 from which the common product stream C is obtained as a sidedraw. This information is used to draw the basic distillation configuration shown in Figure 5c. Additional thermally coupled distillation configurations can be derived from a basic configuration by considering all possible instances of the presence or absence of heat exchangers associated with transfer streams. Figure 5d shows a thermally coupled configuration derived from the basic configuration shown in Figure 5c.

To implement the procedure of converting a 0–1 upper triangular matrix to a distillation configuration in a computer program, we assign a numerical identity to each stream. For instance, for a five component separation, Figure 6a shows the convention used by us to assign numerical identities. Therefore, the matrix shown in Figure 5b can be represented mathematically by the matrix shown in Figure 6b. In this article, we refer to this type of matrix as a topology matrix or Z_{mat} matrix. A topology matrix corresponds uniquely to each feasible 0/1 matrix and allows easy enumeration of the splits and subsequent assignment to distillation columns in an automated fashion. The main advantage is that the space of 0–1 variables is now significantly smaller than that of super-structure based methods which introduce a binary variable for each type of split possible. For instance, the information summarized in Figure 6c can be obtained from the matrix shown in Figure 6b using a computer program. In Figure 6c, the first column of this matrix is the split number, the second column is the feed to the corresponding split represented by its topology matrix, the third and fourth columns

$$\begin{bmatrix} ABCD & 0 & AB & A \\ 0 & 0 & 0 & B \\ 0 & 0 & CD & C \\ 0 & 0 & 0 & D \end{bmatrix} \quad \begin{bmatrix} 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Figure 4. Stream and 0–1 upper triangular matrices corresponding to the feasible configuration shown in Figure 2.

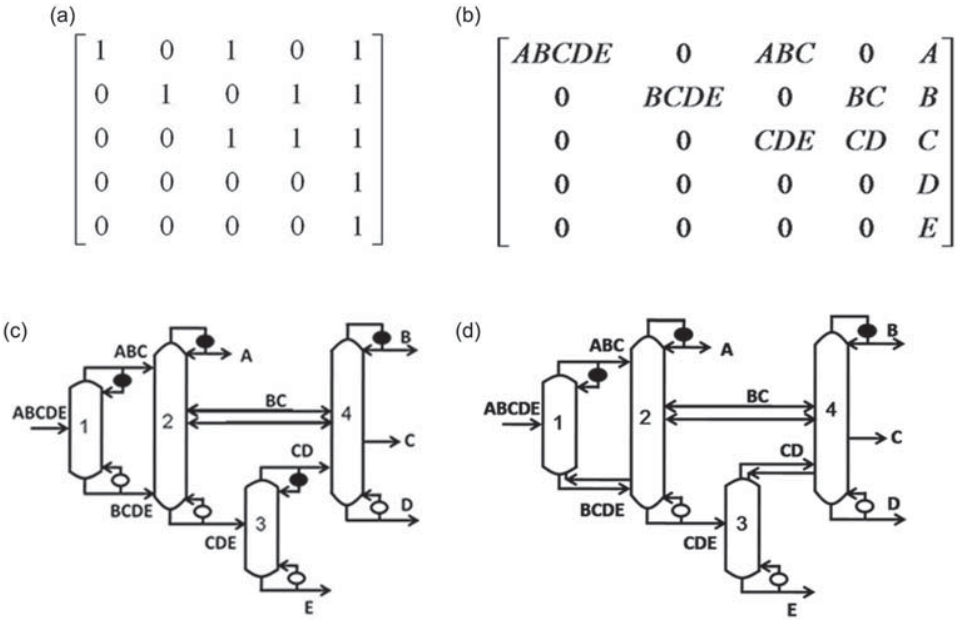

Figure 5. (a) A 0–1 upper triangular matrix corresponding to a feasible distillation configuration for a five component separation. (b) Stream matrix corresponding to the upper triangular matrix shown in Figure 4a. (c) Basic distillation configuration corresponding to the matrix shown in Figures 4a, b. Heat exchangers associated with transfer stream BCDE and CD are replaced by thermal coupling links. (d) One possible thermally coupled configuration derived from the basic configuration shown in Figure 4c.

are the top and bottom products of the corresponding split, and the fifth column represents the distillation column number to which the split is assigned. Because of the information it contains, this type of matrix is referred to as a connectivity matrix. We can thus algorithmically generate a connectivity matrix for each feasible 0–1 upper triangular matrix. The connectivity matrices then allow us to algorithmically formulate an NLP problem for each distillation configuration in our search space.

NLP Formulation

Any optimization problem is described by: (1) the decision variables, (2) the objective function, and (3) the constraints. In the following sections, we present equations for the objective function and the constraints. The parameters, subscripts, variables, and variable sets that we have used in writing these equations are defined in Appendix A. In all these equations, the components are numbered as 1, 2, …, n in the decreasing order of their volatilities. We shall also discuss how these equations can be automatically derived using the connectivity matrix. In Appendix B, we provide an example detailing the equations needed to formulate the nonlinear program for configuration in Figure 5d.

Objective Function

The objective function is a mathematical expression of the desired optimization goal. Since we have only considered

(a)

$$\begin{bmatrix} ABCDE & ABCD & ABC & AB & A \\ 0 & BCDE & BCD & BC & B \\ 0 & 0 & CDE & CD & C \\ 0 & 0 & 0 & DE & D \\ 0 & 0 & 0 & 0 & E \end{bmatrix} \leftrightarrow \begin{bmatrix} 1 & 2 & 4 & 7 & 11 \\ 0 & 3 & 5 & 8 & 12 \\ 0 & 0 & 6 & 9 & 13 \\ 0 & 0 & 0 & 10 & 14 \\ 0 & 0 & 0 & 0 & 15 \end{bmatrix}$$

(b)

$$z_{mat} = \begin{bmatrix} 1 & 0 & 4 & 0 & 11 \\ 0 & 3 & 0 & 8 & 12 \\ 0 & 0 & 6 & 9 & 13 \\ 0 & 0 & 0 & 0 & 14 \\ 0 & 0 & 0 & 0 & 15 \end{bmatrix}$$

(c)

(*Split*)	(*Feed*)	(*Distillate*)	(*Bottom*)	(*Column*)
1	1	4	3	1
2	3	8	6	2
3	4	11	8	2
4	6	9	15	3
5	8	12	13	4
6	9	13	14	4

Figure 6. (a) Assigning numerical identities to the streams. (b) Topology matrix or Zmat matrix corresponding to the stream matrix shown in Figure 4b. (c) Connectivity matrix for the distillation configuration corresponding to the feasible configuration represented by 0–1 matrix in Figure 4a.

basic and thermally coupled distillation configurations in our search space, the capital costs of these configurations are not expected to be drastically different from each other. For many applications, the operating costs of these configurations can differ by significant amounts. Here we assume, as is reasonable, that the operating cost of a configuration is proportional to the sum of the vapor flows generated at each reboiler of the configuration.[11] A more detailed treatment of the relation between minimum vapor flow and capital cost will be discussed in a later manuscript.

The sum of the vapor flows generated at each reboiler in a configuration is referred to as the total vapor duty requirement of the configuration. The minimum total vapor duty requirement of a configuration is simply the total vapor duty requirement of the configuration calculated under minimum reflux conditions. The minimum total vapor duty requirement assumes infinite stages, which despite being a theoretical simplification, produces a reasonable benchmark for comparing the operating cost of the configurations. The main advantage of this simplification is that it makes the computation more tractable. While this approach will not give an exact value of actual cost for a configuration, it can be used to rank-list and compare different arrangements. Therefore, we use the minimum vapor duty requirement as the objective function for each distillation configuration. A general representation for the objective function is:

$$\sum_{s \in \mathrm{COLR}} V_s^{\mathrm{bot}}$$

COLR is the set of all the splits which both occur as the bottom split within a column and have a reboiler at their bottom product withdrawal location. The optimization solver is tasked with minimizing this objective function. If the assumption of minimum reflux is relaxed, the vapor duty requirement of a distillation configuration can be estimated by optimizing a rigorous tray-by-tray model. Such a procedure would be equivalent to optimizing a rigorous ASPEN Plus RADFRAC simulation for each configuration and can be relatively time consuming. Since the number of feasible configurations in the search space is very large, we recommend using the minimum reflux assumption since it avoids tray-by-tray computations. Our approach thus provides a quick screening tool to do a first level screening of the large number of configurations and identifies a handful of attractive candidates which can then be studied using a computationally intensive tray-by-tray model. We use the classical equations derived by Underwood[12] to estimate the minimum total vapor duty requirement. These equations provide a distillation column section based calculation method, that is, they do not involve tray-by-tray computations of compositions, temperatures, and flows to estimate the vapor duty requirement. The equations assume ideal liquid and vapor phase behaviors, constant relative volatilities of components, and constant and equal latent heats of vaporization for all components in the mixture. These assumptions are thus implicit in our model.

Decision Variables

We define the decision variables in a general manner, thereby ensuring that they are capable of describing each feasible distillation configuration in the search space. Conversely, the constraints, the objective function and variable sets are uniquely tailored to each distillation configuration based on the corresponding connectivity matrix.

1. **Stream flow rates** (X_m): Any distillation column must satisfy material balances. To write these constraints we need total molar flow rates of each stream. There are $n\times(n+1)/2$ upper triangular elements (or streams) in an $n \times n$ matrix corresponding to an n-component separation. We thus declare $n\times(n+1)/2$ optimization variables for the total molar flows of these streams. These variables are represented as X_m in this article, and describe the total molar flow of stream m. For a five component separation, 15 X_m variables, one for each stream will be created.

