Synthesis of Heat-Integrated Thermally Coupled Distillation Systems for Multicomponent Separations

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · AUGUST 2003

Impact Factor: 2.59 · DOI: 10.1021/ie030302k

3 AUTHORS, INCLUDING:

Ben-Guang Rong
University of Southern Denmark

Andrzej Kraslawski
Lappeenranta University of Technology

Synthesis of New Distillation Systems by Simultaneous Thermal Coupling and Heat Integration

Ben-Guang Rong* and Ilkka Turunen

Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, FIN-53851 Lappeenranta, Finland

Distillation systems with simultaneous thermal coupling and heat integration can significantly reduce both energy and capital costs compared with systems employing either thermal coupling or heat integration alone. Predefinition of all such new systems will provide a much better alternatives space in optimization when searching an optimal system for a given application. In a previous work (Rong et al. *Ind. Eng. Chem. Res.* **2003**, *42*, 4329−4339), a strategy for heat integration between heat exchangers associated with a single middle component in the thermally coupled configurations was presented, from which the heat-integrated partially coupled (HIPC) distillation systems were obtained. In this work, new strategies for simultaneous thermal coupling and heat integration have been approached, where heat integrations are performed between heat exchangers associated with both single middle components and submixtures of middle components. A large number of new heat-integrated thermally coupled (HITCs) distillation systems are synthesized. In the new HITCs, all the thermal couplings are located at the ends of columns, and all the heat integrations are implemented at the intermediate locations of the combined columns. Compared with the original thermally coupled configurations (OTCs), the new HITCs have the distinct features of (1) a reduction in the number of thermal couplings; (2) a reduction in the number of heat exchangers; and (3) a reduction in the number of columns. As a consequence, the new HITCs have the potential to further reduce energy and capital costs or to improve the operability of the OTCs. In this paper, all of the new HITCs for quaternary distillations are first generated. Then, a procedure is formulated to synthesize new HITCs for an *n*-component mixture. Finally, it is shown that the new HITCs produce distinct thermodynamically equivalent structures to those produced by the OTCs.

1. Introduction

Distillation is the most widely used separation method in the process industry, whereas it is the largest energy consumer among process units and simultaneously needs a large capital investment. New distillation systems with the potential to significantly reduce both energy consumption and capital investment are desired. Specifically, systematic synthesis of new distillation configurations can provide a much better alternatives space in optimization, from which an optimal alternative can be guaranteed for a specific application.

For an ideal or nearly ideal multicomponent mixture, a traditional distillation configuration was obtained by determining a separation sequence with sharp splits for the feed mixture.[1] A condenser and a reboiler are used for each of the columns in the traditional configuration. Traditional distillation configurations suffer from both high energy consumption and large capital investment. Conventionally, there are two ways to improve the economic performance of a traditional distillation configuration. One is through *heat integrations* among the condensers and reboilers of the simple columns.[2] Another is to use *thermal couplings* to eliminate some of the condensers and reboilers in the traditional configuration.[3] A heat-integrated distillation configuration can reduce energy consumption but very often increases capital investment.[2] A thermally coupled distillation configuration has the potential to reduce both energy and capital costs but tends to be more difficult in control and operation when too many thermal couplings are involved.[4]

In a recent work, we found that thermal coupling and heat integration can simultaneously be used in the design of distillation systems.[5] The opportunity for heat integration was found for partially coupled configurations in which there simultaneously exist a lighter middle component reboiler and a heavier middle component condenser between different columns, from which the heat-integrated partially coupled distillation systems (HIPCs) were produced. The HIPCs take advantage of both thermal coupling and heat integration simultaneously. In certain cases, they can significantly reduce both energy and capital costs versus systems with either thermal coupling or heat integration alone. Synthesis of all such HIPCs was presented.[5] A case calculation has fully demonstrated the advantages of the HIPCs. Therein, the heat integration has also been used to reduce the number of columns by implementing heat integration inside a column shell. The number of columns in an HIPC can be lower than that of its original thermally coupled configuration (OTC) for an *n*-component distillation (i.e., $<(n-1)$ columns).

For a multicomponent distillation, all of the traditional distillation configurations can be formulated by identifying the distinct separation sequences with both sharp and sloppy splits.[6] There are a certain number of condensers and reboilers in each of the traditional distillation configurations. A condenser for the most-volatile component and a reboiler for the least-volatile component are needed in any distillation configuration. Then, for any traditional distillation configuration, all the other heat exchangers can be classified into the following four categories: (1) heat exchangers associated with submixtures involving the most-volatile component; (2) heat exchangers associated with submixtures involving the least-volatile component; (3) heat exchangers associated with submixtures of only middle components; and (4) heat exchangers associated with a single middle component. In the previous work,[5] an OTC was first generated

* To whom correspondence should be addressed. Tel.: +358-5-621-6113. Fax: +358-5-621-2199. E-mail: benguang.rong@lut.fi.

10.1021/ie050493m CCC: $33.50
Published on Web 04/20/2006

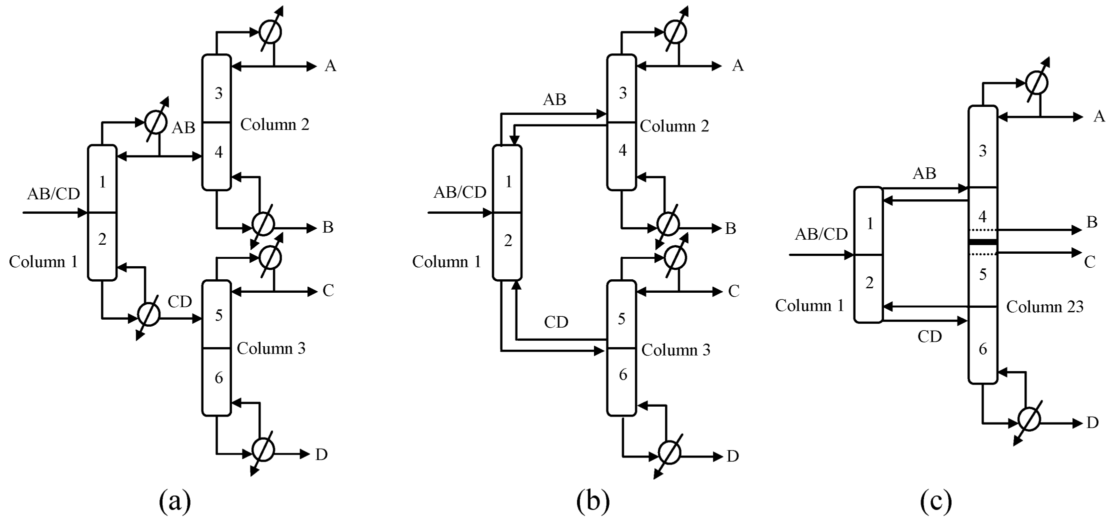

Figure 1. (a) Traditional distillation configuration; (b) thermally coupled configuration of Figure 1a; and (c) HIPC configuration of Figure 1b for a quaternary mixture.

for each of the traditional distillation configurations by eliminating all of the heat exchangers associated with submixtures of two or more components. The heat integrations were then performed among the remaining heat exchangers associated with only single middle components. Therein, thermal coupling and heat integration were successively introduced into a traditional distillation configuration in such a way that the heat integrations did not affect the thermal couplings of the OTCs. As a result, only one HIPC was found for a four-component mixture.[5] However, when thermal coupling and heat integration are simultaneously considered ab initio to deal with all the heat exchangers in the four categories, one realizes that there is the flexibility to deal with the heat exchangers with submixtures of only middle components. For some traditional distillation configurations, one can use either a thermal coupling to eliminate such a heat exchanger or one can perform a heat integration between such a heat exchanger and a heat exchanger of another column. In other words, thermal coupling and heat integration can be simultaneously used *ab origine* to deal with all of the heat exchangers in a distillation configuration. This will produce distinct new heat-integrated thermally coupled distillation systems (HITCs). Compared with the OTCs, the new HITCs can bring the merits of (1) a reduction in the number of thermal couplings; (2) a reduction in the number of heat exchangers; and (3) a reduction in the number of columns. As a consequence, the HITCs have the potential to further reduce energy and capital costs or to improve operability because of the reduced number of thermal couplings.

The main objective of this work is to systematically synthesize the new HITCs for zeotropic mixtures with four or more components. The work will first generate all of the new HITCs for quaternary distillations. Then, a procedure is formulated to generate the new HITCs for an *n*-component mixture. Finally, the generation of thermodynamically equivalent structures for the new HITCs is presented.

2. Generation of the New HITC Configurations for Quaternary Distillations

2.1. Simultaneous Thermal Coupling and Heat Integration for a Multicomponent Distillation. To understand the mass and heat transfers in a multicomponent distillation, let us first examine the quaternary HIPC configuration. In the earlier work,[5] we presented the HIPCs for the partially coupled configurations of an *n*-component mixture. Because heat integration was considered between a condenser associated with a heavier middle component and a reboiler associated with a lighter middle component, only one HIPC was found for a quaternary mixture which is shown in Figure 1c. There are two columns and two heat exchangers in the configuration of Figure 1c.

