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Synthesis of Functionally Distinct Thermally Coupled Configurations for Quaternary Distillations

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The synthesis of the functionally distinct thermally coupled distillation configurations for quaternary mixtures is presented. The concept of the intended individual splits has been presented to formulate a distinct separation sequence, with which a functionally distinct thermally coupled configuration can be generated for a multicomponent distillation. Twenty-two functionally distinct thermally coupled distillation configurations for quaternary mixtures have been identified. They include the possible thermally coupled configurations in the available superstructures for quaternary distillations. Moreover, some new feasible thermally coupled configurations have been found which are not included in the known superstructures. These functionally distinct thermally coupled configurations constitute a unique space with which the other possible thermally coupled schemes can be generated. It provides a more complete search space of the possible alternatives to synthesize the global optimum distillation systems for quaternary separations.

1. Introduction

Thermal coupling has been used in the design of multicomponent distillation systems to significantly reduce both energy consumption and capital costs when compared with conventional simple column configurations. The dividing-wall column with thermal coupling was first patented by Wright.[1] Petlyuk et al.[2] introduced the thermal coupling for ternary distillations and presented a fully thermally coupled configuration (FC; Petlyuk column). There is a considerable amount of literature on the analysis of the relative advantages of the thermally coupled schemes for ternary separations.[3–10] Specifically, the thermally coupled dividing-wall column has been successfully used in many industrial separations for ternary mixtures.[11] Recently, the effort has focused on finding new thermally coupled configurations based on energy savings as well as operability.[12] Upon evaluation of the alternatives for ternary mixtures, a critical issue is the construction of a complete search space that will guarantee the optimal design for a specific ternary mixture.[13]

In industrial processes, the mixtures to be separated often contain four or more components. The industrial experience shows that if the optimum alternative is not predefined, it will not be found.[11] On the other hand, for some specific distillation systems, Eliceche and Sargent[14] have shown that it is not obvious a priori whether some substructures are less expensive than others. Thus, the optimal design of the thermally coupled distillation configurations for four or more component mixtures will depend on the ability to define all of the possible alternatives a priori. The literature has focused on the completeness of the possible distillation configurations for ternary mixtures, and there were only a few studies on thermally coupled schemes for four or more component mixtures.[15] Sargent and Gaminibandara[16] presented a Petlyuk-type fully thermally coupled scheme for a four-component mixture. Kaibel[17] and Christiansen et al.[15] have introduced distillation columns with vertical partitions for multicomponent separations. Agrawal[18] presented some satellite column arrangements of fully coupled schemes for four or more component mixtures. Agrawal[19] also illustrated how to draw thermodynamically equivalent fully thermally coupled schemes through rearrangement of the Petlyuk FC configuration and the satellite column FC configuration for four- and five-component mixtures. The recent studies have shown that the known four-component thermally coupled schemes are useful in specific cases.[15,20] Because the FC configuration is only one possibility among all thermally coupled schemes for multicomponent distillations, some other configurations may have advantages in terms of operating and capital costs, as well as operability. Specifically, there might be different product specifications for a multicomponent separation with respect to the number of the products, the purities of the products, the properties of the products, etc. The main objective of this work is to find a procedure to predefine all of the possible functionally distinct thermally coupled configurations for quaternary mixtures. All of the functionally distinct separation sequences for quaternary mixtures are first generated based on the intended individual splits. Then, the functionally distinct thermally coupled configurations are generated from the identified distinct separation sequences. The other possible thermodynamically equivalent structures of the functionally distinct thermally coupled configurations are also discussed in this work.

2. Functionally Distinct Separation Sequences for a Multicomponent Distillation

Note that essentially all of the thermally coupled distillation systems for ternary mixtures are generated from three distinct separation sequences, i.e., the direct sequence, the indirect sequence, and the prefractionation sequence.[21] Thus, to understand how to generate all possible thermally coupled distillation schemes for

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a multicomponent mixture, it is necessary first to understand how a multicomponent mixture can be separated using a feasible separation sequence. For a nonazeotropic multicomponent mixture, the total number of the different submixtures, including the feed and the products, is given as $n(n + 1)/2$.[22] However, it is well-known that a feasible distillation configuration normally does not include all of the feasible submixtures of the multicomponent mixture. The submixtures in a feasible distillation configuration are determined by the specific individual splits of the separation sequence. Thus, to generate all of the possible distillation configurations for a multicomponent mixture, it is first necessary to see how many possible individual splits can be generated for a multicomponent mixture. Typically, there are two ways to perform a separation for a nonazeotropic multicomponent mixture: the *sharp splits* and the *sloppy splits.* A sharp split takes place when the two key components are adjacent and each component in the feed appears in significant amounts only in one of the two products. A sloppy split occurs when the two key components are nonadjacent and there is at least one middle component distributed between the top and bottom products. In this paper, a sloppy split for a specific submixture (including feed) is represented in such a way that an underline is used to indicate the distributed middle key components; that is, ABCD means that a sloppy split is performed for the submixture ABCD, with the two middle components B and C distributed in top (ABC) and bottom (BCD) products. A sharp split is represented with an oblique line between the two adjacent keys; that is, AB/CD means that a sharp split is introduced between B and C for the submixture ABCD, with the top product being AB and the bottom product being CD. Obviously, for a ternary mixture ABC, a total of three individual splits can be used to perform a separation of the feed mixture, that is, two sharp splits of A/BC and AB/C and one sloppy split of ABC.