2. **Component flow rates** ($X_{m,k}$): Underwood's equations are solved for each split in the configuration. To estimate the vapor duty requirement of a split using Underwood's equations, we need the compositions and flow rates of the feed stream and the top product stream for each split. If the flow rates of each component in these streams are available, then the total flow rate of each stream and its composition can be calculated. Therefore, we declare the molar flow rate of each component in each stream as a decision variable. These variables are manipulated by the optimization solver as it tries to minimize our objective function. For $n\times(n+1)/2$ possible streams, we thus declare $n\times(n+1)/2\times n$ optimization variables for the molar flow of each component in each stream. These variables are denoted as $X_{m,k}$, and describe the flow of component k in each stream m. For a five component separation, 75 $X_{m,k}$ variables, one for each stream-component pair, will be created.

3. **Liquid and vapor flow rates** (L_m andV_m): The thermal quality or thermodynamic state of a stream is the fraction of the feed flow that is in the liquid phase. To solve Underwood's equations, we need to know the thermal qualities of the feed streams of each split in a configuration. Since the n final product streams cannot be feed streams to a split, we declare $2\times[n\times(n+1)/2-n]$ optimization variables that correspond to vapor and liquid flows associated with each possible feed stream. For each stream m, these variables are referred to as $L_m$and V_m, respectively. For a five component separation, there are a total of ten such stream flows and for each feed streamL_m and V_m variables are created to account for flows in both directions. The thermal quality of each stream can be easily calculated from these L_m and V_m variables. In the first part of this series of articles,[10] we have defined the thermal quality for various types of streams including streams that act as thermal coupling links and streams that are side-draws. The same convention is used in this article.

4. **Minimum vapor duty requirements for splits** ($V_s^{\min}$) **and Underwood roots** ($\theta_{s,r}$): The $X_{m,k}$, L_m, and$V_m$variables can be used to formulate Underwood's equations. These equations are defined as constraints that relate the minimum vapor duty requirement, $V_s^{\min}$ variables to variables $X_{m,k}$ and $\theta_{s,r}$. The $\theta_{s,r}$ variables are referred to in the literature as the "Underwood roots." If the feed stream to a split s has p components, the corresponding Underwood's equation has $p-1$ Underwood roots. For each split these are defined as decision variables and will be referred to using the symbol θ in this article.

5. **Actual split vapor flow at top** (V_s^{top}) **and bottom** (V_s^{bot}): V_s^{top} and V_s^{bot}, respectively, are the vapor flows in the rectifying and stripping section associated with split s. We thus require that V_s^{top} be no less than $V_s^{\min}$, and V_s^{top} is

related to V_s^{bot} through a material balance on vapor flow. When multiple splits (e.g., s and s') are present in the same column—where we assume s is right above s'—a material balance on vapor also links $V_{s'}^{top}$ of a lower section with V_s^{bot} of the section immediately above it, and hence $V_{s'}^{top}$ is related to V_s^{top}. Since the vapor flow in the rectifying section of one split is related to the vapor flow in the rectifying section of another split in the same column, that is, in our example, since V_s^{top} is related to $V_{s'}^{top}$, the minimum vapor flow of a particular split (say V_s^{min} for split s) can influence the vapor flow in every other section of the column containing multiple splits. For each split, $V_{s'}^{top}$ and V_s^{bot} are thus defined as decision variables.

6. **Split-specific distillate component flow rates** ($\bar{X}_{s,k}$): When a stream is produced by two splits, it acts as the bottom product for one split and the top product for the other split. In such a case, the feed streams of both the splits can contribute to the compositions of the common product stream (see Appendix C). Therefore, one or more of the component flow rates may not be representative of the separation of each split and cannot be used directly in Underwood's equations for the split. For minimum vapor duty requirement calculations, we thus need to estimate the portion of the component flows that are contributed only by the split under consideration. These component flows are split-specific component flows and we need separate variables to represent them. Thus, if there are n_s splits in a configuration that separates a feed mixture into n product streams, we declare $n_s \times n$ optimization variables for the split-specific distillate component flow rates. For a five component separation using the configuration shown in Figure 5c, the number of splits is 6 and the number of local distillate component flow rate variables will be 30.

Constraints

A distillation configuration has to satisfy phase equilibrium and mass balance rules. A mathematical expression of these rules gives rise to constraints. The following sign convention is used for writing these constraints.

1. For all splits in a configuration, the order of the splits is determined by the Z_{mat} number corresponding to their feed stream. A split fed by a stream with $Z_{mat} = 10$ will have a higher split number than a split fed by a stream with $Z_{mat} = 4$.

2. Every flow leaving a lower-numbered split as a product is either a pure final product or a feed to a higher-numbered split. In either case, a flow is considered positive when leaving the column containing the lower-numbered split that produces it. The net flow of such streams will always be positive. Liquid (or vapor) flow variables can be negative; that is, they can return to the column in a stream that has a net flow leaving the column, given the presence of a larger opposing flow of vapor (or liquid), respectively.

3. In any molar balance around a particular envelope, terms associated with any stream whose net flow is entering the envelope are added to the left hand side of the balance; terms associated with any stream whose net flow is leaving the envelope are subtracted from the left hand side of the balance. The right hand side of the balance contains only accumulation terms and is always zero.

With this convention, we can list the physical rules and the type of constraints they give rise to. It will be clear that the constraints corresponding to some rules will be different for each configuration.

1. **Material balance across columns**: In the absence of chemical reactions, non-condensables, and leaks, the total molar flow entering a distillation column must equal that leaving the column. Similarly the total molar flow of any component entering a distillation column must equal that leaving the column. These rules give rise to the following two types of linear equality constraints

$$\sum_{m \in \mathrm{FEEDC}_c} X_m = \sum_{m' \in \mathrm{PRODC}_c} X_{m'} \quad \forall c = 1, \ldots, n-1 \tag{1}$$

$$\sum_{m \in \mathrm{FEEDC}_c} X_{m,k} = \sum_{m' \in \mathrm{PRODC}_c} X_{m',k} \quad \forall c = 1, \ldots, n-1; \quad \forall k = 1, \ldots, n-1 \tag{2}$$

Here the FEEDC_c variable set contains all the feed streams entering the distillation column c, and the PRODC_c variable set contains all the product streams leaving distillation column c. The connectivity matrix corresponding to the configuration under consideration contains this information.

2. **Total stream flow constraints**: The total flow of any stream is equal to the sum of the flows of each component in the stream, and results in linear equality constraints.

$$X_m = \sum_{k=1}^{n} X_{m,k} \quad \forall m = 1, \ldots, n \times (n+1)/2 \tag{3}$$

3. **Feed definition constraints**: The flow rate F_k of each component k in the main feed stream F is specified by the user as a part of the problem definition. These values are assigned to the corresponding decision variables via n linear equality constraints. One of the requirements for a feed specification is the feed quality q_f. This must also be defined in an equation.

$$X_{1,k} = F_k \quad \forall k = 1, \ldots, n \tag{4}$$

$$V_1 = \sum_{k=1}^{n} F_k (1 - q_f); L_1 = \sum_{k=1}^{n} F_k (q_f) \tag{5}$$

4. **Constraints for streams that do not exist**: In a given configuration some streams may be absent. For such streams, if we retain the variables in the formulation, we must set the total stream flow and the component flows as 0. This gives rise to two types of linear equality constraints.

$$X_m = 0 \quad \forall m \in \mathrm{ABSENTS} \tag{6}$$

$$X_{m,k} = 0 \quad \forall m \in \mathrm{ABSENTS}; \quad \forall k = 1, \ldots, n \tag{7}$$

Here, the ABSENTS variable set contains all the feed streams that are absent in a given distillation configuration. The connectivity matrix corresponding to the configuration under consideration contains this information.

5. **Constraints for definite absence of components in streams**: All the streams except the main feed stream have some components absent. For instance, for a four component separation, the main feed stream is denoted as ABCD since it has some flow of each of the four components. In our model, any other stream such as BC is assumed to have no flow of some components such as A and D. In an actual distillation, all the components will be present in all the streams, in at least trace amounts. However, because of assumption of infinite theoretical stages in our model, streams with trace amounts of components may be treated as

not containing those components. The variables associated with the corresponding component flow rates are set to zero:

$$X_{m_s,k}=0 \quad \forall j=1,\ldots,n; \quad \forall i=1,\ldots,j; \quad \forall k=1,\ldots,i-1 \tag{8}$$

$$X_{m_s,k}=0 \quad \forall j=1,\ldots,n; \quad \forall i=1,\ldots,j; \quad \forall k=n+i-j+1,\ldots,n \tag{9}$$

6. **Net stream flow constraints**: For each stream, the sum of its liquid and vapor portions must equal its net flow. Also, the final product streams are liquid-only streams in our model. Furthermore, transfer streams associated with condensers are vapor-only streams, while transfer streams associated with reboilers are liquid-only streams in our model. These lead to four types of linear equality constraints.

$$X_m=L_m+V_m \quad \forall m=1,\ldots,\frac{n(n+1)}{2} \tag{10}$$

$$\left.\begin{aligned} X_m&=L_m \\ V_m&=0 \end{aligned}\right\} \quad \forall m=\frac{n(n-1)}{2}+1,\ldots,\frac{n(n+1)}{2} \tag{11}$$

$$\left.\begin{aligned} X_m&=L_m \\ V_m&=0 \end{aligned}\right\} \quad \forall m \in \text{REBOILERS} \tag{12}$$

$$\left.\begin{aligned} X_m&=V_m \\ L_m&=0 \end{aligned}\right\} \quad \forall m \in \text{CONDENSERS} \tag{13}$$

Here, the CONDENSERS and REBOILERS variable set contains the stream numbers of streams that originate from condensers or reboilers excluding the final product streams.