The separation sequence of the HIPC in Figure 1c has three intended individual splits (AB/CD → A/B → C/D). Each individual split designates a simple column. A simple column is defined as a column with one feed and two column sections: one rectifying section with a top condenser for the light product and one stripping section with a bottom reboiler for the heavy product. A simple column can perform any intended individual split in a separation sequence, either a sharp or a sloppy split. In this work, *a traditional distillation configuration* (TDC) is defined as a distillation configuration in which a simple column is used for each of the intended individual splits in the separation sequence. As a consequence, the number of simple columns in a TDC is equal to the number of the intended individual splits. The number of column sections, as well as the number of heat exchangers in a TDC, is twice the number of the intended individual splits in the separation sequence. For example, Figure 1a illustrates the traditional distillation configuration for the separation sequence of a quaternary mixture. There are three simple columns for the three intended individual splits in the TDC. As a consequence, there are six column sections and six heat exchangers in the TDC as shown in Figure 1a. There are two heat exchangers associated with a submixture in the TDC of Figure 1a. Such heat exchangers with submixtures have inevitable remixing at the ends of columns and cause separation inefficiency. According to Petlyuk et al.,[3] the separation inefficiency can be improved by eliminating the submixture heat exchanger and interlinking the columns by two-way vapor and liquid streams, i.e., *thermal coupling*. This produces thermally coupled configurations for multicomponent distillations. Such thermally coupled configurations can reduce both the energy and capital costs. Systematic synthesis of all of the thermally coupled configurations can be done for a multicomponent mixture by replacing the submixture heat exchangers with thermal couplings.[6] For example, the thermally coupled configuration for the TDC in Figure 1a is illustrated in Figure 1b.

Two thermal couplings in Figure 1b are introduced by eliminating the condenser AB and the reboiler CD of the TDC. In Figure 1b, the two-way thermal coupling AB connects column

1 and column 2. A vapor stream AB flows from column 1 to column 2 as the feed of column 2, and a liquid stream AB flows from column 2 to column 1 as the reflux of column 1. At the same time, the two-way thermal coupling CD connects column 1 and column 3. A liquid stream CD flows from column 1 to column 3 as the feed of column 3, and a vapor stream CD flows from column 3 to column 1 as the boilup of column 1. Thus, by thermal coupling AB, the condenser A in Figure 1b will provide both refluxes for column 2 and column 1. Similarly, by thermal coupling CD, the reboiler D in Figure 1b will provide both boilups for column 3 and column 1. Therefore, each thermal coupling can *laterally* coordinate two separation units of the TDC.

A distinct feature of such *thermal coupling* is that it brings forth direct material flows between the thermally linked columns. This will designate *the same nominal pressure* between the two thermally linked columns. For ternary mixtures, Linnhoff et al.[7] indicated that the same nominal pressure of the two thermally linked columns would be a disadvantage when considering heat integration between the columns and the background process. However, for four or more component mixtures, such a nominal pressure is advantageous when considering heat integrations between the columns within the thermally coupled configurations.[5] Nevertheless, to provide a driving force for vapor transports between two thermally coupled columns, the pressure of the column withdrawing the vapor should be a little higher than that of the column receiving the vapor stream. Such a pressure difference can avoid the use of expensive compressors to transport vapor flows.[8] Moreover, we will discuss later that such a pressure difference is also beneficial in providing a sufficient temperature driving force for heat integration between the columns.

In Figure 1b, there are four heat exchangers associated with a single component. One condenser for the most-volatile component and one reboiler for the least-volatile component are always needed in a distillation system. The most-volatile component condenser will designate the extreme cold utility with the lowest temperature, and the least-volatile component reboiler will designate the extreme hot utility with the highest temperature for the whole separation task. The other two heat exchangers will need heating or cooling temperatures between the lowest and the highest temperatures. Since the thermally linked columns have the same nominal pressure, the temperature of condenser C is certainly higher than that of reboiler B. Thus, *heat integration* can be implemented between condenser C and reboiler B for further energy savings. Furthermore, if heat integration between column 2 and column 3 is implemented inside one column shell, then the HIPC can have only two columns. This column number (i.e., $<(n-1)$) is less than that of both the TDC in Figure 1a ($n-1$ columns) and the OTC in Figure 1b ($n-1$ columns). Therefore, it becomes clear that the principal idea of such heat integration in Figure 1c is two-fold: first, it can further save energy than the thermally coupled configuration, and second, it can combine simple columns to reduce the total number of columns. Thus, such new HITC configurations have the potential to significantly reduce both energy and capital costs versus configurations with either thermal coupling or heat integration alone.

A distinct feature of such *heat integration* in Figure 1c is that it uses the intrinsic temperature difference between a condenser of a lower column and a reboiler of an upper column. The temperature difference is due to the fact that the feed submixture of the lower column is heavier than that of the upper column. Furthermore, as discussed above, the temperature driving force for such heat integration can be amplified by the pressure difference for vapor transports of the thermally linked columns. There is a fundamental difference between such heat integration in the thermally coupled configuration and that in the traditional simple column configurations. In traditional heat-integrated simple column configurations (e.g., ref 2), the pressure of one column was significantly increased in order to make its condenser work as a heat source of a reboiler of another column. As a consequence, the mass transfer of the simple columns is usually deteriorated because of the decreases in the relative volatilities by the pressure increments. Therefore, although it usually gives energy savings in a heat-integrated simple column configuration, its capital cost is very often higher than that of the corresponding simple column configuration.

It is clear that thermal coupling and heat integration can simultaneously be used to coordinate the mass and heat transfers between the multiple separation units, from which the new HITCs can be synthesized. The heat integration in Figure 1c was performed between a condenser with a heavier middle component of one column and a reboiler with a lighter middle component of another column. It was the only HIPC found for quaternary mixtures.[5] However, we will show in the next section that a heat integration can be performed between a pair of a condenser and a reboiler associated with any single middle components or any submixtures of middle components. For mixtures with four or more components, there are quite many opportunities where thermal coupling and heat integration can simultaneously be used to produce the new HITCs.

2.2. New HITC Configurations for Quaternary Distillations. Clearly, thermal coupling and heat integration represent *two distinct mechanisms* to coordinate the mass and heat transfers between the multiple separation tasks in a distillation system. A thermal coupling can *laterally* coordinate two individual tasks by replacing a heat exchanger associated with a submixture with the two-way thermal coupling streams. A heat integration, on the other hand, can *vertically* combine two columns by implementing the heat exchange between a condenser of one column and a reboiler of another column inside a combined column. The two distinct mechanisms dictate that there need to be at least three individual tasks in the separation sequence where thermal coupling and heat integration can simultaneously be employed. Therefore, the true opportunities for simultaneous use of thermal coupling and heat integration appear among the functionally distinct configurations for mixtures with four or more components.

For an n-component distillation, the number of the intended individual splits in the distinct separation sequences is between the minimum number of $n-1$ and the maximum number of $n(n-1)/2$.[6] If a simple column is used for each of the intended individual splits, then the number of the heat exchangers in a TDC is between the minimum number of $2(n-1)$ and the maximum number of $n(n-1)$. For an n-component mixture ($n \geq 4$), except the most-volatile component and the least-volatile component, all the other components are called middle components. Thus, for an n-component mixture, there are $n-2$ middle components.[5] The $n-2$ middle components can generate $(n-1)(n-2)/2$ distinct intermediate volatility subgroups (including the subgroups with a single middle component). This means that there will be a certain number of condensers and reboilers associated with the intermediate volatility subgroups among the TDCs. As known, a condenser for the most-volatile component and a reboiler for the least-volatile component must be needed in any distillation configuration. The other heat exchangers in the TDCs can be classified into the following four categories:

Category 1. Heat exchangers associated with submixtures involving the most volatile component;

Category 2. Heat exchangers associated with submixtures involving the least volatile component;

Category 3. Heat exchangers associated with submixtures composed of only middle components; and

Category 4. Heat exchangers associated with a single middle component.

For the heat exchangers in the four categories, there are opportunities to use either thermal coupling or heat integration to coordinate the intended individual splits in the separation sequence. To systematically synthesize the new distillation systems by simultaneous thermal coupling and heat integration, the following *rules* have been formulated to deal with the heat exchangers in the TDCs.

Rule 1. *The heat exchangers of Categories 1 and 2 in a TDC can only be dealt with via thermal couplings*. A heat exchanger of Category 1 with a submixture involving the most-volatile component will always appear as a top condenser of a column. Conversely, a heat exchanger of Category 2 with a submixture involving the least-volatile component will always appear as a bottom reboiler of a column in a TDC. There is no opportunity for heat integration between these heat exchangers of Categories 1 and 2. (Do not consider Rathore et al.[2] multieffect schemes).

Rule 2. *The heat exchangers of Category 3 in a TDC can be dealt with either via thermal couplings or heat integrations.* A submixture associated with only middle components can be obtained from either a top condenser of a column, a bottom reboiler of a column, or both a top condenser of one column and a bottom reboiler of another column in a TDC. There are opportunities to use either thermal coupling or heat integration for the heat exchangers of Category 3.