Mixtures with four or more components contain more than one middle component; thus, there exists flexibility in determining the distribution of the middle components in a sloppy split. One can simultaneously distribute all of the middle components or distribute only one or two or any combination of the adjacent middle components. The former will produce two equal size subgroups, while the latter results in two unequal size ones. To distinguish these two different types of sloppy splits, we defined the former as *a symmetric sloppy split* and the latter as *an asymmetric sloppy split.* For example, for a four-component mixture ABCD, a symmetric sloppy split, which simultaneously distributes the two middle components B and C, will create two equal size subgroups of ABC and BCD (i.e., the individual split ABCD), while an asymmetric sloppy split, which distributes only one of the two middle components (let us say B), will produce two unequal size subgroups of AB and BCD (i.e., the individual split ABCD).

Obviously, for each of the submixtures with binary or more components (including feed), one should designate a specific individual split for it in order to formulate a feasible separation sequence. However, we can use a different number of *intended individual splits* to accomplish a separation task for a multicomponent distillation. The minimum number of individual splits is achieved by including the minimum number of submixtures with binary or more components (including feed)

Table 1. Minimum and Maximum Number of Individual Splits in a Distillation Sequence for an *n*-Component Mixture

no. of components n	min no. of individual splits $n - 1$	max no. of individual splits $n(n - 1)/2$
3	2	3
4	3	6
5	4	10
6	5	15
7	6	21
8	7	28
9	8	36
10	9	45

in the separation sequence, and this accounts for $n - 1$ individual splits. The maximum number of individual splits is achieved by including all of the possible submixtures with binary or more components (including feed) in the separation sequence, and this accounts for $n(n - 1)/2$ individual splits. Table 1 presents the minimum and maximum number of individual splits in a feasible separation sequence for an *n*-component mixture. It can be seen that the spread (maximum−minimum) in the number of individual splits in a feasible separation sequence increases dramatically as the number of the components in the feed mixture increases. It is likely that other feasible separation sequences will have a number of individual splits between the minimum number $n - 1$ and the maximum number $n(n - 1)/2$. Furthermore, all three types of individual splits, i.e., the sharp split, the symmetric sloppy split, and the asymmetric sloppy split, will appear in all of the possible separation sequences for four or more component mixtures.

In the following section, we will show that the number of functionally distinct thermally coupled schemes for a multicomponent distillation is determined by the number of functionally distinct separation sequences which can be generated for that multicomponent mixture. A *functionally distinct separation sequence* is defined as a separation sequence where at least one of its individual splits is different from other feasible separation sequences.

To generate all of the distinct separation sequences for a multicomponent distillation, we need to identify the number of distinct sets of intended individual splits that represent the different separation sequences. *A set of intended individual splits* is defined as a list of ranked individual splits introduced into a multicomponent mixture with which a feasible separation sequence is determined for the whole separation task. For example, for a ternary mixture, there are three distinct sets of intended individual splits, i.e., (A/BC, B/C), (AB/C, A/B), and (ABC, A/B, B/C). Thus, it is the number of distinct sets of intended individual splits generated for a multicomponent mixture that finally determines all of the functionally distinct separation sequences.

For the generation of all possible separation sequences for a multicomponent mixture, a submixture (including feed) with ternary or more components can be separated in all of its feasible ways with respect to the three types of splits during the identification of a set of feasible individual splits for a multicomponent separation task. Obviously, for a given multicomponent mixture, one has the flexibility to define the *first split* in the formulation of a feasible separation sequence, provided one simultaneously takes into account all of the three types of splits, namely, the sharp split, the

Table 2. First Splits and Their Functionally Distinct Separation Sequences for Quaternary Mixtures

first splits	distributed middle component(s)	no. of schemes
A/BCD	none	3
AB/CD	none	1
ABC/D	none	3
A$\overline{B}$CD	B	3
A$\overline{B}\overline{C}$D	C	3
A$\overline{B}\overline{C}$D	BC	9
		total: 22

symmetric sloppy split, and the asymmetric sloppy split. The number of first splits for an n-component mixture is calculated as $n(n-1)/2$,[23] and each first split will determine a branch for the generation of the possible separation sequences for the feed mixture. This is done by further determining the individual splits for the submixtures generated from the first split with ternary or more components, again simultaneously taking into account all of the three types of splits. Finally, based on this procedure, remaining will be only the binary submixtures that are then separated as sharp splits. Table 2 illustrates the generation of all functionally distinct separation sequences for quaternary mixtures based on the definition of a first split for the feed mixture. In total, six first splits are identified that include three sharp splits, two asymmetric sloppy splits, and one symmetric sloppy split. Table 3 presents all of the 22 functionally distinct separation sequences for quaternary mixtures.