7. **Distillation constraints**: Based on the Z_{mat} matrix demonstrated in Figure 6, it is clear that for any $(i,j) < n$ the stream number corresponding to $Z_{mat}(i,j)$ is given by $Z_{mat}=\binom{j}{2}+i=\frac{j(j-1)}{2}+i$. Likewise for any stream m the ROW and COL variables uniquely identify the values of i and j which satisfy $m=\binom{j}{2}+i$; $n \geq j \geq i$; in other words, ROW and COL read the location of stream m in the Z_{mat} matrix.

In non-azeotropic distillation processes, the top product of a split must get enriched in at least one of the light components and the bottom product of a split must get enriched in at least one of the heavy components, relative to the feed stream. For instance, for the split of ABCD to ABC/BCD, we must ensure the following inequality constraint in our model.

$\frac{x_{B,\text{dist}}}{x_{C,\text{dist}}} \geq \frac{x_{B,\text{feed}}}{x_{C,\text{feed}}}$, where $x_{j,\text{stream}}$ is the mole fraction of component j in the stream.

A similar constraint is created for each pair of consecutive overlapping components (where applicable) in the product streams of each split. Each side of the constraint equation involves a ratio of component mole fractions belonging to the same stream. Therefore, these mole fraction terms can be replaced by the corresponding component flow rate terms. A rearrangement of terms then converts the constraint to a bilinear inequality constraint.

$$\begin{aligned} &\forall s \in \text{DISTC} \\ &m=\text{FEEDS}_s; m'=\text{DISTS}_s \\ X_{m,k-1}\times X_{m',k} \leq X_{m,k}\times X_{m',k-1}; \; &i=\text{ROW}(m); i'=\text{ROW}(m') \\ &j=\text{COL}(m); j'=\text{COL}(m') \\ &\forall k=3,\ldots,n-j+i \end{aligned} \tag{14}$$

These distillation constraints are applicable only when the product streams of a split have at least two overlapping components. The DISTC variable set contains all the splits which meet this criterion, and can be generated in a computer program by using the information in the corresponding connectivity matrix. In Eq. 14, i and j represent the row and column number corresponding to the distillate stream under consideration in the $n \times n$ matrix. The term $n-j+i$ corresponds to the last component in a stream at the location (i, j) in the matrix. FEEDS and DISTS give the stream number of the feed and distillate streams. When coupled with the molar balance, Eq. 14 ensures that the bottom stream of a split is also enriched in at least one heavy component.

8. **Thermal coupling constraints**: For streams that serve as thermal coupling links, the vapor portions of their flows must match the vapor flow entering or exiting the appropriate corresponding distillation column. Therefore, for a thermal coupling link connected to the top of a distillation column, the vapor portion of the flow must be set equal to the actual vapor flow above the feed of the top split of the distillation column. Similarly, for a thermal coupling link connected to the bottom of a distillation column, the vapor portion of the flow must be set equal to the actual vapor flow below the feed of the bottom split of the distillation column. These result in two types of linear equality constraints.

$$V_s^{\text{bot}}=-V_m \quad \forall m \in \text{TCBOTT}; \quad c=\text{CVECT}(m); \quad s=\text{SBOT}_c \tag{15}$$

$$V_s^{\text{top}}=V_m \quad \forall m \in \text{TCTOP}; \quad c=\text{CVECT}(m); \quad s=\text{STOP}_c \tag{16}$$

The TCBOTT variable set contains the stream numbers for the streams which serve as thermally coupled links at the bottom of a distillation column. Similarly the TCTOP variable set contains the stream numbers for the streams which serve as thermally coupled links at the top of a distillation column. The CVECT variable set contains information about which distillation column number produces stream m. SBOT_c and STOP_c give the splits that produce (respectively) the bottom and top produt of column c.

9. **Underwood's equations as constraints**: For every split in the configuration, we have to ensure two types of constraints that represent Underwood's equations. The first constraint is referred to as the Underwood feed constraint and is given by Eq. 17. It can be seen that this constraint is an $(n-j+1)^{\text{th}}$ order polynomial in θ (where j is the column number of the feed stream according to Z_{mat}). Basically, this equation is applied for each feed stream in the distillation configuration and the order of the polynomial in θ is the number of components in the corresponding feed stream. For a feed with p components, the constraint can be written as a p^{th} order polynomial in θ. Let these roots be $\theta 1 \geq \ldots \geq \theta \text{p}$. Then, Underwood showed that for $\alpha_{i+k} \leq \theta_k \leq \alpha_{i+k-1}$ for $k=1,\ldots,p-1$. The active root is further used to estimate the vapor duty requirement in the second Underwood constraint equation as shown in Eq. 18a. In Eq. 18a, $V_s^{\min}$ represents the minimum vapor duty requirement in the rectifying section of the split under consideration.

We have observed that it is not necessary to be able to identify this active root of a split (θ_a). We can instead estimate $V_s^{\min}$ for not just the active Underwood root, but instead for all other Underwood roots as well. The Underwood

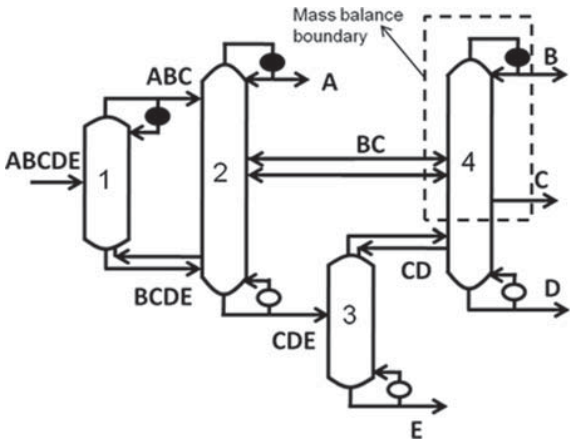

Figure 7. Example distillate component balance constraint boundary for split CD to C/D.

root(s) that results in the largest $V_s^{\min}$ value has always been observed to be the active root. The largest value of $V_s^{\min}$ thus corresponds to the minimum vapor duty requirement in the rectifying section of the split under consideration. Therefore, to avoid the difficulty of algorithmically identifying the active root (θ_a) of a split, we use the abovementioned observation and replace the Underwood vapor flow constraint by the equivalent inequality constraint as given by Eq. 18b.

$$\sum_{k=i}^{n-j+i} \frac{\alpha_k X_{m,k}}{\alpha_k - \theta_{s,r}} = V_m \qquad \begin{array}{l} \forall s=1,\ldots,ns; \quad \forall r=1,\ldots,n-j+i; \\ m=\text{FEEDS}_s; \quad i=\text{ROW}(m); \quad j=\text{COL}(m) \end{array} \tag{17}$$

$$\sum_{k=i}^{n-j+i} \frac{\alpha_k \bar{X}_{s,k}}{\alpha_k - \theta_{s,r}} = V_s^{\min} \qquad \begin{array}{l} \forall s=1,\ldots,ns; \quad \forall r=i,\ldots,n-j+i; \\ i=\text{ROW}(\text{DISTS}_s); \quad j=\text{COL}(\text{DISTS}_s) \end{array} \tag{18a}$$

$$\sum_{k=i}^{n-j+i} \frac{\alpha_k \bar{X}_{s,k}}{\alpha_k - \theta_{s,r}} \le V_s^{\min} \qquad \begin{array}{l} \forall s=1,\ldots,ns; \quad \forall r=i,\ldots,n-j+i; \\ i=\text{ROW}(\text{DISTS}_s); \quad j=\text{COL}(\text{DISTS}_s) \end{array} \tag{18b}$$

In these equations i corresponds to the first component of the stream under consideration and the term "$n-j+i$" corresponds to the last component of the stream under consideration. The variables $\bar{X}_{s,k}$ are split-specific distillate component flow rates.

Two separate cases are encountered in the course of the algorithm. When a split is such that components r and $r+1$ are found in both the top and bottom products of the split, Eq. 18a applies. When r and $r+1$ are not found in both top and bottom product, Eq. 18b will be used. Equation 18b can be thought of as more general; the applicability of Eq. 18a in the previously described cases has been demonstrated in literature.[13]

10. **Split-specific distillate component flow estimation constraints**: These constraints are essentially mass balance calculations across an envelope that covers the top of a distillation column and extends below until it includes the top product of the split under consideration. For example, the envelope for split CD to C/D in the distillation configuration of Figure 5d is shown in Figure 7. The calculations estimate the portions of the component flow rates ($\bar{X}_{s,k}$) in the top product of the split under consideration that originate only from the feed of the split under consideration. This ensures that we do not include flow contributions from other splits while estimating the vapor duty requirement of the split under consideration using the Eq. 18b.

$$\bar{X}_{s,k} = \sum_{m \in LPRODA_s} X_{m,k} - \sum_{m \in FEEDA_s} X_{m,k} \qquad \begin{array}{l} \forall s=1,\ldots,ns \\ i \in \text{ROW}(\text{DISTS}_s) \\ j \in \text{COL}(\text{DISTS}_s) \\ k=i,\ldots,n-j+i \end{array} \tag{19}$$

$$\bar{X}_{s,k} \le X_{m,k} \qquad \begin{array}{l} \forall s=1,\ldots,ns \\ m=\text{DISTS}_s \\ i \in \text{ROW}(\text{DISTS}_s) \\ j \in \text{COL}(\text{DISTS}_s) \\ k=i,\ldots,n-j+i \end{array} \tag{20}$$

DISTS_s is the distillate product stream of each split s. The LPRODA_s variable set contains the product streams that are above the split s within the same distillation column and the distillate product stream of the split s. The FEEDA_s variable set contains all the feed streams above the split s within the same distillation column.