Rule 3. *The heat exchangers of Category 4 in a TDC can only be dealt with via heat integrations*. A middle component product can be obtained from either a top condenser of a column, a bottom reboiler of a column, or both a top condenser of one column and a bottom reboiler of another column in a TDC. Also, it is known that thermal couplings are used to deal with the heat exchangers associated with submixtures of binary or more components in a TDC.

At the same time, the heat integration can be implemented between a condenser associated with a subgroup of one or more middle components in one column and a reboiler associated with a subgroup of one or more middle components in another column. Therefore, there will be opportunities for heat integrations in the following *four cases*:

Case 1. Heat integration between a condenser of a single middle component and a reboiler of a single middle component (heat exchangers in Category 4);

Case 2. Heat integration between a condenser of a submixture of middle components and a reboiler of a submixture of middle components (heat exchangers in Category 3);

Case 3. Heat integration between a condenser of a single middle component and a reboiler of a submixture of middle components (heat exchangers in Categories 3 and 4); and

Case 4. Heat integration between a condenser of a submixture of middle components and a reboiler of a single middle component (heat exchangers in Categories 3 and 4).

Depending on the subgroups associated with the condenser and the reboiler, there are two different ways to combine the simple columns through heat integrations. When the condenser and the reboiler are associated with the same subgroup, there is allowed mass communication at the heat-integrated location along the combined column. Meanwhile, the same subgroup is withdrawn at a single location of the combined column. It is seen that most of the OTCs with sloppy split(s) derived in the earlier work belong to such cases where a middle-component product was withdrawn at a single location of a combined column.[6] Conversely, when the condenser and the reboiler are associated with two different subgroups, there is not allowed mass communication at the heat-integrated location within the combined column. Meanwhile, the two different subgroups are withdrawn at two different locations of the combined column. This can prevent the remixing of the two different subgroups around the heat-integrated location in a combined column (e.g., Figure 1c). The former with mass communication at the heat-integrated location is defined as *open heat integration* (OHI) (a thin horizontal line will be used to denote mass communication between column sections in the following figures). The latter without mass communication at the heat-integrated location is defined as *closed heat integration* (CHI) (a thick horizontal line denotes no mass communication between column sections, e.g., Figure 1c).

Obviously, for heat integrations in Cases 1 and 2, if the condenser and the reboiler are associated with the same single middle component or the same submixture of middle components, then there will be OHI to combine the two-section columns. Otherwise, there will be CHI to combine the two-section columns. For Cases 3 and 4, there will be always CHI to combine the two-section columns.

In previous works,[5,6] the opportunity for heat integration among the thermally coupled configurations has only been found for the previously mentioned Case 1. However, when considering Cases 2−4, there are certainly new opportunities for heat integrations among the functionally distinct thermally coupled configurations. For a quaternary mixture, there will be produced many new distillation systems with simultaneous thermal couplings and heat integrations. When considering heat integrations of Case 2 among all of the OTCs for a quaternary mixture, four OTCs were found which can further use heat integrations to produce new HITCs. The original OTCs are presented in parts a−d of Figure 2. The corresponding new HITCs are presented in parts a−d of Figure 3. When considering heat integrations of Cases 3 and 4 among all of the OTCs for a quaternary mixture, four other OTCs were found which can further use heat integrations to produce new HITCs. The original OTCs are presented in parts e−h of Figure 2. The corresponding new HITCs are presented in parts e−h of Figure 3.

For each configuration in parts a−d of Figure 3, the heat integration is implemented for the intermediate transferring submixture BC. This corresponds to the heat integration of Case 2 where both the condenser and the reboiler are associated with the same submixture of middle components. In each such configuration, the intermediate submixture BC is produced from both a reboiler of an upper column and a condenser of a lower column in the TDC. Thus, an OHI can be implemented between this pair of condenser and reboiler. *With heat integration, we designate that the intermediate transferring stream withdrawn from the heat-integrated location is a liquid flow*. A liquid flow (compared to a vapor flow) can cope well with the pressure disturbances of the combined columns and is advantageous for the system's control and operation. Note that, except the two-way vapor and liquid transfers by thermal coupling and the one-way liquid transfer by heat integration for the intermediate submixture BC, there are exactly the same structures for the configurations between parts a−d in Figure 2 and parts a−d in

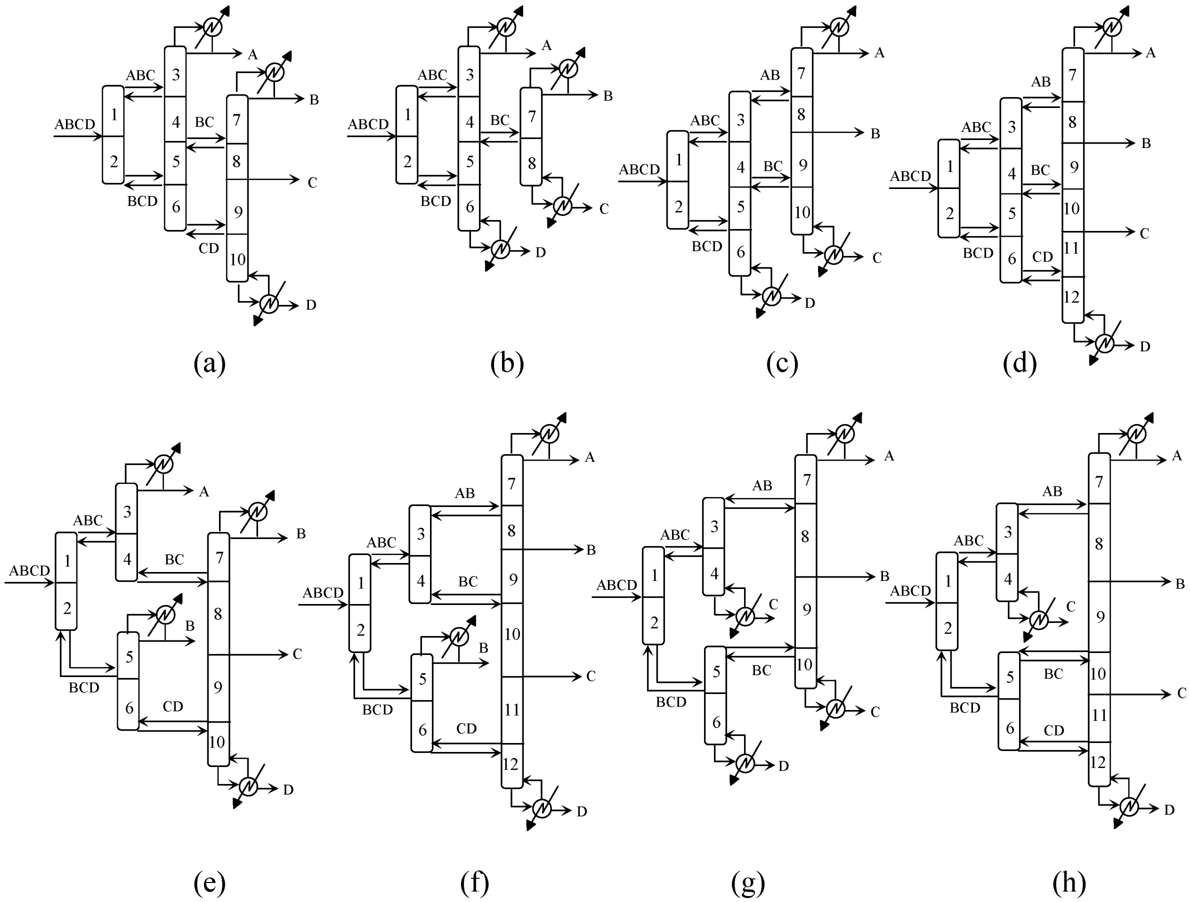

Figure 2. Original functionally distinct thermally coupled configurations for quaternary mixtures.