Among the 22 distinct separation sequences, there are five sequences (a, b, and d−f) that contain a minimum number of three individual splits; they formulate the subspace of the well-known simple column sequences with only sharp splits. There are seven sequences (c, g, h, i, k, l, and o) with four individual splits; each of them includes only one sloppy split. There are seven sequences (j, m, n, p, q, s, and u) with five individual splits; each of those sequences j, m, n, and q includes two sloppy splits, and each of the other three includes only one symmetric sloppy split. There are three sequecnes (r, t, and v) containing the maximum number of six individual splits. The sequence r includes all sloppy splits for the submixtures with ternary or more components.

3. Functionally Distinct Thermally Coupled Distillation Configurations for Quaternary Mixtures

The traditional design of a distillation system for a multicomponent separation is to use only the simple columns. A simple column is defined as a column with (a) one feed and top and bottom products and (b) one condenser and one reboiler. It can perform a sharp or a sloppy split depending on whether each component appears in only one product in significant quantities.[23] The separation of an n-component mixture into pure products requires at least $n-1$ simple columns,[24] which means only sharp splits are used in the separation sequence, and totally $2(n-1)$ condensers and reboilers. Furthermore, the use of sloppy splits in submixture separations with ternary or more components will increase the number of columns in a conventional multicomponent separation system, which will also result in an increased number of condensers and reboilers. However, Petlyuk et al.[2] have shown that the separation "inefficiency" in the conventional simple column configurations for a multicomponent distillation results from the irreversibility occurring during the mixing of streams at both the feed locations and the ends of the columns. This separation "inefficiency" can be decreased by using both sloppy splits and the thermal coupling for a multicomponent distillation system. The sloppy splits reduce the thermodynamic irreversibility during the mixing of the streams at the feed locations, while thermal couplings can reduce the thermodynamic irreversibility during the mixing of the streams at the ends of columns. More importantly, in most cases by using thermal couplings one can introduce sloppy splits for the submixtures of ternary or more components, while keeping the same number of column units in a thermally coupled configuration as that in a conventional simple column configuration, e.g., $n-1$. Moreover, an additional benefit is a reduction in the number of condensers and reboilers required in the thermally coupled system when compared to the traditional simple column configuration. Thus, for each of the functionally distinct sequences identified in Table 3, one can draw a corresponding functionally distinct thermally coupled configuration to perform the multicomponent separation. By *a functionally distinct thermally coupled distillation configuration,* it is meant that at least one of the individual splits in the separation system is different from other possible thermally coupled schemes. Also, all of the column units in the distillation system are thermally coupled, which implies that there are no simple columns included in a functionally distinct thermally coupled distillation scheme. These thermally coupled configurations have the potential to significantly reduce both energy consumption and capital costs when compared to the traditional simple column configurations. Obviously, for ternary mixtures there are three functionally distinct thermally coupled schemes which are the well-known side stripper, side rectifier, and Petlyuk column. Past studies have shown that the sloppy split fully coupled column (i.e., the Petlyuk column), on average, can have a 30% energy savings