11. **Vapor balance equations within column**: Once $V_s^{\min}$ is known for all splits within a column, these minimum vapor requirements must be coupled with a series of vapor balances to determine how much vapor is required at the column reboiler. This is achieved by the following three sets of equations:

$$V_s^{\text{top}} \ge V_s^{\min} \quad \forall s=1,\ldots,ns; \tag{21}$$

$$V_s^{\text{top}} = V_s^{\text{bot}} + V_m \quad \forall s=1,\ldots,ns; \quad \forall m \in \text{FEEDS}_s; \tag{22}$$

$$V_j^{\text{top}} = V_i^{\text{bot}} + V_m \quad \forall i \in \text{TOP}_c; j \in \text{BOT}_i; m \in \text{SD}_{i,j} \tag{23}$$

Equation 21 dictates that the actual top vapor flow must always exceed the minimum vapor requirement as calculated by Underwood's method. Equation 22 sets the difference between the top and bottom flows of vapor within a split equal to the amount of vapor added or withdrawn by the feed. In Eq. 23, TOP_c is a list of all splits in column c excluding the bottom split, while the BOT_i variable set returns the split j which is immediately below any split i. This equation enforces the mass balance of vapor at the boundary of two splits using variable set $\text{SD}_{i,j}$ which is the stream number corresponding to the side draw stream between split i and split j.

This completes the description of the objective function and the constraints of our optimization formulation for any given distillation configuration. It can be seen that the objective function is a linear function and all the constraints are linear except Constraints 14, 17, and 18b. The nonlinearity arises in constraint (14) because of the bilinear terms involved in it. The nonlinearity in constraint (17) arises from the fact that it is a polynomial in θ. The nonlinearity in constraint (18b) is because it involves fractional terms. Our optimization problem thus has a linear objective function with linear and nonlinear constraints, making it a NLP problem.

For each distillation configuration, a unique NLP problem can be algorithmically generated as described above. The formulation works with any non-azeotropic n-component

separation problem using $n-1$ columns and includes configurations with and without thermal coupling. We automatically generate an NLP problem for each configuration on the fly and solve it to global optimality, with current state-of-the-art solvers. Solving these NLP problems to global optimality is significantly easier than solving a single MINLP problem to global optimality. Our approach then provides a global optimization based rank-list of all possible basic and thermally coupled distillation configurations with respect to their total minimum vapor duty requirements.

Ensuring Global Optimality

NLP optimization solvers such as GAMS/BARON[14] guarantee global optimality as long as the formulation uses nonlinear functions such as bilinear, fractional, or logarithmic functions and the search space is compact. In our experience, the polynomial inequality (17) can pose a challenge to these solvers. We have therefore reformulated the equation to a more tractable form.

As mentioned before, Underwood showed that all the $p-1$ Underwood roots of a p^{th} order polynomial lie in between consecutive volatilities of the p feed components. Mathematically, this results for feed m with $i = \text{Row(m)}$:

$$\alpha_k \geq \theta_{s,k} \geq \alpha_{k+1} \tag{24}$$

GAMS/BARON solver has well defined convex relaxations for standard bilinear/fractional nonlinear functions.[15] These convex relaxations are used in the solver to arrive at the global minimum solution of the NLP through standard branch and bound method[16,17] based global optimization techniques.

One of the disadvantages of using branch and bound techniques is that the convergence can be quite slow. The GAMS/BARON optimization solver overcomes this limitation by using optimality and feasibility based range reduction techniques[18] to speed up the convergence.

Feasible Initial Guesses

The optimization solver benefits from a feasible and preferably good quality initial guess solution for each configuration's NLP problem. This is particularly true because of the singularity when θ_k approaches one of the relative volatilities. We ensure this by obtaining an initial guess using the SMA algorithm that was presented in detail in the first part of this series of articles.[10] The SMA involves analytical calculations only. Therefore, it quickly provides a feasible initial guess solution to the optimization solver. In fact, for some configurations, this solution also turns out to be the optimal solution.[10]

Improving the Speed of Convergence

The speed of convergence for Branch and Bound based techniques can be improved significantly by providing upper and lower bounds as close as possible to the global optimal solution, for all the optimization variables. In this section, we present some physical insights that can be used to generate good bounds for some key decision variables. For all other decision variables, basic insights from mass and material balance can be used to arrive at the appropriate best bounds.

1. The configuration with highest vapor duty requirement in the search space has to be a sharp split configuration without thermal coupling.[8]

In a sharp split configuration, all splits involved are sharp splits (i.e., each split does not have any components distributing between its distillate and bottom streams). The sharp split configurations without thermal coupling constitute a very small fraction of search space, and can be solved to global optimality analytically without any optimization iterations.[10] The sharp split configuration without thermal coupling and having the highest vapor duty requirement can thus be easily identified. Let us refer to this vapor duty requirement as Worst of sharp split (W_{SS}) vapor duty. This vapor duty requirement provides an upper bound for the total minimum vapor duty requirement for all the configurations in the search space, and thus provides an upper bound to the objective function in our formulation. It also provides a loose upper bound for the minimum vapor duty requirement for each split of each configuration ($V_s^{\min}$) in the search space.

2. The maximum vapor flow that can occur anywhere in a configuration equals the sum of the W_{SS} vapor duty and the vapor flow in the main feed stream.

We know that the upper bound of the minimum vapor duty requirement for any configuration is the W_{SS} vapor duty requirement. Since apart from the vapor produced in the reboilers, the only point at which additional vapor can enter a configuration is the main feed point in the first distillation column, the maximum vapor flow that can occur in any section of the configuration is given by the sum of W_{SS} and the vapor flow in the feed stream. Let us refer to this vapor flow as W_{SS+F}. This vapor flow value can be used as the upper bound for vapor flow in sidedraw streams and thermal coupling links.

3. The configuration with the lowest vapor duty requirement in the search space has to be the fully thermally coupled configuration (FTC).

The FTC is one in which all possible streams of the n-component separation are present; it has thermal coupling links at all the transfer streams. The global minimum vapor duty for this configuration can be calculated by the SMA method.[10] This configuration has the lowest vapor duty in the search space.[13,19,20] Observe that this configuration may not be practical to operate due to the presence of so many thermal couplings. Regardless, its vapor flow requirement is a mathematical lower bound for the total minimum vapor duty requirement for any configurations in the search space. This also provides a lower bound to the objective function in our formulation.

4. The vapor duty requirement of any split in a distillation configuration is greater or equal to its analytical transition split solution.

While this is true for any split in any configuration, we can exploit this fact only for the first split. This is because the feed to this split is the main feed stream which is completely defined *a priori*. The other splits in the configuration have feeds which may take many different values. The transition split solution for the minimum vapor duty requirement of the first split is easily calculated using the SMA algorithm.[10] This value is used as the lower bound for the corresponding vapor duty variable ($V_1^{\min}$).

5. The Underwood roots can be bounded more tightly using the bounds on corresponding component flows and vapor flows.

From Eq. 17, it can be seen that the Underwood root (θ) depends on the component flows in the feed to the split and the amount of vapor in the feed stream. Also, these roots lie

between consecutive relative volatilities of the feed components. However, we can get tighter lower and upper bounds for these roots by analyzing the bounds of the variables in Eq. 17 itself. The term (V_m) on the right hand side of Eq. 17 represents the vapor flow portion of the feed stream. The following two cases are considered for getting good bounds on this vapor flow.

Case 1: The feed stream is associated with a heat exchanger. A stream associated with a reboiler is a saturated liquid (thermal quality = 1) and a stream associated with a condenser is a saturated vapor (thermal quality = 0). This information can be used with the upper and lower bounds of the stream's individual component flows to estimate the upper and lower bounds for the variable, V_m.

Case 2: The feed stream is a thermal coupling link or a sidedraw stream. In this case, the vapor flow can be changed during each optimization iteration. Therefore, we use W_{SS+F} as the upper bound for this vapor flow.

Equation 17 relates the vapor flow entering a split with the variables X and $\theta_{s,r}$. Since $f(X,\theta_{s,r})$, the function given by the left hand side of Eq. 17, is increasing in $\theta_{s,r}$, it follows that the lower bound of the variable $\theta_{s,r}$ can be calculated by replacing the vapor flow term in Eq. 17 by its lower bound. Similarly, the upper bound of $\theta_{s,r}$ can be calculated by replacing the vapor flow term in Eq. 17 by its upper bound. For a fixed right hand side value in Eq. 17, $\theta_{s,r}$ will be lowest when each variable X is at its the upper bound in terms within the summation which are known to be positive, and at its the lower bound in terms within the summation which are known to be negative. Therefore we get:

$$\sum_{k=i}^{r}\frac{\alpha_k X^U_{s,k}}{\alpha_k-\theta^L{}_{s,r}}+\sum_{k=r}^{n-j+i}\frac{\alpha_k X^L_{s,k}}{\alpha_k-\theta^L{}_{s,r}}=V^L_s \tag{25}$$

A similar argument can be used to derive Eq. 28 for the upper bound of $\theta_{s,r}$:

$$\sum_{k=i}^{r}\frac{\alpha_k X^L_{s,k}}{\alpha_k-\theta^U{}_{s,r}}+\sum_{k=r}^{n-j+i}\frac{\alpha_k X^U_{s,k}}{\alpha_k-\theta^U{}_{s,r}}\le V^U_s \tag{26}$$

For example, consider a split with feed stream AB, we can find lower and upper bounds of Underwood root θ_1 that lies between α_A and α_B using the bounds of the component flow variables and the vapor flow variables in the Underwood feed equation as shown in Eqs. 27 and 28.

$$\frac{\alpha_A X^U_{AB,A}}{\alpha_A-\theta^L_1}-\frac{\alpha_B X^L_{AB,B}}{\theta^L_1-\alpha_B}=V^L_{AB} \tag{27}$$

$$\frac{\alpha_A X^L_{AB,A}}{\alpha_A-\theta^U_1}-\frac{\alpha_B X^U_{AB,B}}{\theta^U_1-\alpha_B}=V^U_{AB} \tag{28}$$

Following this procedure, we obtain tighter bounds of the Underwood roots for all splits in the configuration. This variable bound tightening is important because it avoids the singularities associated with $\theta_{s,k}$ becoming equal to one of the volatilities.