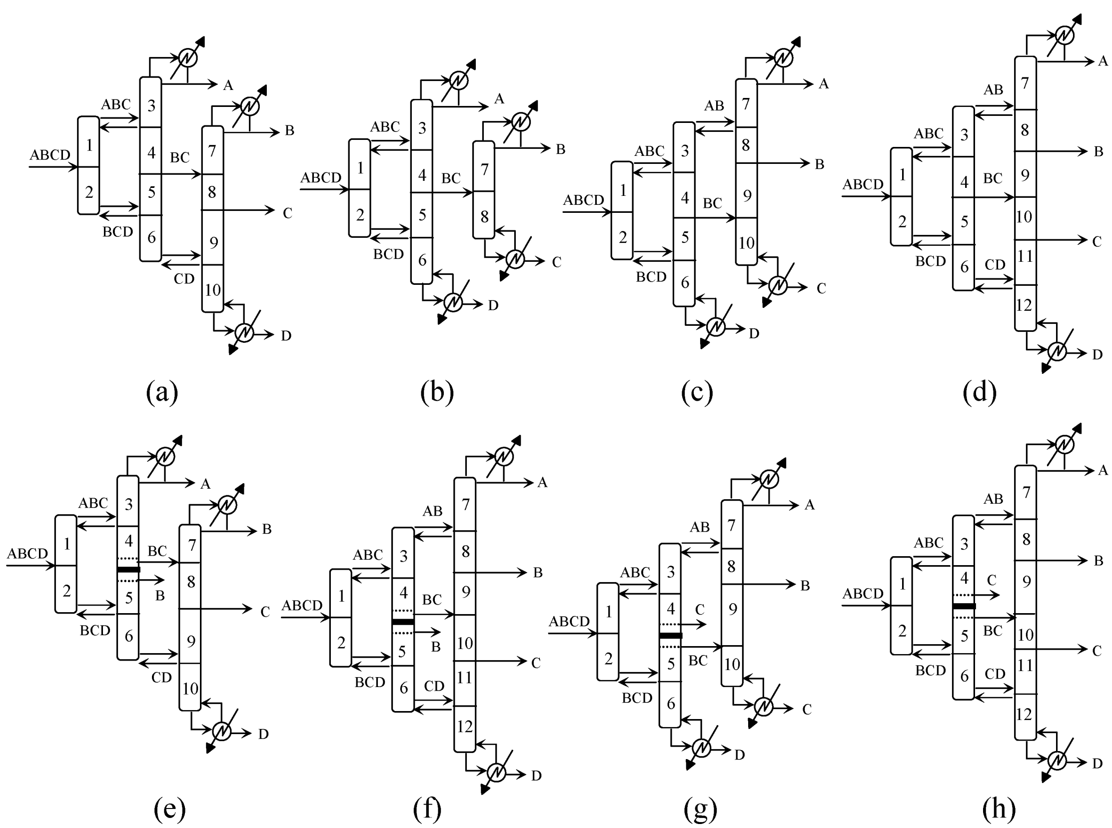

Figure 3. New HITCs for the OTCs in Figure 2.

Figure 3. One can expect that there will be similar energy and capital costs for the configurations in parts a−d of Figure 3 and the corresponding ones in parts a−d of Figure 2. However, there is a reduced number of thermal couplings in the configura-

Table 1. Distinct Separation Sequences from Each First Split for a Five-Component Mixture

	first split	distinct separation sequence	no. of splits	no. of column sections
1	A/BCDE	A/BCDE → B$\underline{\text{CD}}$E → B$\underline{\text{C}}$D → C$\underline{\text{D}}$E → B/C → C/D → D/E	7	14
2	AB/CDE	AB/CDE → C$\underline{\text{D}}$E → A/B → C/D → D/E	5	10
3	ABC/DE	ABC/DE → A$\underline{\text{B}}$C → A/B → B/C → D/E	5	10
4	ABCD/E	ABCD/E → A$\underline{\text{BC}}$D → A$\underline{\text{B}}$C → B/CD → A/B → B/C → C/D	7	14
5	A$\underline{\text{B}}$CDE	A$\underline{\text{B}}$CDE → B$\underline{\text{CD}}$E → B$\underline{\text{C}}$D → CD/E → A/B → B/C → C/D	7	14
6	AB$\underline{\text{C}}$DE	AB$\underline{\text{C}}$DE → AB/C → C$\underline{\text{D}}$E → A/B → C/D → D/E	6	12
7	ABC$\underline{\text{D}}$E	ABC$\underline{\text{D}}$E → A$\underline{\text{BC}}$D → A/BC → B$\underline{\text{C}}$D → B/C → C/D → D/E	7	14
8	A$\underline{\text{BC}}$DE	A$\underline{\text{BC}}$DE → B$\underline{\text{CD}}$E → AB/C → B$\underline{\text{C}}$/D → C$\underline{\text{D}}$E → A/B → B/C → C/D → D/E	9	18
9	AB$\underline{\text{CD}}$E	AB$\underline{\text{CD}}$E → AB/CD → CD/E → A/B → C/D	5	10
10	A$\underline{\text{BCD}}$E	A$\underline{\text{BCD}}$E → A$\underline{\text{BC}}$D → B/CDE → AB/C → BC/D → C$\underline{\text{D}}$E → A/B → B/C → C/D → D/E	10	20

tions in Figure 3. Thus, the new configurations will be more flexible than the corresponding original ones in terms of operability.[4,9] Moreover, we will show later that the reduction in the number of thermal couplings will significantly affect the rearrangements of column sections in the thermodynamically equivalent structures.

For configurations in parts e and f of Figure 3, the heat integration is implemented between a reboiler associated with the intermediate submixture BC of an upper column and a condenser associated with the single middle component B of a lower column. This corresponds to the heat integration of Case 4, and it is a CHI. Similarly, for the configurations in parts g and h of Figure 3, the heat integration is implemented between a reboiler associated with the single middle component C of an upper column and a condenser associated with the intermediate submixture BC of a lower column. This corresponds to the heat integration of Case 3, and it is a CHI. Note that there are dramatic structural changes between the configurations in parts e−h of Figure 3 and those in parts e−h of Figure 2. One heat integration for each configuration in parts e−h of Figure 2 can result in the following: (1) a reduction of one thermal coupling of submixture BC, (2) a reduction of one heat exchanger of a single middle component (B or C), and (3) a combination of two columns to one combined column. Thus, there needs to be three columns (i.e., $n - 1$) in the new HITCs in parts e−h of Figure 3 with an extra middle-component product. Whereas, in the original OTCs in parts e−h of Figure 2, there needs to be four columns (i.e., $>(n - 1)$) for an extra middle-component product. These distinct features make the new HITCs in parts e−h in Figure 3 advantageous compared to the OTCs in parts e−h in Figure 2 in terms of both energy and capital costs.

It is interesting to note that there are completely symmetric structures between the HITCs of parts a and e of Figure 3, between parts c and g of Figure 3, and between parts d and f and parts d and h of Figure 3. The only difference is the use of an OHI or a CHI for the transfer of the intermediate submixture BC. An additional middle-component product will be obtained in the CHI case. However, they are produced from functionally distinct separation sequences with inherently different intended individual splits. There is one different intended individual split for the submixture BCD between parts a (i.e., B$\underline{\text{C}}$D) and e (i.e., B/CD) of Figure 3, for the submixture ABC between parts c (i.e., A$\underline{\text{B}}$C) and g (i.e., AB/C) of Figure 3, for the submixture BCD between parts d (i.e., B$\underline{\text{C}}$D) and f (i.e., B/CD) of Figure 3, and for the submixture ABC between parts d (i.e., A$\underline{\text{B}}$C) and h (i.e., AB/C) of Figure 3. Note that the functionally distinct separation sequences are unchanged in the HITCs of Figure 3 compared to those of the corresponding OTCs of Figure 2. In other words, there are the same inherent intended individual splits between the HITCs in Figure 3 and the corresponding OTCs in Figure 2. However, there are no such symmetric structures among the OTCs in Figure 2. Thus, *heat integration can lead to substantial changes in the structures of the distillation systems*.

It is important to pay special attention to the transfer of an intermediate submixture between intermediate locations of two columns (e.g., the intermediate submixture BC in Figures 2 and 3). In the OTCs in Figure 2, such an intermediate submixture BC is transferred in a two-way communication due to thermal coupling, whereas in the HITCs in Figure 3, such an intermediate submixture BC is transferred in a one-way communication due to heat integration. Therefore, one can say that thermal coupling and heat integration represent two distinct mechanisms in the determination of a one-way or two-way communication for transferring an intermediate submixture. Clearly, these two mechanisms are crucial for the systematic synthesis of all functionally distinct distillation configurations for any *n*-component mixture.

3. New HITC Configurations for an *n*-Component Mixture

3.1. New HITC Configurations for Five or More Component Mixtures. For mixtures with five or more components, the HITCs can be generated whenever thermal coupling and heat integration can simultaneously be used in the distillation systems. For any TDC of an *n*-component mixture, one can readily identify all of the heat exchangers based on the intended individual splits in its distinct separation sequence. All of the heat exchangers can then be classified into the four categories presented in Section 2, whereby the three *rules* are then used to deal with the heat exchangers in each category. Whenever the opportunities for heat integrations in the four cases appear, they can be implemented to produce the new HITC systems. Thus, one can be sure that the new HITCs can be systematically generated by identifying all of the functionally distinct separation sequences for any *n*-component mixture. This can be done by determining the *first splits* for the feed mixture. Each first split will designate a branch to generate the functionally distinct separation sequences for the feed mixture.[6] To do so, the following procedure is formulated for the generation of the feasible HITCs from the functionally distinct separation sequences.

Step 1. Choose a first split among all of the $n(n - 1)/2$ first splits for an *n*-component mixture. For example, there are 10 first splits for a five-component mixture, as shown in Table 1.

Step 2. Formulate a distinct separation sequence by determining the intended individual splits for the subgroups generated from the first split.

Step 3. Determine the TDC by using a simple column for each of the intended individual splits in the identified separation sequence. This will determine all of the heat exchangers in the TDC.

Step 4. Identify the types of heat exchangers in the TDC. Except the condenser for the most-volatile component and the reboiler for the least-volatile component, all the other heat exchangers are classified into the four categories presented in Section 2.

Step 5. Identify the heat exchangers in Categories 1 and 2. These heat exchangers are associated with the submixtures involving the two extreme volatility components of the feed mixture. According to Rule 1, these heat exchangers in Categories 1 and 2 can be eliminated by introducing corresponding thermal couplings.