Table 3. Functionally Distinct Separation Sequences for Quaternary Mixtures

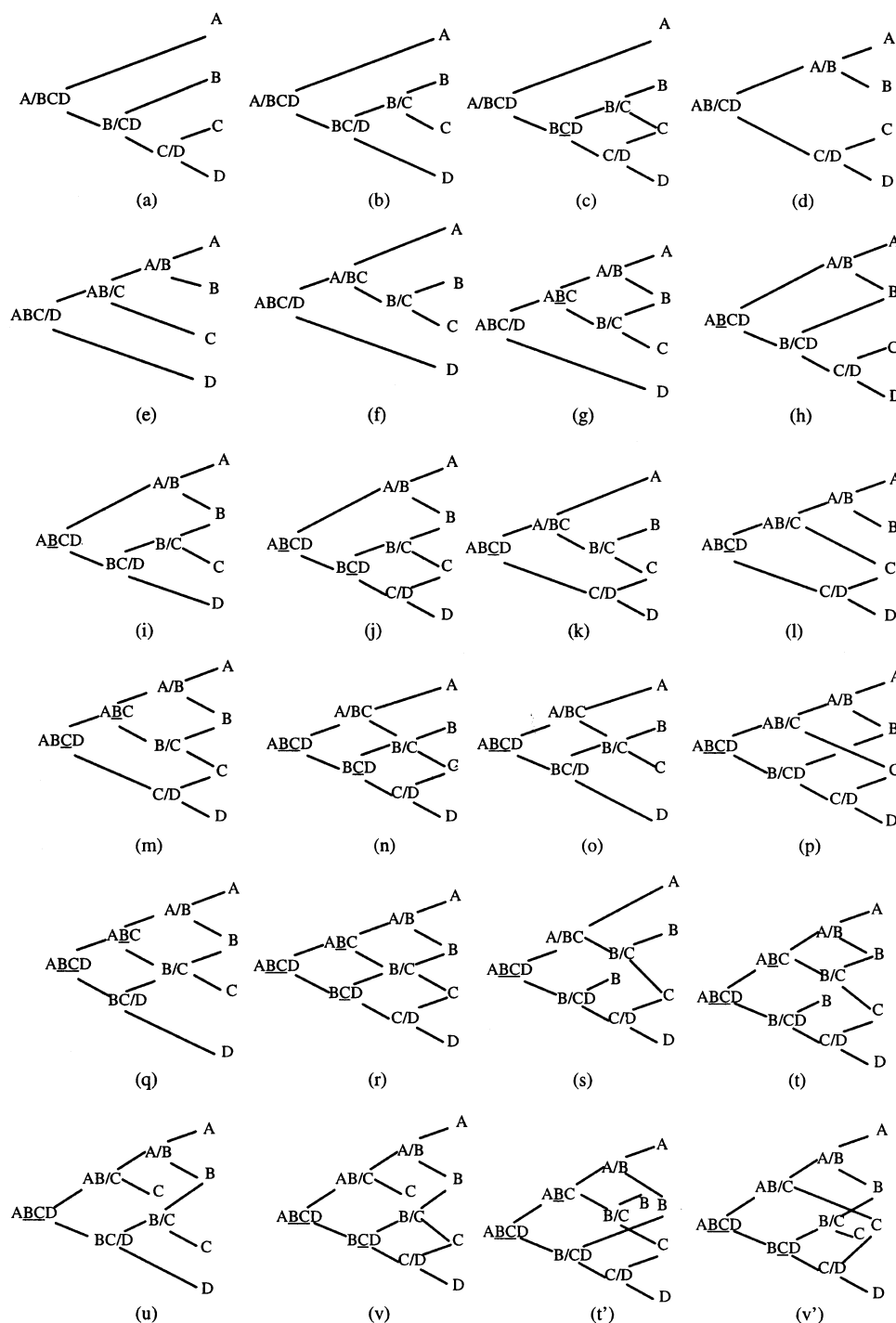| no. of sequences	separation sequence	no. of sequences	separation sequence
a	A/BCD → B/CD → C/D	l	ABCD → AB/C → A/B → C/D
b	A/BCD → BC/D → B/C	m	A$\overline{B}$CD → A$\overline{B}$C → A/B → B/C → C/D
c	A/BCD → B$\overline{C}$D → B/C → C/D	n	A$\overline{B}$CD → A/$\overline{B}$C → B$\overline{C}$D → B/C → C/D
d	AB/CD → A/$\overline{B}$ → C/D	o	A$\overline{B}$CD → A/BC → B$\overline{C}$/D → B/C
e	ABC/D → AB/C → A/B	p	A$\overline{B}$CD → AB/C → B/CD → A/B → C/D
f	ABC/D → A/BC → B/C	q	A$\overline{B}$CD → A$\overline{B}$C → BC/D → A/B → B/C
g	ABC/D → A$\overline{B}$C → A/B → B/C	r	A$\overline{B}\overline{C}$D → A$\overline{B}$C → B$\overline{C}$D → A/B → B/C → C/D
h	ABCD → B/$\overline{C}$D → A/B → C/D	s	A$\overline{B}$CD → A/$\overline{B}$C → B/$\overline{C}$D → B/C → C/D
i	A$\overline{B}$CD → BC/D → A/B → B/C	t	A$\overline{B}\overline{C}$D → A$\overline{B}$C → B/CD → A/B → B/C → C/D
j	A$\overline{B}$CD → B$\overline{C}$D → A/B → B/C → C/D	u	A$\overline{B}\overline{C}$D → A$\overline{B}$/C → BC/D → A/B → B/C
k	A$\overline{B}$CD → A/$\overline{B}$C → B/C → C/D	v	A$\overline{B}\overline{C}$D → AB/C → B$\overline{C}$D → A/B → B/C → C/D

Figure 1. Network representations of the distinct separation sequences for quaternary mixtures.