6. The minimum vapor duty of a split can be bounded more tightly using the bounds on the corresponding distillate component flows and Underwood roots.

It can be seen that the minimum vapor duty of a split depends on the distillate component flows and the Underwood roots. Since we already know how to calculate tighter bounds on Underwood roots, we can now get tighter bounds on the minimum vapor duty requirement. For example, for a split s with feed stream ABC to AB/BC, we can find lower and upper bounds of the minimum vapor flow variable using the bounds of the distillate component flow variables and the bounds on each active Underwood root. Equations 29 and 30 give the first set of limiting values on minimum vapor flow if active Underwood root is θ_1. In the same way, we can get a second set of limiting values on minimum vapor flow assuming θ_2 is the active Underwood root. The maximum of these limiting values gives the upper bound and the minimum of these limiting values gives the lower bound on the minimum vapor flow requirement for this split.

$$\frac{\alpha_A \overline{X}^U_{s,A}}{\alpha_A-\theta^L_{s,1}}-\frac{\alpha_B \overline{X}^L_{s,B}}{\theta^L_{s,1}-\alpha_B}-\frac{\alpha_C \overline{X}^L_{s,C}}{\theta^L_{s,1}-\alpha_C}=V^U_s \tag{29}$$

$$\frac{\alpha_A \overline{X}^L_{1,A}}{\alpha_A-\theta^U_1}-\frac{\alpha_B \overline{X}^U_{1,B}}{\theta^U_1-\alpha_B}-\frac{\alpha_C \overline{X}^U_{1,C}}{\theta^U_1-\alpha_C}=V^L_s \tag{30}$$

Results

To demonstrate the use of our GMA, we apply it to the problem of petroleum crude distillation. Petroleum crude oil is typically separated into the following five fractions: Naphtha (A), Kerosene (B), Diesel (C), Gas Oil (D), and Residue (E). In this article, we consider the heavy crude oil feed parameters that were used by Shah and Agrawal[2]. The relative volatility of each component A, B, C, and D, with respect to E is assumed to be 45.3, 14.4, 4.7, and 2.0, respectively. The feed mixture is assumed to contain 14.4% A, 9.3% B, 10.1% C, 3.9% D, and 62.3% E on a molar basis. The feed is a two phase mixture, with the flow corresponding to 90% of the heaviest component (E) being in the liquid phase and the remainder of the flow being in the vapor phase.

For this five component separation, the method of Shah and Agrawal[2,3] is used to enumerate the complete search space of basic and thermally coupled distillation configurations. We thus obtain 203 basic configurations and 5925 additional configurations that range from partial to complete thermal coupling, resulting in a total of 6128 candidate configurations. Throughout this section, the configurations are drawn in fully operable arrangements by the method of Agrawal[21,22] these arrangements are completely equivalent in terms of vapor to those such as the configuration drawn in Figure 7. We formulate the optimization problem in MATLAB and call the GAMS/BARON optimization solver through the GAMS/MATLAB interface provided by Ferris et al.[23].

To demonstrate the need for GMA algorithm, we run the optimization problem in the following three scenarios:

Scenario 1

Here, we solve our NLP optimization problem using the NLP solver GAMS/MINOS, without any inputs like feasible initial guesses from our SMA algorithm and without our tighter bounds. An NLP problem is generated and solved for all the 6128 candidate configurations. The following are the key observations from the results of this run.

1. MINOS could get globally optimal solutions only for 2378 candidate configurations out of the search space of 6128 configurations.

2. MINOS concludes that the problem is infeasible for 1625 candidate configurations.

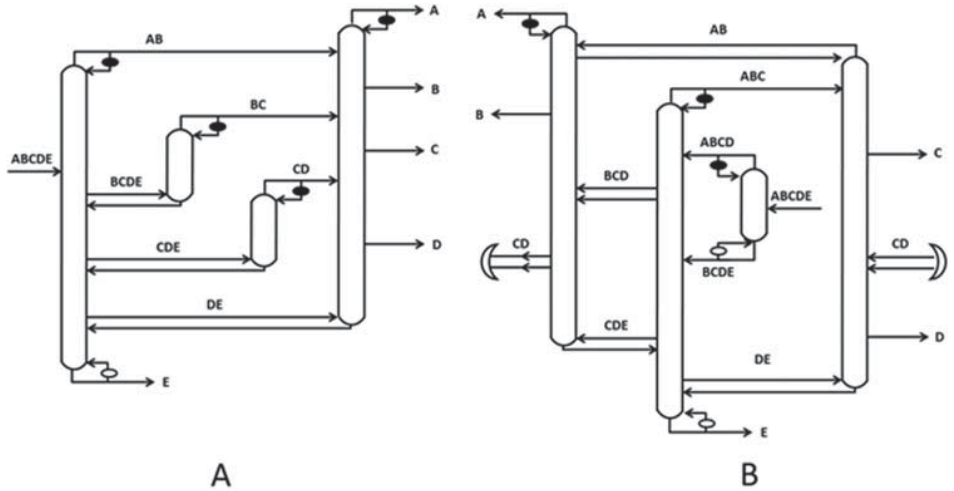

Figure 8. A/B: Fully operable arrangement of two distillation example configurations for which GAMS/MINOS gets only a locally optimal solution.

3. MINOS gets locally optimal solutions (i.e., those for which a superior solution can be identified using GMA) for 2125 candidate solutions. Figure 8a shows a configuration from this set. For this configuration MINOS gets only an intermediate local solution of 1.3678 moles of vapor duty requirement per mole of feed flow, which is higher than the true optimal solution of 0.7452 moles per mole of feed flow for this configuration by 83.5%. Figure 8b shows another configuration for which MINOS gets only a locally optimal solution of 1.3678 moles of vapor per mole of feed flow, which is higher than the globally optimal solution of 0.6996 moles per mole of feed flow for this configuration by 95.5%.

4. Of the 2125 locally optimal solutions, the maximum percentage by which the NLP solution is higher than the globally optimal solution is 95.5%.

Scenario 2:

Here we solve each of the 6128 NLP optimization problems using the NLP solver GAMS/MINOS with initial guesses from our SMA algorithm and with tighter bounds on the variables.

1. MINOS now could obtain the optimal solutions for 4447 configurations. It terminates infeasible solutions for 345 configurations and gets only locally optimal solutions for 1336 configurations.

2. In this run MINOS finds the optimal solution for the configuration shown in Figure 8a. For the configuration shown (Figure 8b), it gets only a slightly improved intermediate solution of 1.2224 moles per mole of feed flow, which is still higher than the globally optimal solution by 64.3%. The reason for this is, that as seen in Figure 8b, this configuration is a "satellite" configuration with streams transferred in opposite directions between two columns. Thus the initial guess from the SMA solution is not a very good starting point for the optimization solver.

Scenario 3

Here, we solve each of the 6128 NLP optimization problems using the global solver GAMS/BARON with initial guesses from our SMA method and with tighter bounds on variables.

1. The global optimization solver could get a locally optimal solution as good as that in scenario 2 for all 6128 configurations. 5640 of these configurations were solved to global optimality that was certifiably within 2% optimality tolerance in just 100 s of computational time per configuration on a Dell Precision T5500. Feasible local optima were reached for all remaining configurations and further examination revealed the majority of these could also be solved globally with additional time.

All of the above results clearly demonstrate the importance of the GMA method and a global optimization solver like BARON to obtain a reliable and guaranteed true rank-list of distillation configurations. We have found our GMA algorithm to be robust to different feed conditions and different number of components; in contrast to local solution methods, all configurations tested returned feasible answers.

Advantages of the Enumeration Strategy

For the heavy crude oil distillation example, we obtained a global optimization based rank-list of all configurations with respect to their minimum total vapor duty requirements. The lowest vapor duty requirement for this separation is found to be 0.6996 moles per mole of feed flow. Since we have access to a complete rank-list, we could observe that 175 configurations have this same minimum vapor duty requirement. Therefore, any of these configurations is the globally optimal configuration for this separation with respect to our objective function of total minimum total vapor duty requirement. These 175 configurations of course include the FTC shown in Figure 9. This configuration involves all transfer streams and has no transfer stream exchanger. However, several of the other configurations have significantly fewer transfer streams and significantly fewer thermal coupling links while having the same minimum total vapor duty requirement. For instance, five such configurations are shown in Figure 10. Therefore, having access to a global optimization based rank-list can significantly help process engineers to identify efficient distillation configurations that might be more suitable in other dimensions which are not easily quantified in a mathematical model, such as process safety and controllability.