Step 6. Identify the heat exchangers in Categories 3 and 4. These heat exchangers are associated with either submixtures of only middle components or a single middle component. According to Rules 2 and 3, they could provide opportunities for heat integrations.

Step 7. For the heat exchangers in Categories 3 and 4, identify the pairs of condensers and reboilers based on the four cases for heat integrations presented in Section 2. Whenever a reboiler in an upper column and a condenser in a lower column are identified, then the opportunity for heat integration appears. This will determine the actual heat integrations in the final configurations.

Step 8. Determine the HITC systems by performing the identified heat integrations in Step 7.

As examples, Table 1 presents a distinct separation sequence for each of the 10 first splits for a five-component mixture. The corresponding HITC systems are presented in Figure 4, respectively.

Like the configurations in Figure 3, for each HITC in Figure 4, the two-way communications between columns are the vapor and liquid streams from thermal couplings, and the one-way communications are the liquid streams from heat integrations. It is seen that the HITCs can have a different number of columns. Each of the HITCs in parts b, c, f, and i of Figure 4 has three columns ($<(n-1)$ columns), and each of the HITCs in parts a, d, e, g, h, and j of Figure 4 has four columns ($n-1$ columns). It is also seen that the HITCs can have a different number of heat exchangers. Each of the HITCs in parts b, c, f, h, and j of Figure 4 has two heat exchangers, i.e., one condenser for the most-volatile product A and one reboiler for the least-volatile product E. Each of the HITCs in parts a, d, e, g, and i of Figure 4 has one or more heat exchangers for the intermediate volatility products. The number of column sections in each of the HITCs in Figure 4 is determined by its distinct separation sequence shown in Table 1. The number of column sections in each HITC is twice the number of the intended individual splits in the distinct separation sequence.

3.2. Structural Features of the New HITC Configurations. Unlike the OTCs, all of the thermal couplings in the HITCs are located at the ends of the columns. All heat exchangers are also located at the ends of the columns. This means that the two ends of a column in a HITC will have either two thermal couplings, or two heat exchangers, or a thermal coupling and a heat exchanger. On the other hand, all of the heat integrations are implemented at intermediate locations of the columns. This means that those columns with more than two sections are combined columns through heat integrations. It also dictates that an intermediate submixture transferring between intermediate locations of two columns in an HITC is a one-way liquid stream. At the same time, each heat integration will increase two sections in a combined column. A column with two sections has no heat integration, one with four sections has one heat integration, and one with six sections has two heat integrations. The number of column sections will increase by two with one more heat integration included.

Like the OTCs, for each HITC in Figures 3 and 4, a counterpart of two column sections is designated to one intended individual split in the separation sequence. The odd numbers represent the rectifying sections and the even numbers represent the stripping ones. Similarly, the column units in the HITCs of Figures 3 and 4 are *sequentially* arranged based on the intended individual splits in the distinct separation sequences. These structural arrangements are similar to the simple column configurations in which the simple columns are *sequentially* arranged based on the individual splits in the separation sequences. Specifically, the first column in each of the HITCs in Figures 3 and 4 implements only the first split of the feed mixture. The subsequent columns implement the other intended individual splits in the separation sequence. The column unit with more than two sections is a combined column with heat integrations(s). We define the HITC configurations in Figures 3 and 4 as the *original HITC configurations* with regard to the intended individual splits in the distinct separation sequences. It will distinguish them from the other possible thermodynamically equivalent arrangements.

It is worthwhile to further compare the HITCs with the OTCs and TDCs in terms of both the number of columns and the number of heat exchangers. The number of columns in any HITC is $\leq(n-1)$, while the number of columns in the TDCs is between the minimum number of $n-1$ and the maximum number of $n(n-1)/2$ (i.e., the number of intended individual splits in the separation sequence). The number of columns in the OTCs is $\geq(n-1)$.[6] On the other hand, the number of heat exchangers in the HITCs is equal to or less than that in the OTCs but is always less than that in the TDCs. Note that there are the same number of column sections between the HITCs and the corresponding OTCs and TDCs. In other words, both thermal couplings and heat integrations in the HITCs will not change the column sections of the OTCs and the TDCs. There are some HITCs (like the one in Figure 1c) which are distinct from any other possible distillation configurations in terms of both the number of columns and the number of sections. As shown in Figure 1c, for four or more component mixtures, some of the HITCs with only one condenser and one reboiler have a minimum number of $2(n-1)$ column sections. At the same time, they have $<(n-1)$ columns. Like Figure 1c, such HITCs (one condenser and one reboiler, minimum number of $2(n-1)$ sections, $<(n-1)$ columns) were produced from those distinct separation sequences with only sharp splits.[5] They are distinct from both Petlyuk fully coupled configurations[3] (one condenser and one reboiler, $n(n-1)$ sections, $n-1$ columns) and Agrawal's satellite column configurations[10] (one condenser and one reboiler, $4n-6$ sections, $n-1$ columns). Furthermore, like the configurations in parts e−h of Figure 3 and in parts d, f, h, and j of Figure 4, some of the HITCs can produce one or more additional intermediate volatility products. They are more flexible when products with different purities or different properties are needed.

4. Thermodynamically Equivalent Structures of the New HITCs

Thermodynamically equivalent structures (TESs) are the distinct features of thermally coupled distillation configurations. Optimal synthesis of the TESs will not only ensure savings on energy and capital costs but also improve hydraulic performance and operability of the thermally coupled distillation systems.[11] The heat integrations in the HITCs will significantly affect the TESs. For a distillation system involving thermal couplings, the thermal couplings will bring forth structural degrees of freedom

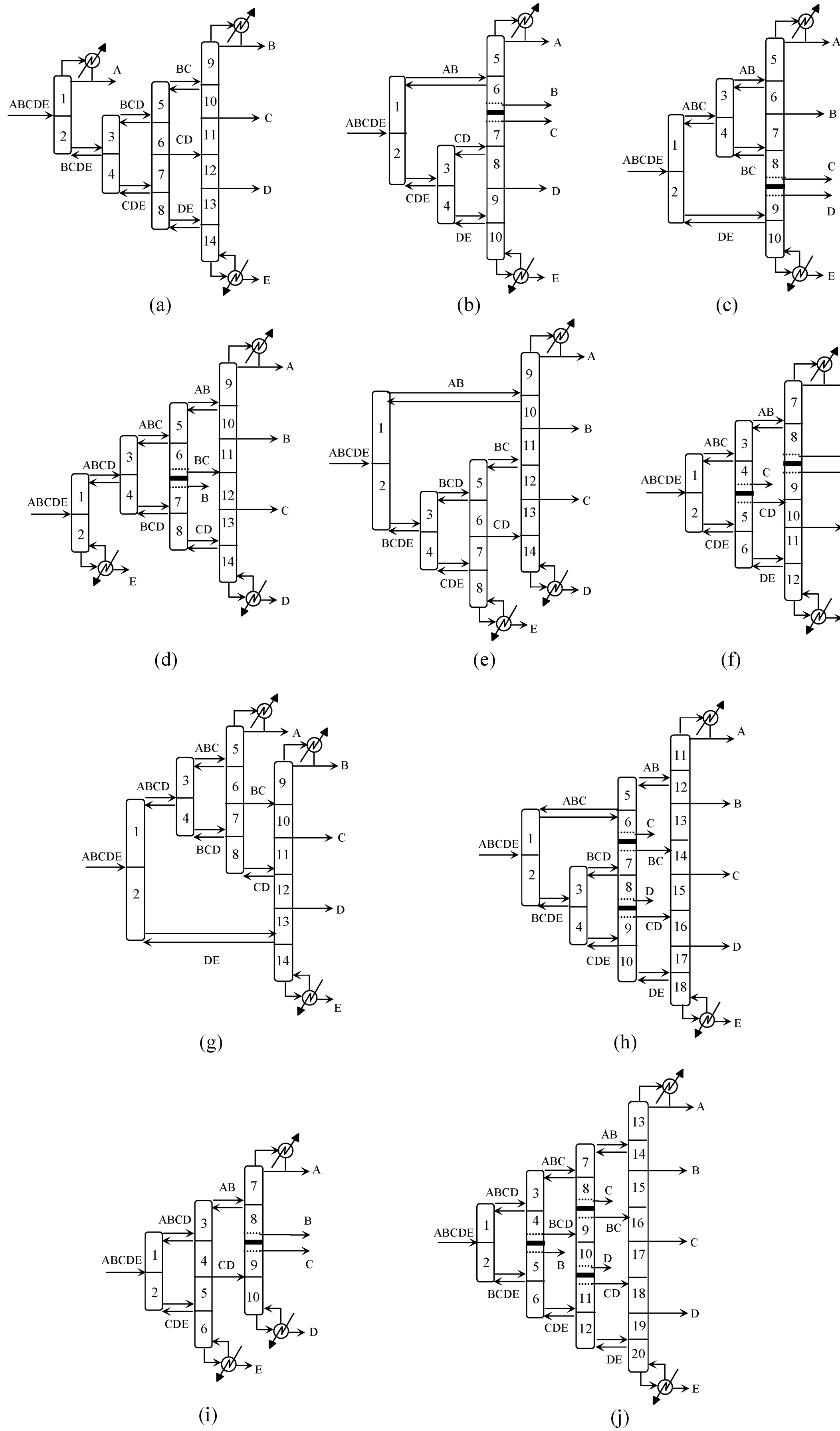

Figure 4. Functionally distinct HITCs from the distinct sequences in Table 1 for a five-component mixture.