when compared to a simple column system.[2,25] Specifically, the thermodynamically equivalent dividing-wall column has been successfully used in many industrial processes.[10,26]

To generate the functionally distinct thermally coupled configurations from the identified functionally distinct separation sequences shown in Table 3, a representation of each separation sequence in terms of intended individual splits is introduced, with which the relationships of all of the submixtures (including feed and products) in that separation sequence can be clearly visualized. Hu et al.[23] presented a network representation of Sargent and Gaminibandara's[16] general scheme for a four-component mixture. This network has been extended to represent the simple column configurations

and the FCs with satellite columns for multicomponent distillations.[18] We also found that a network representation of a feasible separation sequence shown in Table 3 uniquely defines a functionally distinct thermally coupled configuration for a multicomponent distillation. Figure 1 presents the network representations of all of[46] the 22 functionally distinct thermally coupled schemes that correspond to the functionally distinct separation sequences shown in Table 3 for quaternary mixtures. In a network representation, each node (except product nodes with a single component) represents an individual split of the separation sequence. Each node of an individual split emanates two lines indicative of its two subgroups. The combinations of the same submixtures (for example, the submixtures of BC and C in Figure
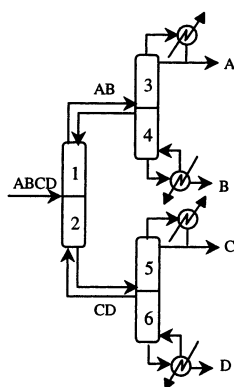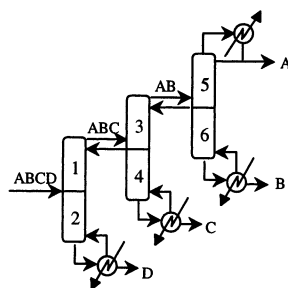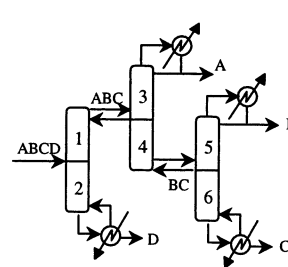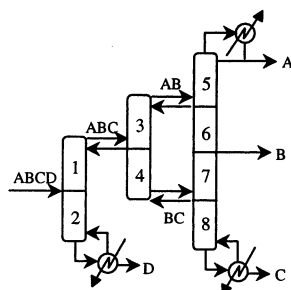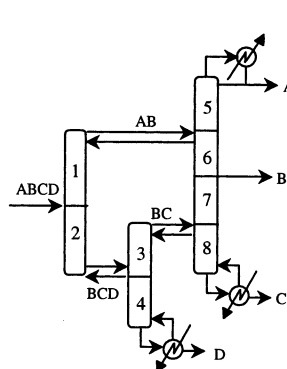
(a)

(b)

(c)
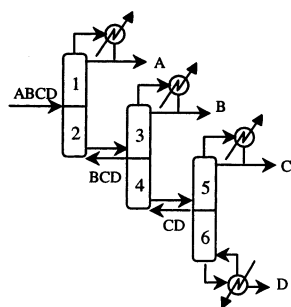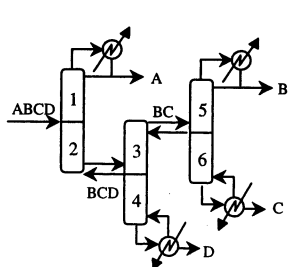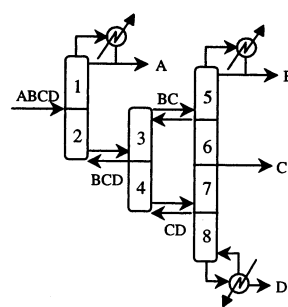
(d)

(e)

(f)

(g)
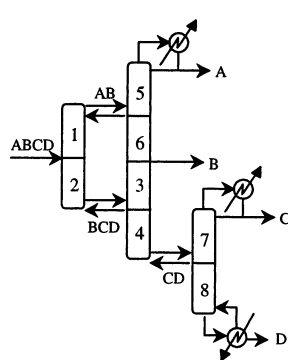
(h)