If maximum ease of operability and controllability is known to be important, the tools described in this article can be easily tailored to produce solutions strong in these aspects with minimum computing time. For instance, consider another example

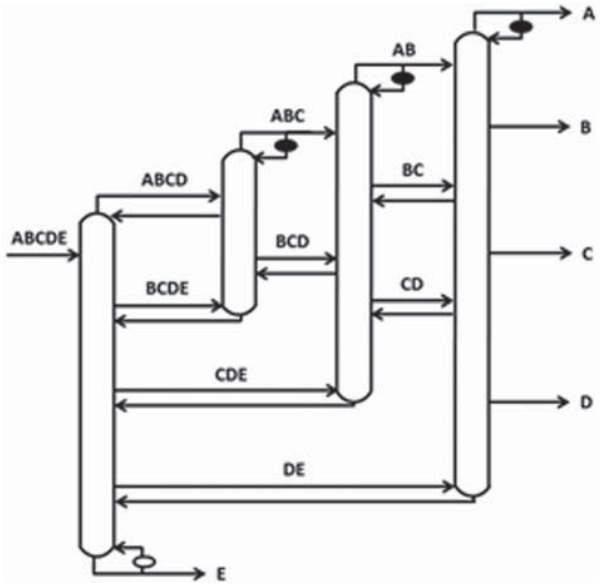

Figure 9. Fully operable arrangement of fully thermally coupled configuration.

using a general five-component liquid equimolar mixture with relative volatilities of components A, B, C, and D with respect to E being 39.0625, 15.625, 6.25, and 2.5, respectively. We know that the configuration with the minimum total vapor requirement will be the FTC, but the fact that this configuration contains six thermal coupling links can create difficulty in constructing and operating it. This ranklist tool can be adapted to synthesize alternatives with a vapor requirement within 5% of the FTC configuration via the following steps:

1. For a feed flow rate of 100 kmol/h, the minimum total vapor duty requirement of the FTC is 105.156 kmol/h. This value is set as the global lower bound.

2. The global upper bound is set as 1.05 times the global lower bound. This will ensure that we only capture those solutions which fall within 5% of the FTC configuration. We avoid solving every possible configuration in our search space to optimality, saving significant computing time.

3. The 203 CTC arrangements in the search space are first solved to global optimality. CTC arrangements are those with each transfer stream reboiler and condenser replaced by a thermal coupling link. The FTC configuration is the CTC configuration that contains all possible transfer streams.[24]

4. Twenty-six CTC configurations had a vapor requirement within 5% of the global optimum. For a basic configuration, conversion of a condenser or a reboiler to a thermal coupling link is known to generally lead to a decrease but never an increase in the overall heat duty of the configuration.[13,19,20] Therefore, for any configuration that does not belong to the set of 26 CTC configurations, if a thermal coupling were to be replaced with the corresponding reboiler or the condenser, the overall vapor requirement will never fall within 5% of the FTC vapor requirement. However, there are several thermal coupling links within the set of 26 CTC configurations noted above, which when replaced will either not contribute to an increase in the overall vapor requirement or, even with the increase, the overall vapor requirement may still be within 5% of the FTC vapor requirement.[25,26] Thus, for these 26 configurations, all partially thermally coupled variants with the same topology matrix were optimized using the same global upper and lower bounds. This approach yielded a total of 340 configurations with a minimum vapor requirement within 5% of the globally optimal vapor requirement. Solving

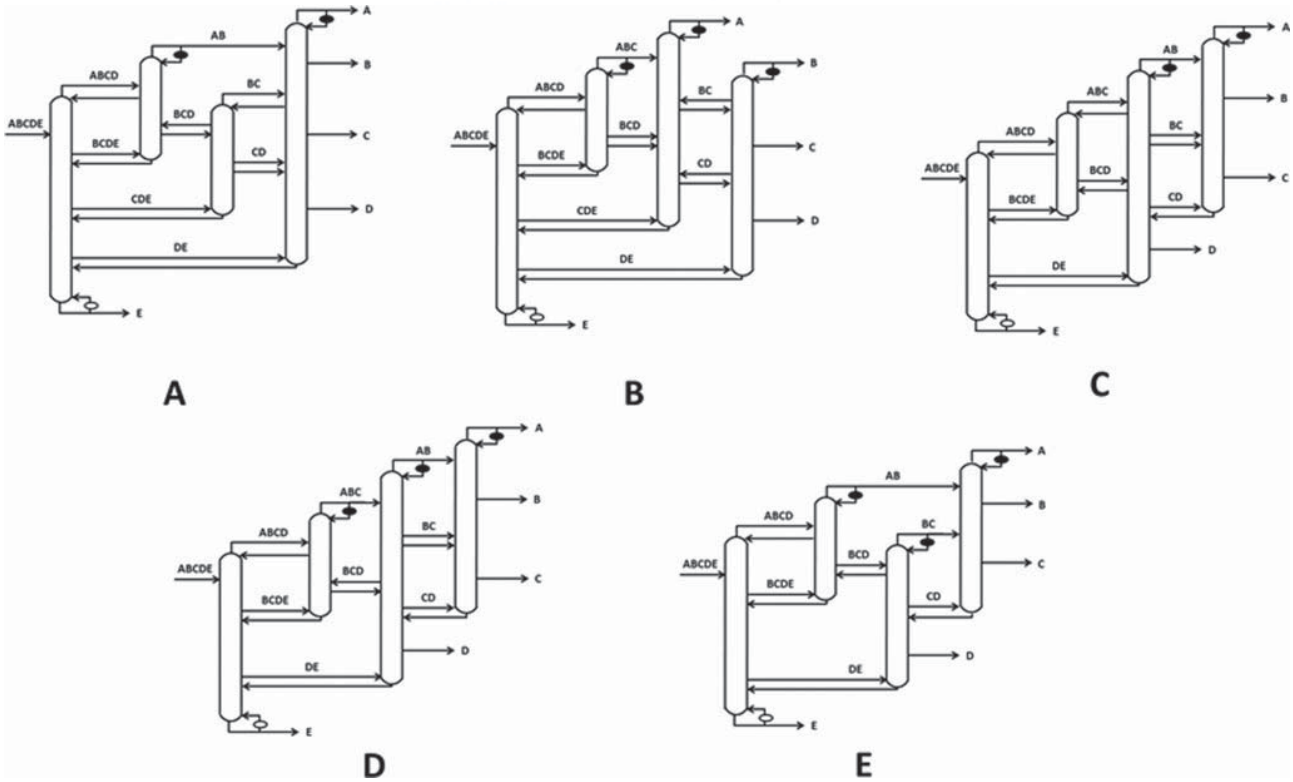

Figure 10. A/E: Fully operable arrangement of five distillation configurations from the list of the top 175 configurations that have the same global minimum total vapor duty requirement.

only 340 configurations out of 6128 configurations in our search space to global optimality results in a significant reduction in computing time.

After following this method, it was found that for this case 338 configurations converged to within 2% optimality tolerance, and the remaining two configurations converged to within 4.6% optimality tolerance within 100 s. Of these 338 configurations, 82 have the same vapor requirement as the FTC configuration (105.156 kmol/h), but use fewer thermal couplings. Of these 82 configurations, we can identify ten configurations which use only three thermal coupling links (plus one two-way side draw stream), compared to the six thermally coupled links (plus three sidedraw streams) used by the FTC configuration. One of these configurations is pictured in Figure F11 11. There also exist multiple configurations with only two thermally coupled links (plus one two-way sidedraw stream), which are within 5% of the globally optimal vapor duty. Figure 12 shows one such configuration with two thermal coupling links, which has a minimum vapor duty requirement of 107.948 kmol/h. This has 2.7% more vapor duty than the global minimum. Thus a practicing engineer can evaluate the trade-off between energy savings and reduced complexity from the point of easy operation and stability and make an informed decision that best suits the design needs of the application.

This example illustrates how the use of a ranklist with the GMA method and BARON solver helps identify the right configuration by considering the design and operability in tandem with the energy efficiency of the system in a reasonable computing time. We have also developed a visual tool that simplifies such a selection process. The tool allows quick selection of a subset of configurations by specifying constraints such as heat duty range of interest, number of acceptable thermal coupling links, and presence or absence of specific splits. By specifying such filters, one can quickly and visually observe flowsheets fulfilling these requirements. This allows an engineer to narrow the choice from thousands of available configurations to a select few on the fly.

In some situations, there may be significant uncertainty in the composition and flow rate of the feed mixture. In such a situation, one can generate global optimization based ranklists for some representative feed conditions, and then identify a configuration that is close to optimal for many of these different feed conditions.

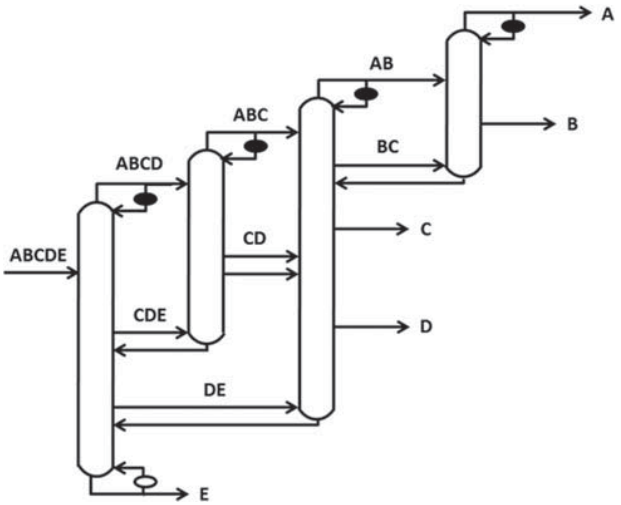

Figure 11. Fully operable arrangement—a five-component configuration with globally minimum vapor duty and only three thermally coupled links.