from which some column sections are movable. The movable column sections are designated by the thermal couplings. The TESs are generated by movement of the movable column sections between the columns. Recently, we developed *two rules*

Table 2. Thermal Couplings, Movable Sections, Number of TESs for the HITCs in Figures 1c and 3, and Number of TESs for OTCs in Figures 1b and 2

configs	thermal couplings	movable column sections	no. of TESs of HITCS	configs	no. of TESs of OTCs
1c	AB, CD	3, 6	4	1b	4
3a	ABC, BCD, CD	3, 6, 10	8	2a	16
3b	ABC, BCD	3, 6	4	2b	8
3c	ABC, BCD, AB	3, 6, 7	8	2c	16
3d	ABC, BCD, AB, CD	3, 6, 7, 12	16	2d	32
3e	ABC, BCD, CD	3, 6, 10	8	2e	16
3f	ABC, BCD, AB, CD	3, 6, 7, 12	16	2f	32
3g	ABC, BCD, AB	3, 6, 7	8	2g	16
3h	ABC, BCD, AB, CD	3, 6, 7, 12	16	2h	32

to account for the number of structural degrees of freedom and the number of movable column sections in a thermally coupled configuration.[11] Using the two rules, all possible TESs for a thermally coupled configuration can be systematically generated.

The two rules are valid for any thermally coupled configurations, including the HITCs, to generate all the TESs. However, the heat integrations in the HITCs will cause them to have a different number of structural degrees of freedom, as well as a different number of movable column sections, than the OTCs. This will significantly affect the rearrangements of column sections as well as the number of the TESs. As seen from Figures 3 and 4, the HITCs have thermal couplings only at the ends of the columns. The intermediate submixtures transferred between intermediate locations of two columns in the HITCs will have no structural degrees of freedom. This means that the HITCs will have no counterparts of the movable column sections from the intermediate transferring submixtures. Therefore, in any HITC, each thermal coupling will designate one movable column section to produce the TESs. However, if the designated movable column section is combined with another column section via heat integration, then this pair of column sections must be moved together. For example in Figure 4b, thermal coupling CD will designate a pair of combined column sections 6 and 7 to be moved together. Similarly in Figure 4e, thermal coupling BC will designate a pair of combined column sections 10 and 11 to be moved together. In other words, *a pair of column sections combined via heat integration (either OHI or CHI) in a HITC must stay together in the TESs*. Like in the OTCs, the two column sections with the feed mixture must stay together in any TESs of the HITCs.

Now, all of the TESs for any HITC can be readily generated with the two rules. First, the number of thermal couplings in the HITC is counted. Then, the movable column section corresponding to each of the thermal couplings is identified. Finally, the TESs can be obtained by systematically moving the movable column sections in a combinatorial way. The number of the TESs (TES_n) for any HITC of an n-component mixture can be calculated using the following eq 1 (NTC = number of thermal couplings).[11]

$$TES_n = \sum_{i=0}^{NTC} C_{NTC}^{i} = 2^{NTC} \quad (1)$$

Table 2 presents the thermal couplings, the corresponding movable sections, and the number of the TESs for the HITCs in Figures 1c and 3, respectively. The number of the TESs for the OTCs in Figures 1b and 2 are also presented in Table 2. Table 3 presents the thermal couplings, the corresponding movable sections, and the number of TESs for the HITCs in Figure 4.

Table 3. Thermal Couplings, Movable Sections, and Number of TESs for the HITCs in Figure 4

configs	thermal couplings	movable column sections	no. of TESs
4a	BCDE, BCD, CDE, BC, DE	4, 5, 8, 9, 14	32
4b	AB, CDE, CD, DE	5, 4, 6+7, 10	16
4c	ABC, DE, AB, BC	3, 10, 5, 8+9	16
4d	ABCD, ABC, BCD, AB, CD	3, 5, 8, 9, 14	32
4e	AB, BCDE, BCD, CDE, BC	9, 4, 5, 8, 10+11	32
4f	ABC, CDE, AB, DE	3, 6, 7, 12	16
4g	ABCD, DE, ABC, BCD, CD	3, 14, 5, 8, 12+13	32
4h	ABC, BCDE, BCD, CDE, AB, DE	5, 4, 6+7, 10, 11, 18	64
4i	ABCD, CDE, AB	3, 6, 7	8
4j	ABCD, BCDE, ABC, CDE, AB, DE	3, 6, 7, 12, 13, 20	64

From Table 2, it is seen that, for the HITCs with a reduced number of thermal couplings, the number of TESs is sharply reduced compared with the corresponding OTCs. The number of TESs of each HITC in Figure 3 (one thermal coupling reduced) is reduced by half that of the corresponding OTC in Figure 2. The number of the TESs of Figure 1c is the same as that of Figure 1b, because there are the same thermal couplings in the two configurations. From eq 1, one can predict that any further reduction in thermal couplings will dramatically reduce the number of possible TESs.

Another significant change resulting from heat integration is *the thermodynamically equivalent side-column structures* of the HITCs. As illustrated, for any thermally coupled configuration, a *unique* thermodynamically equivalent side-column structure can be produced by simultaneous movement of all its movable column sections.[6,11] For example, the corresponding thermodynamically equivalent side-column structures for the OTCs in Figures 1b and 2 are presented in Figure 5.[6] Similarly, by simultaneous movement of all of the movable column sections in the HITCs, a subspace of thermodynamically equivalent side-column structures can be obtained. Each HITC produces a *unique* thermodynamically equivalent side-column structure. For example, part i of Figure 6 presents the side-column structure for the HITC in Figure 1c, and parts a−h of Figure 6 present the corresponding side-column structures for the HITCs in Figure 3, respectively. Figure 7 presents the corresponding side-column structures for the HITCs in parts a−j of Figure 4, respectively.

Compared with the thermodynamically equivalent side-column structures of the OTCs shown in Figure 5, each thermodynamically equivalent side-column structure of the HITCs shown in Figure 6 has the following distinct features:

(1) A main column with feedstock is used to produce the most-volatile product at the top and the least-volatile product at the bottom. There is the same main column in the side-column structures between a HITC shown as in Figure 6 and its corresponding OTC shown as in Figure 5 (including the corresponding column sections).

(2) The intermediate volatility products are produced from the side columns in the configurations of Figure 6. Some side columns do not produce products, while others can produce one or more middle-component products. This is different from the side-column structures of the OTCs in Figure 5, where each side column produces one single middle product.

(3) There is a main condenser at the top end associated with the most-volatile product and a main reboiler at the bottom end associated with the least-volatile product in the main column. The other heat exchanger(s) are at the ends of the side columns associated with the intermediate volatility products.

(4) Each side column in the thermodynamically equivalent side-column structure of a HITC has at least two column