(i)
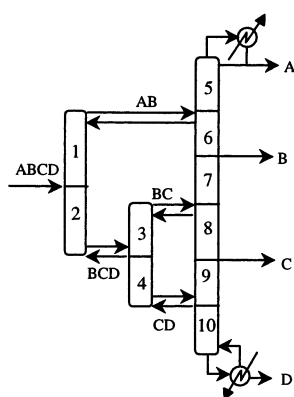
(j)
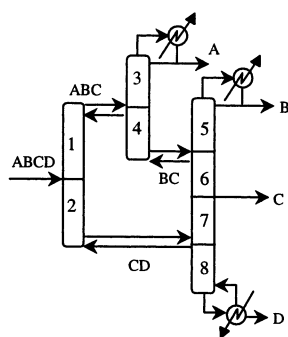
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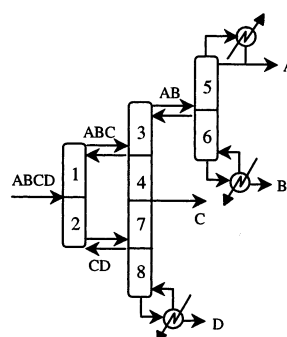
(l)
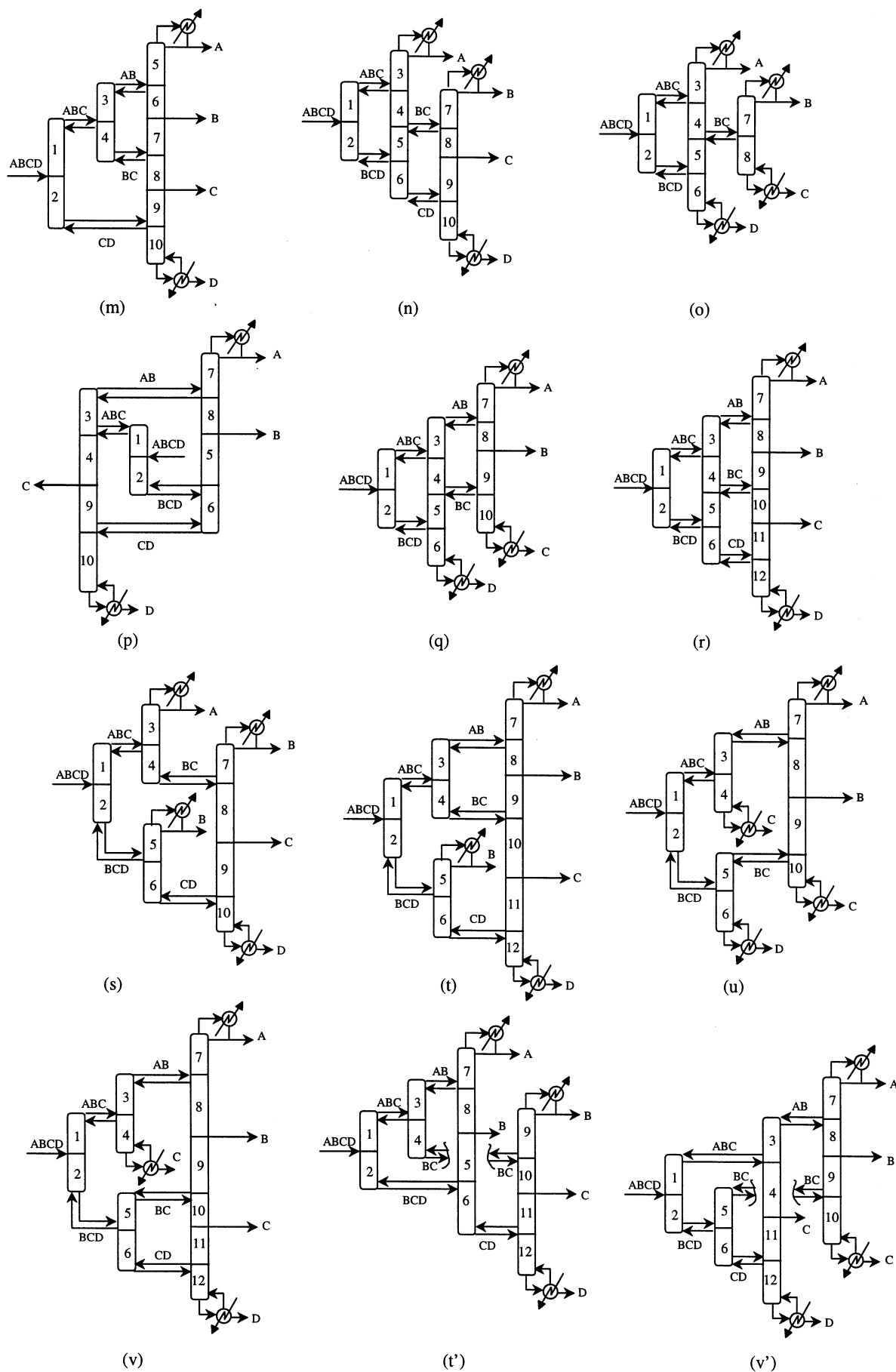
Figure 2. Functionally distinct thermally coupled distillation configurations for quaternary mixtures.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

(k)