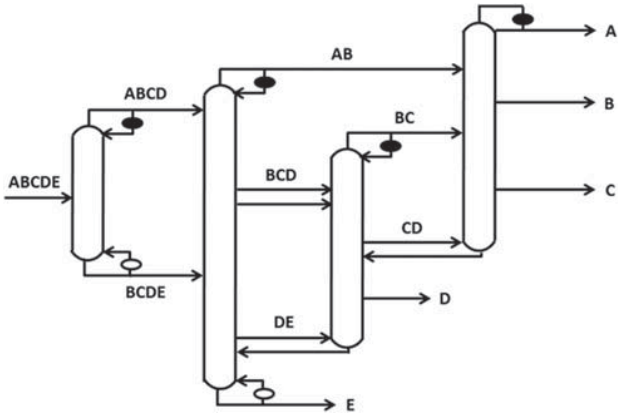

Figure 12. Fully operable arrangement—available five-component configuration with 1.027 times minimum vapor duty and two thermally coupled links

Conclusions

Previous work has demonstrated the need for a GMA due to the lack of optimality guarantee from sequential methods.[10] We have presented a general GMA that utilizes a reformulation of Underwood's equation to obtain a global optimization based rank-list of basic and thermally coupled configurations. We have used the minimum total vapor duty requirement as the objective function in our analysis. Our approach provides for the first time, a global optimization framework to identify optimal and near-optimal distillation configurations for ideal or near-ideal multicomponent separations. Our results demonstrate the limitations of using local optimization based NLP solvers. We also presented strategies based on fundamental and physical insights to improve the robustness and the speed of convergence of the distillation sequencing algorithm. Our approach relies on the enumeration of all the configurations in the search space, and allows practicing engineers to select optimal or near-optimal configurations while also taking into account difficult-to-quantify aspects such as control, operability, safety, and feed fluctuations.

Our general framework can be easily tailored to include capital cost and utility costs for specific distillation applications. We shall detail such enhancements in a subsequent paper.

Acknowledgments

The authors thank the US Dept. of Energy, award DE-FG36-06GO16104 for providing financial support for this work. The authors also thank Zheyu Jiang for his work on improving convergence and robustness of the optimization program.

Literature Cited

1. Giridhar AV, Agrawal R. Synthesis of distillation configurations: II. A search formulation for basic configurations. *Comp Chem Eng*. 2010;34:84–95.
2. Shah VH, Agrawal R. A matrix method for multicomponent distillation sequences. *AIChE J*. 2010;56(7):1759–1775.

3. Shah VH, Agrawal R. Conceptual design of zeotropic distillation processes. In: Gorak A, Sorensen E, editors. *Distillation: Fundamentals and Principles, Ch. 7*. Academic Press, 2014: 271–303.
4. Caballero JA, Grossmann IE. Generalized disjunctive programming model for optimal synthesis of thermally linked distillation columns. *Ind Eng Chem Res*. 2001;40:2260–2274.
5. Caballero JA, Grossmann IE. Design of distillation sequences: from conventional to fully thermally coupled distillation systems. *Comp Chem Eng*. 2004;28:2307–2329.
6. Agrawal R. Synthesis of multicomponent distillation configurations. *AIChE J*. 2003;49:379–401.
7. Shenvi AA, Shah VH, Zeller JA, Agrawal R. A synthesis method for multicomponent distillation sequences with fewer columns. *AIChE J*. 2012;58(8):2479–2494
8. Giridhar AV, Agrawal R. Synthesis of distillation configurations: I. Characteristics of good search space. *Comp Chem Eng*. 2010;34:73–83.
9. Turkay M, Grossmann IE. A logic based outer approximation algorithm for MINLP optimization of process flowsheets. *Comp Chem Eng*. 1996;20:959.
10. Nallasivam U, Shah VH, Shenvi AA, Tawarmalani M, Agrawal R. Global optimization of multicomponent distillation configurations: 1. Need for a reliable global optimization algorithm. *AIChE J*. 2013; 59(3):971–981.
11. Rod V, Marek J. Separation sequences in multicomponent rectification. *Coll Czech Chem Commun*. 1958;24:3240.
12. Underwood AJV. Fractional distillation of multicomponent mixtures. *Chem Eng Prog*. 1948;44(8):603–614.
13. Fidkowski ZT, Agrawal R. Multicomponent thermally coupled systems of distillation columns at minimum reflux. *AIChE J*. 2001;47: 2713–2724.
14. Tawarmalani M, Sahinidis NV. The branch-and-reduce optimization navigator (BARON), GAMS solver for global optimization of nonlinear (NLP) and mixed-integer nonlinear programs (MINLP), 2005.
15. Tawarmalani M, Sahinidis NV. *Convexification and Global Optimization in Continuous and Mixed-Integer Nonlinear Programming*. Kluwer Academic Publishers, 2002.
16. Edgar TF, Himmelblau DM, Lasdon LS. *Optimization of Chemical Processes*. McGraw-Hill Chemical Engineering Series, McGraw-Hill Book Company, 2001.
17. Horst R, Tuy H. *Global Optimization: Deterministic Approaches*. Springer, 1996.
18. Sahinidis NV. Global optimization and constraint satisfaction: the branch-and-reduce approach. COCOS 2002, LNCS 2003;2861:1–16.
19. Fidkowski ZT, Krolikowski L. Thermally coupled system of distillation columns: optimization procedure. *AIChE J*. 1986;32:537–546.
20. Halvorsen IJ and Skogested S. Minimum energy consumption in multicomponent distillation. 3. More than three products and generalized Petlyuk arrangements. *Ind Eng Chem Res*. 2003;42:605–615.
21. Agrawal R, Fidkowski ZT. More operable arrangements of fully thermally coupled distillation columns. *AIChE J*. 1998;44(11):2565–2568.
22. Agrawal R. A method to draw fully thermally coupled distillation column configurations for multicomponent distillation. *Chem Eng Res Des*. 2000;78(3):454–464.
23. Ferris MC, Jain R, Dirkse S. GDXMRW: interfacing GAMS and MATLAB. http://research.cs.wisc.edu/math-prog/matlab.html, 2011.
24. Agrawal R. Synthesis of distillation column configurations for a multicomponent separation. *Ind Eng Chem Res*. 1996;35:1059–1071.
25. Agrawal, R. Thermally coupled distillation with reduced number of intercolumn vapor transfers. *AIChE J*. 2000;46:2198–2210.
26. Shah, VH, Agrawal, R. Are all thermal coupling links between multicomponent distillation columns useful from an energy perspective? *Ind Eng Chem Res*. 2011;50:1770–1777.

Appendix A

In this section, we define the input parameters, subscripts, variables and variable sets that have been used in the formulation.

Input Parameters

q_f = thermal quality (or liquid fraction) in the main feed stream
F_k = molar flow rate of component k in the main feed stream
n = number of components in the main feed stream
$\alpha_k Z$ = relative volatility of component k with respect to the heaviest component

Subscripts Used in the Model Definition

c = distillation column number: 1,. . ., $n-1$
i = row number in $n \times n$ matrix: 1,. . ., n
j = column number in $n \times n$ matrix: 1,. . ., n
k = component number: 1,. . ., n
ns = number of splits in a given configuration
m = stream number: 1,. . ., $n\times(n+1)/2$
r = underwood root number
s = split number

Variables

L_m = liquid portion of the flow of stream m
X_m = total flow of a stream m
$X_{m,k}$ = flow of component k in stream m
$\bar{X}_{s,k}$ = flow of distillate component k contributed by split s
V_m = vapor portion of the flow of stream m
V_s^{bot} = actual vapor flow below the feed of split s
$V_s^{\min}$ = minimum vapor duty requirement for the split s
V_s^{top} = actual vapor flow above the feed of split s
θ_a = active Underwood root for a split
$\theta_{s,r}$ = underwood root r of the split s

Variable Sets

Note: The examples given here for each variable set corresponds to the distillation configuration in Figure 5d.