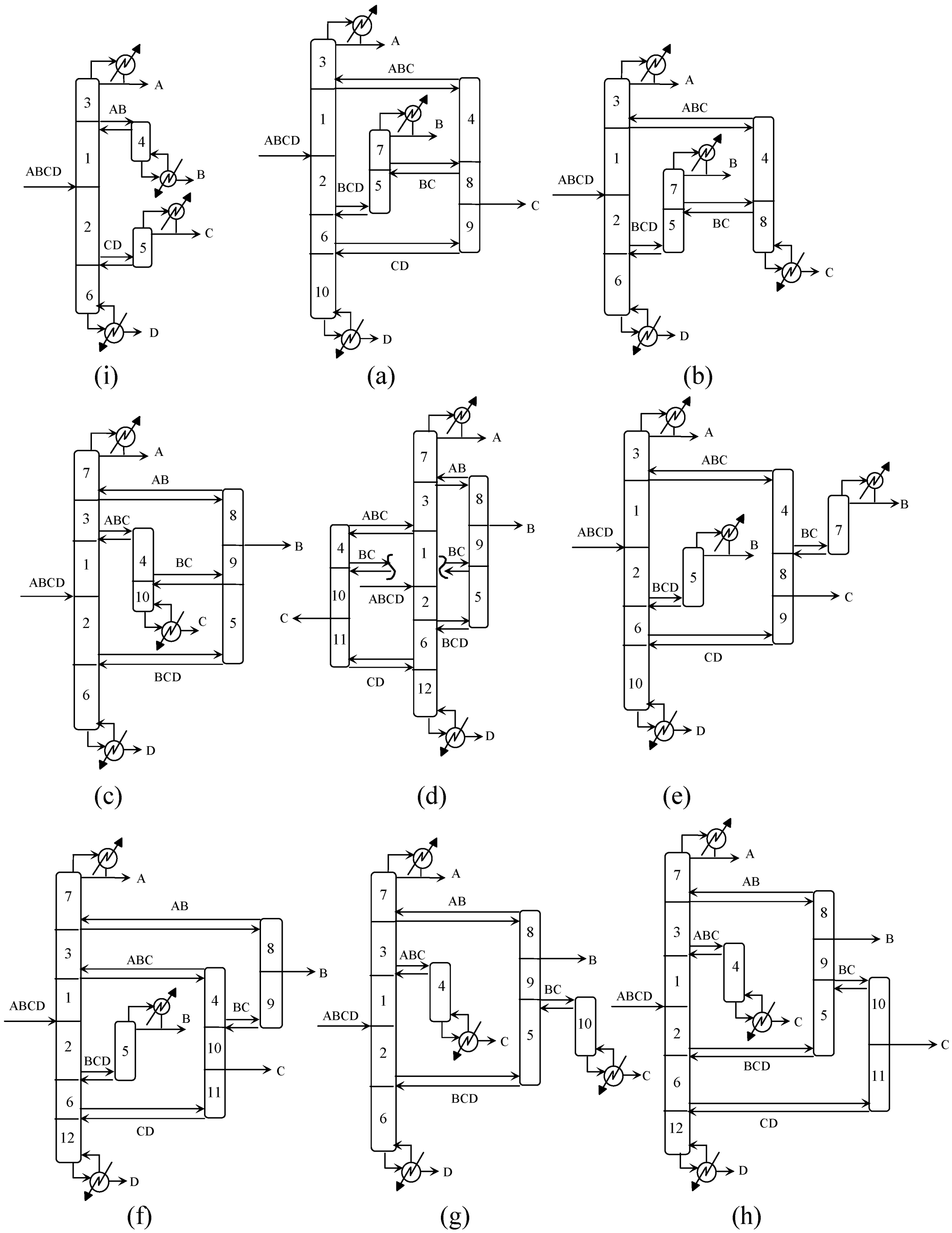

Figure 5. Thermodynamically equivalent side-column structures of the OTCs: (i) for Figure 1b and (a−h) for Figure 2.

sections, while a side column in the thermodynamically equivalent side-column structure of an OTC can have only one column section.

(5) The number of columns in the thermodynamically equivalent side-column structure of a HITC is equal to the number of columns in its original HITC ($n - 1$ or $<(n - 1)$ columns). Note that the number of columns in the thermodynamically equivalent side-column structure of an OTC is also equal to the number of columns in its OTC ($n - 1$ or $>(n - 1)$ columns).

As in the original HITCs of Figure 3, there are completely symmetric structures between the thermodynamically equivalent side-column structures of parts a and e of Figure 6, between parts c and g of Figure 6, and between parts d and f and parts d and h of Figure 6. The only difference is the use of an OHI or a CHI to transfer the intermediate submixture BC between the side columns. An additional middle product will be obtained from the CHI case. Similarly, there are no such symmetric structures among the thermodynamically equivalent side-column structures shown in Figure 5 for the OTCs in Figure 2.

Together with the thermodynamically equivalent side-column structures shown in Figure 7 for the HITCs in Figure 4, each thermodynamically equivalent side-column structure of the HITCs in Figures 6 and 7 has the following additional distinct features:

(6) The main column is divided into two parts at the feed location: the upper part above the feed and the lower part below the feed. The column sections in the upper part are the stacked

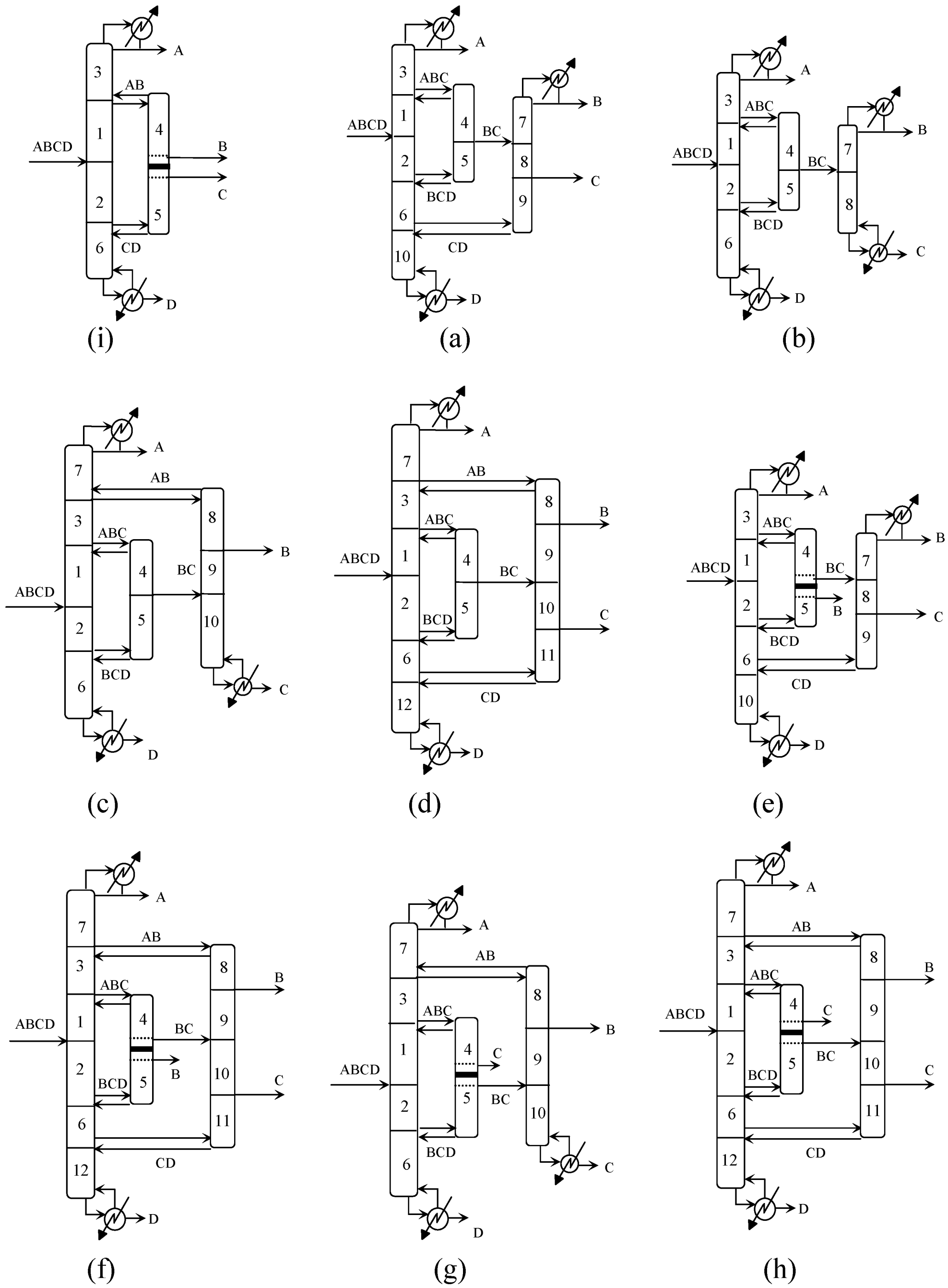

Figure 6. Thermodynamically equivalent side-column structures of the HITCs: (i) for Figure 1c and (a−h) for Figure 3.

rectifying sections, and the column sections in the lower part are the stacked stripping sections.

(7) A submixture involving the most-volatile component is always transferred between the upper part of the main column and the top end of a side column in a two-way thermal coupling. The reflux of such a side column thermally linked with the upper part of the main column is provided by the main condenser in the main column. Conversely, a submixture involving the least-volatile component is always transferred between the lower part of the main column and the bottom end of a side column in a two-way thermal coupling. The boilup of such a side column thermally linked with the lower part of the main column is provided by the main reboiler in the main column.

(8) A submixture composed of only middle components is always transferred between two side columns. When it is transferred from one end of a side colunm to another side column, it is a two-way vapor and liquid communication via thermal coupling. When it is transferred between intermediate locations of two side columns, it is a one-way liquid communication via heat integration.

(9) In the thermodynamically equivalent side-column structure of a HITC, all the heat integrations are implemented within the side columns. The main column has only thermal couplings communicated with the side columns.

For each of the HITCs in Figures 3 and 4, all the other possible TESs between the original HITC (shown in Figures 3 and 4) and its thermodynamically equivalent side-column structure (shown in Figures 6 and 7) can be obtained when a different number of movable column sections (shown in Tables 2 and 3) are moved each time. When considering real applications of these new HITC systems, the TESs can determine the optimal system in terms of not only energy and capital cost savings but also improvements in column equipment design and operability.[11]

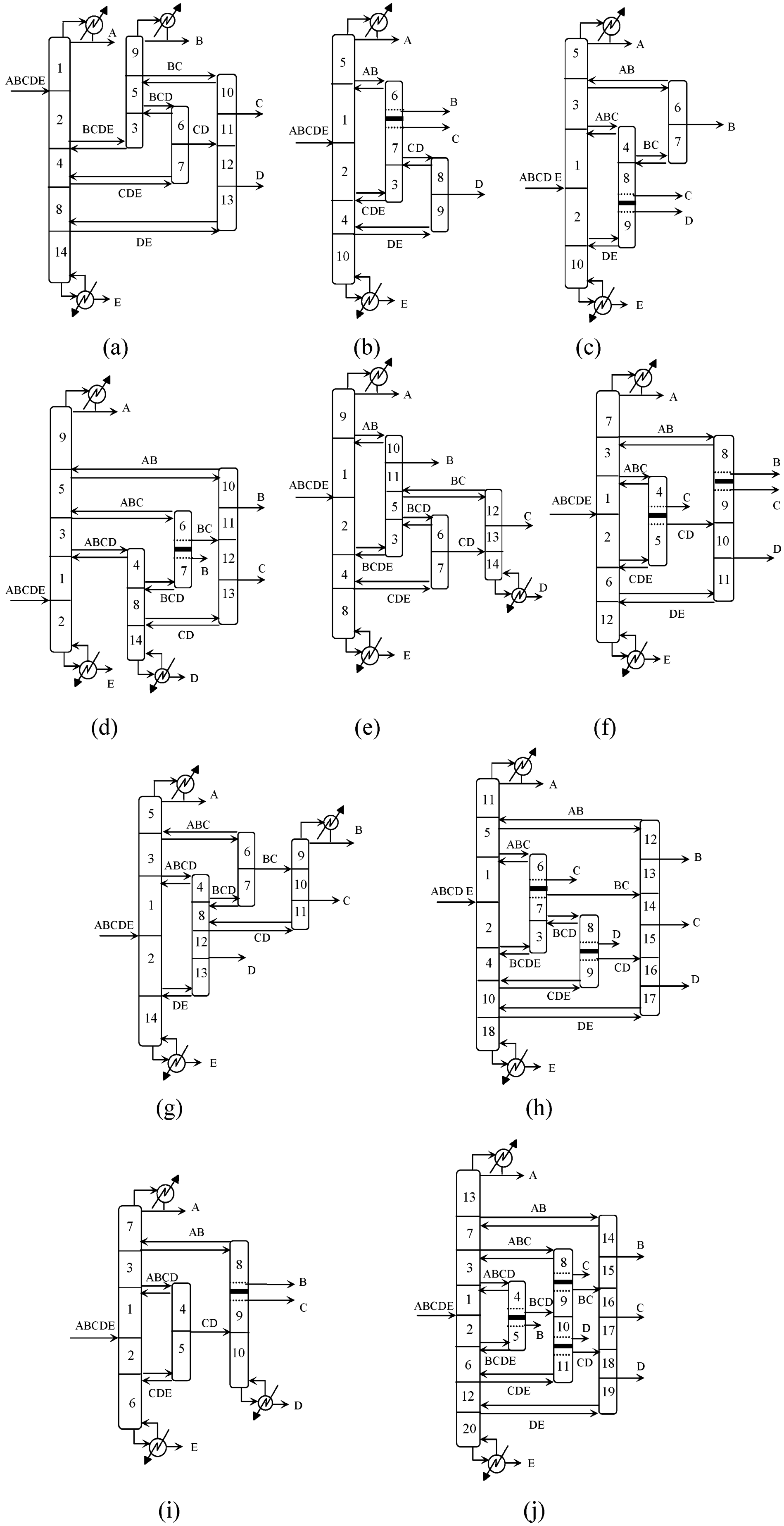

Figure 7. Thermodynamically equivalent side-column structures of the HITCs in Figure 4.

5. Conclusions

Thermal coupling and heat integration are two distinct mechanisms to enhance the mass and heat transfers within a multicomponent distillation system. A thermal coupling laterally coordinates two individual tasks by replacing a heat exchanger associated with a submixture with thermal coupling streams. A heat integration vertically combines two columns by implementing heat exchange between a condenser of one column and a reboiler of another column inside a combined column. The thermal coupling provides a two-way communication for a submixture between columns, while the heat integration provides a one-way communication for a submixture between the columns. Thermal couplings give the structural degrees of freedom to produce TESs. Heat integrations combine the two-section columns to reduce the number of columns in the distillation system. Distillation systems with simultaneous thermal coupling and heat integration have the potential to significantly reduce both energy and capital costs compared with systems with either thermal coupling or heat integration alone.

In this paper, systematic synthesis of the new distillation systems with simultaneous thermal coupling and heat integrations is presented. In the synthesized new HITCs, all the thermal couplings are located at the ends of the columns, and all the heat integrations are implemented at the intermediate locations of the combined columns. The two ends of a column in any HITC are associated with either two thermal couplings, or two heat exchangers, or one thermal coupling and one heat exchanger. For a pair of a condenser and a reboiler standing for heat integration, there are two ways to combine the two-section columns. An open heat integration (OHI) allows mass communication through the heat-integrated location within the combined column. A closed heat integration (CHI) does not allow mass communication through the heat-integrated location within the combined column. The number of columns in the HITC systems is either less than or equal to that of distillation configurations with thermal coupling or heat integration alone. Some HITCs have a lower number of thermal couplings than their corresponding OTCs and are more amenable to operability. Moreover, some HITCs produce one or more additional intermediate volatility products and are more flexible when products with different purities or different properties are required.

In this work, for the TDCs, all the heat exchangers except a condenser and a reboiler with the two extreme volatility components are classified into four categories. Three rules are formulated to deal with the heat exchangers in the four categories with simultaneous thermal coupling and heat integration. Four cases of heat integrations are identified to determine the practical heat integrations in the HITCs systems. All of the new HITCs for quaternary distillations are first generated. Then, a procedure is formulated to synthesize new HITCs for any *n*-component mixture. Finally, the generation of the TESs for the new HITCs is presented.

Recently, rigorous optimization methods have been developed for complex distillation systems, which are capable of searching the optimal structures[12−14] and designing the optimal parameters[15,16] for distillation systems. The new HITCs, together with their TESs, constitute an advantageous alternatives space when looking for an economically efficient system for specific applications.

Acknowledgment

The financial support from the Academy of Finland (Suomen Akatemia) is gratefully acknowledged.

Literature Cited

(1) Thompson, R. W.; King, C. J. Systematic Synthesis of Separation Schemes. *AIChE J.* **1972**, *18*, 941.

(2) Rathore, R. N. S.; Wormer, K. A. V.; Powers, G. J. Synthesis Strategies for Multicomponent Separation Systems with Energy Integration. *AIChE J.* **1974**, *20*, 940.

(3) Petlyuk, F. B.; Platonov, V. M.; Slavinskii, D. M. Thermodynamically Optimal Method for Separating Multicomponent Mixtures. *Int. Chem. Eng.* **1965**, *5*, 555.

(4) Agrawal, R. Thermally Coupled Distillation with Reduced Number of Intercolumn Vapor Transfers. *AIChE J.* **2000**, *46*, 2198.

(5) Rong, B.-G.; Kraslawski, A.; Turunen, I. Synthesis of Heat-Integrated Thermally Coupled Distillation Systems for Multicomponent Separations. *Ind. Eng. Chem. Res.* **2003**, *42*, 4329.

(6) Rong, B.-G.; Kraslawski, A.; Turunen, I. Synthesis of Functionally Distinct Thermally Coupled Configurations for Quaternary Distillations. *Ind. Eng. Chem. Res.* **2003**, *42*, 1204.

(7) Linnhoff, B.; Dunford, H.; Smith, R. Heat Integration of Distillation Columns into Overall Processes. *Chem. Eng. Sci.* **1983**, *38*, 1175.

(8) Carlberg, N. A.; Westerberg, A. W. Temperature−Heat Diagrams for Complex Columns. 2. Underwood's Method for Side Strippers and Enrichers. *Ind. Eng. Chem. Res.* **1989**, *28*, 1379.

(9) Agrawal, R.; Fidkowski, Z. T. New Thermally Coupled Schemes for Ternary Distillation. *AIChE J.* **1999**, *45*, 485.

(10) Agrawal, R. Synthesis of Distillation Column Configurations for a Multicomponent Separation. *Ind. Eng. Chem. Res.* **1996**, *35*, 1059.

(11) Rong, B.-G.; Kraslawski, A.; Turunen, I. Synthesis and Optimal Design of Thermodynamically Equivalent Thermally Coupled Distillation Systems. *Ind. Eng. Chem. Res.* **2004**, *43*, 5904.

(12) Barttfeld, M.; Aguirre, P. A.; Grossmann, I. E. A Decomposition Algorithm for Synthesizing Complex Column Configurations Using Tray-by-Tray GDP Models. *Comput. Chem. Eng.* **2004**, *28*, 2165.

(13) Yeomans, H.; Grossmann, I. E. Disjunctive Programming Model for the Optimal Design of Distillation Columns and Separation Sequences. *Ind. Eng. Chem. Res.* **2000**, *39*, 1637.

(14) Caballero, C. A.; Grossmann, I. E. Design of Distillation Sequences: From Conventional to Fully Thermally Coupled Distillation Systems. *Comput. Chem. Eng.* **2004**, *28*, 2307.

(15) Lang, Y. D.; Biegler, L. T. Distributed Stream Method for Tray Optimization. *AIChE J.* **2002**, *48*, 582.

(16) Grossmann, I. E.; Aguirre, P. A.; Barttfeld, M. Optimal Synthesis of Complex Distillation Columns Using Rigorous Models. *Comput. Chem. Eng.* **2005**, *29*, 1203.

Received for review April 26, 2005
Revised manuscript received December 23, 2005
Accepted March 29, 2006

IE050493M