ABSENTS {Streams that are absent in the configuration}
e.g., {2, 5, 7, 10}

BOT_s {Split located directly below split s in a column}
e.g., {6} $_{\text{for } s = 5}$

BOTTS_s {Bottom product stream of a split s}
e.g., {6} $_{\text{for } s = 2}$

COL {Matrix column locations of streams}
e.g., {1, 2, 2, 3, 3, 3, 4, 4, 4, 4, 5, 5, 5, 5, 5}

COLR {Split numbers which are the bottom split in their respective column AND contain a reboiler at their bottom product}
e.g., {1, 2, 4, 6}

CONDENSERS {Streams associated with condensers except the final product streams}
e.g., {4}

CVECT {Distillation column number that produces the given stream}
e.g., {0, 0, 1, 1, 0, 2, 0, 2, 3, 0, 2, 4, 4, 4, 3}

DISTC {Splits for which distillation constraints are applicable}
e.g., {1}

DISTS_s {Distillate product stream of a split s}
e.g., {8} $_{\text{for } s = 2}$

FEEDA_s {Feed streams above split s within the same column}
e.g., {8} $_{\text{for } s = 6}$

FEEDC_c {Feed streams entering the distillation column c}
e.g., {3, 4} $_{\text{for } c = 2}$

FEEDS_s {Feed stream of a split s}
e.g., {3} $_{\text{for } s = 2}$

LPRODA_s {Product streams above split s within the same column including the split's top product}
e.g., {11, 8} $_{\text{for } s = 2}$

PRODC_c {Product streams exiting the column c}
e.g., {6, 8, 11} $_{\text{for } c = 2}$

REBOILERS {Streams associated with reboilers except the final product streams}
e.g., {6}

ROW {Matrix row locations of streams}
e.g., {1, 1, 2, 1, 2, 3, 1, 2, 3, 4, 1, 2, 3, 4, 5}

$STOP_c$ {Split that produces thermally coupled top product of column c}
e.g., {4} for $c = 3$
$SBOT_c$ {Split that produces thermally coupled bottom product of column c}
e.g., {1} for $c = 1$
$SD_{i,j}$ {Stream number of the side draw stream between split i and split j}
e.g., {8} for $i = 3$ & $j = 2$
TCBOTT {Thermal coupling links replacing reboilers in the configuration}
e.g., {3}
TCTOP {Thermal coupling links replacing condensers in the configuration}
e.g., {9}
TOP_c {List of splits in column c, excluding the bottom split in c}
e.g., {5} for $c = 4$

Appendix B

We provide the objective function equation and all the constraint equations for the configuration shown in Figure 5d.

Objective Function

$$\min\left(V_2^{\text{bot}}+V_4^{\text{bot}}+V_6^{\text{bot}}\right)$$

Constraints

1. *Material balance across columns*
Molar flow balance for distillation column 1:

$$X_1=X_3+X_4 \tag{B1}$$

The component molar flow balance for component 1 for column 1:

$$X_{1,1}=X_{3,1}+X_{4,1} \tag{B2}$$

Where X_1 represents molar flow of stream ABCDE and $X_{1,1}$ represents the molar flow of component A in the stream ABCDE and so on.

2. ***Total stream flow constraints***
For the stream ABC:

$$X_4=X_{4,1}+X_{4,2}+X_{4,3} \tag{B3}$$

3. ***Feed definition constraints***
For component 1:

$$X_{1,1}=F_1 \tag{B4}$$

$$V_1=(1-q_F)\sum_{j=1}^{5}F_j;L_1=(q_F)\sum_{j=1}^{5}F_j \tag{B5}$$

4. ***Constraints for streams that do not exist***

$$X_m=0\ \ \forall m\in\{2,5,7,10\} \tag{B6}$$

$$X_{m.k}=0\ \ \forall m=\{2,5,7,10\};\ \forall k=1,\ldots,5 \tag{B7}$$

5. ***Constraints for definite absence of components in streams***
Constraints for stream 8, that is, stream BC:

$$X_{8,k}=0;k=1 \tag{B8}$$

$$X_{8,k}=0;k=4,5 \tag{B9}$$

6. ***Net stream flow constraints***
For feed stream 8, product stream 11, reboiler stream 6 and condenser stream 4:

$$X_8=L_8+V_8 \tag{B10}$$

$$X_{11}=L_{11};\ V_{11}=0 \tag{B11}$$

$$X_6=L_6;\ V_6=0 \tag{B12}$$

$$X_4=V_4;\ L_4=0 \tag{B13}$$

7. ***Distillation constraints***
For overlapping component B and C in split 1 (ABCDE to ABC/BCDE):

$$X_{1,2}\times X_{4,3}\le X_{1,3}\times X_{4,2} \tag{B14}$$

8. ***Thermal coupling constraints***
For stream BCDE and stream CD:

$$V_1^{\text{bot}}=-V_3 \tag{B15}$$

$$V_3^{\text{top}}=V_9 \tag{B16}$$

9. ***Underwood's equation as constraints***
For split 2 (BCDE to BC/CDE):

$$\frac{\alpha_2X_{3,2}}{\alpha_2-\theta_{2,r}}+\frac{\alpha_3X_{3,3}}{\alpha_3-\theta_{2,r}}+\frac{\alpha_4X_{3,4}}{\alpha_4-\theta_{2,r}}+\frac{\alpha_5X_{3,5}}{\alpha_5-\theta_{2,r}}=V_3\qquad\forall r=1,2,3 \tag{B17}$$

$$\frac{\alpha_2\bar{X}_{2,2}}{\alpha_2-\theta_{2,r}}+\frac{\alpha_3\bar{X}_{2,3}}{\alpha_3-\theta_{2,r}}\le V_2^{\min}\qquad\forall r=1,2,3 \tag{B18}$$

10. ***Local distillate component flow estimation constraints***
For split 2 (BCDE to BC/CDE), for component B:

$$\bar{X}_{2,2}=X_{11,2}+X_{8,2}-X_{4,2} \tag{B19}$$

$$\bar{X}_{2,2}\le X_{8,2} \tag{B20}$$

11. ***Vapor flow balance throughout column***
For column 2:

$$V_2^{\text{top}}\ge V_2^{\min};V_3^{\text{top}}\ge V_3^{\min} \tag{B21}$$

$$V_2^{\text{top}}=V_2^{\text{bot}}+V_3;V_3^{\text{top}}=V_3^{\text{bot}}+V_4 \tag{B22}$$

$$V_3^{\text{bot}}=V_2^{\text{top}}-V_8; \tag{B23}$$

Appendix C

All calculations in this manuscript are performed under the following assumption:

When multiple splits share a column, the minimum vapor flow for each split can be found by solving the Underwood feed and distillate equations corresponding to each split, and then assuming a "mixing section" connecting the two splits; out of this mixing section a single stream is drawn with a composition calculated by completely mixing the products calculated individually for each split. The total vapor flow required by the column is equal to the greater of the two individual vapor flow requirements. This arrangement is assumed to be identical to a system that uses

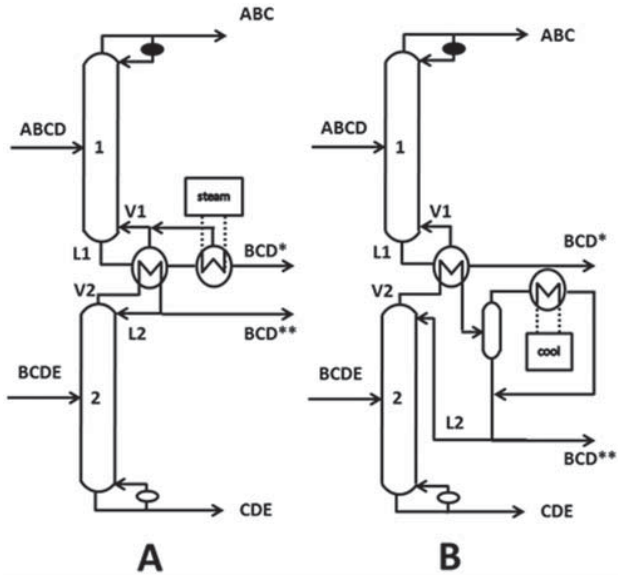

Figure 13. A/B: Possible heat exchange options for operating both splits using [amount of vapor = max(V1,V2)]. A: If V1 > V2, using heat from V2 to create part of V1 leads to a total of only V1 vapor requirement from utility. B/C: If V2 > V1, all of V1 can be generated by heat exchange with V2; the remainder of V2 is condensed using either cool utility or the liquid stream of a nearby thermal coupling.

heat integration to arrive at the same total vapor requirement for performing two separate splits, followed by mixing.

Assume two quaternary splits, S1 and S2, in a system with five components; each is treated separately. Each split produces a product we call BCD; however, when allowed to assume their minimum vapor flows, the compositions of the two BCD streams may differ (we will refer to them generally as compositions BCD* and BCD**).

Figure 13 shows some possible example heat integration arrangements (which assume constant latent heat) that would allow operation of both splits independently at their own vapor duty requirements using only the larger of the two individual vapor requirements as the total vapor requirement. In the case where V_1 (the top split's vapor flow) is higher than V_2 (the bottom split's vapor flow), the heat from the first column can provide part of the second column's duty through heat exchange, resulting in a total vapor requirement from utility of only V_1 rather than $V_1 + V_2$ (Figure 13a).

If $V_2 > V_1$ and the condensation done in the column is associated with cold utility, Figure 13b demonstrates an arrangement which uses part of the heat available in V_2 to vaporize V_1, and uses cold utility only for the condensation of V_2. Once again, this requires only a total of V_2 to be generated by hot utility, rather than $V_1 + V_2$. Thus, it has been demonstrated that there are many arrangements capable of operating two splits at a vapor duty of only $\max(V_1,V_2)$. In choosing instead to use the arrangement of directly transferring vapor within the column to operate at a vapor duty of $\max(V_1,V_2)$ we can be sure that the vapor duty could be duplicated through some form of heat exchange. Throughout this article, we assume that an arrangement such as Figure 13 could be designed for any two splits sharing the same column to achieve the vapor duty achieved by taking the maximum of the two. Due to this assumption, we do not optimize configurations by considering these different heat transfer arrangements. Instead, our model uses the simpler calculation of treating the maximum vapor requirement of all stacked splits (adjusted for feed and product streams as described in the Constraints section) as the column's vapor requirement.

Manuscript received Nov. 29, 2015, and revision received Feb. 5, 2016.

AQ1: Please check whether the author affiliations and corresponding details are OK as typeset.

AQ2: Please provide publisher location for Refs. 3, 15, 16, and 17.

AQ3: Please provide complete publication details for Ref. 14.

AQ4: Please confirm that given names (red) and surnames/family names (green) have been identified correctly.