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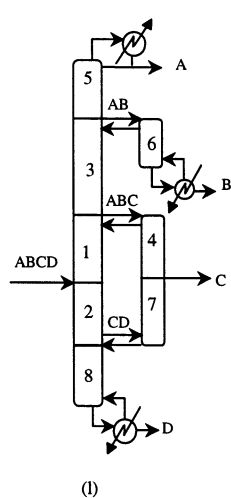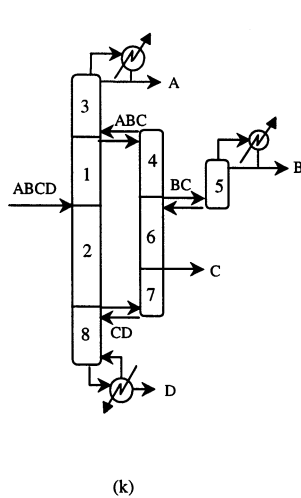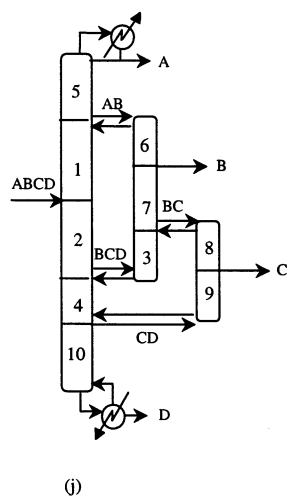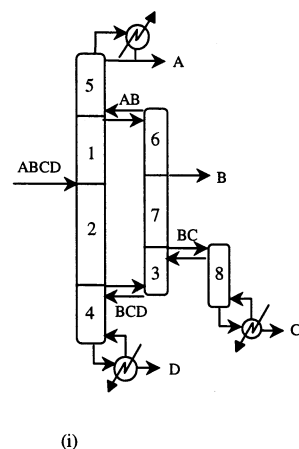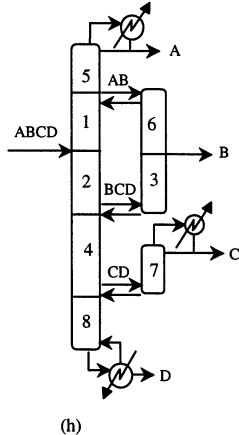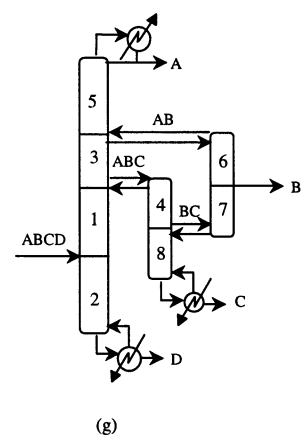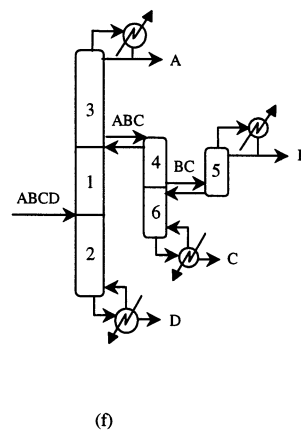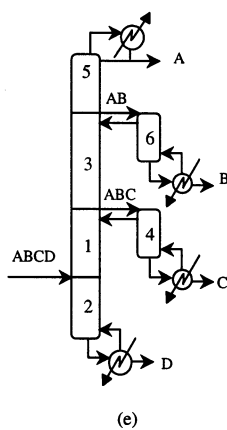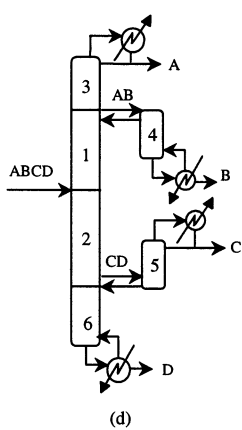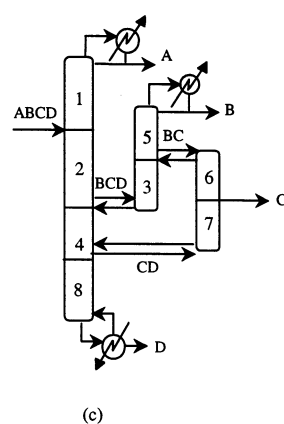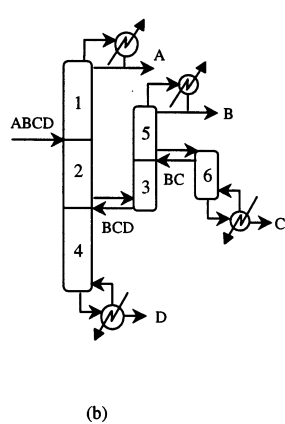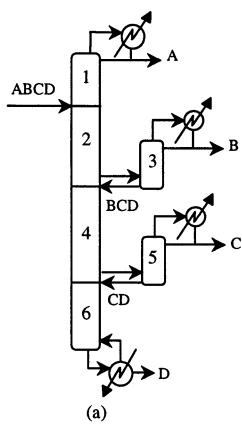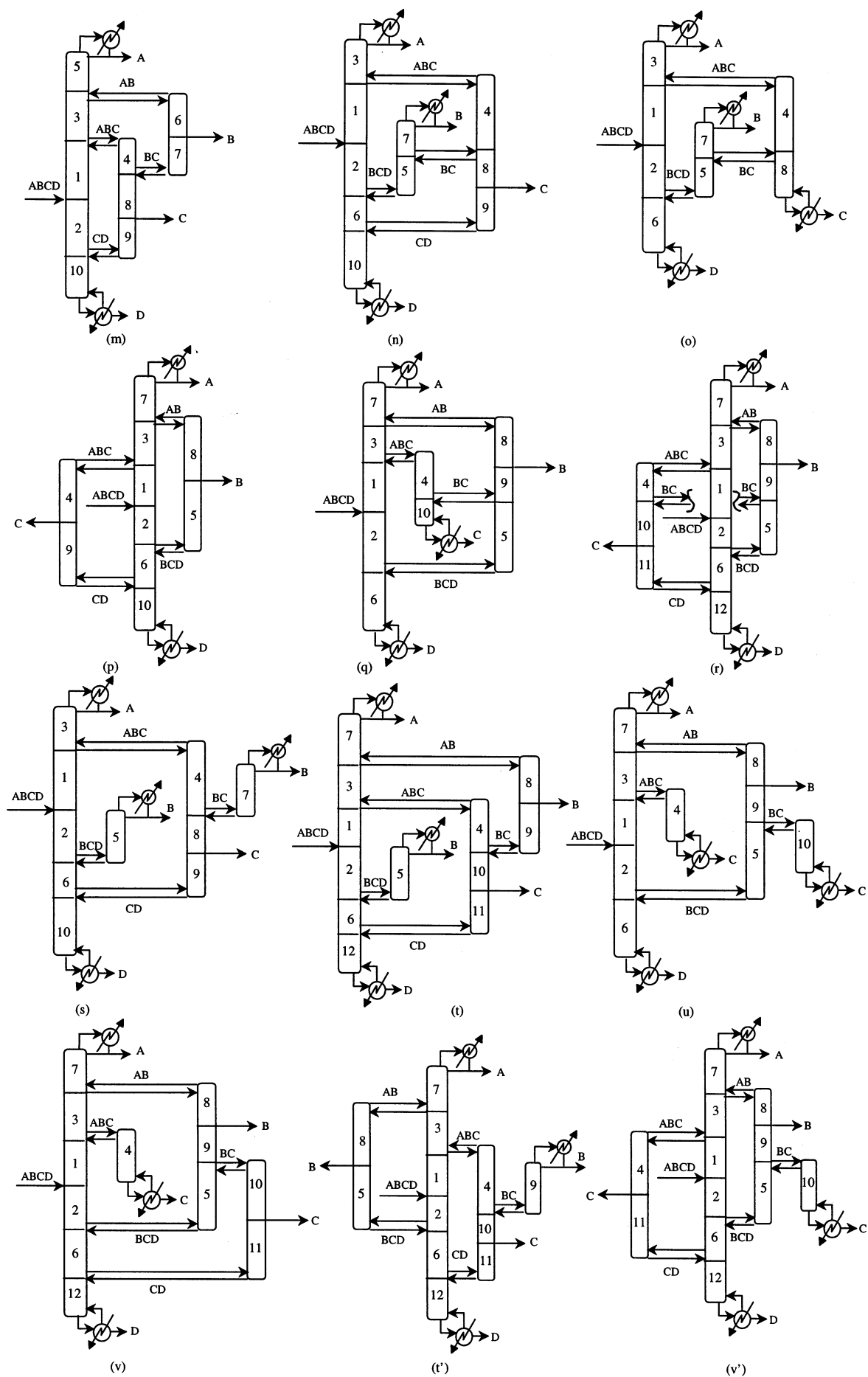
Figure 3. Thermodynamically equivalent side-column arrangements of the thermally coupled configurations from Figure 2.

1n), produced from the different individual splits in a separation sequence, can guarantee that there the minimum number of column units in the thermally coupled system is used. However, for separation sequence t, in Table 3, there is the flexibility to combine the product B from the individual split A/B with product B from the individual split B/C or B/CD. Thus, there is an additional network representation shown as Figure 1t′ for sequence t. The same flexibility exists for product C in sequence v and is shown in the network as Figure 1v′.

Starting from a simple column configuration with all sharp splits, Rong and Kraslawski[21] presented a procedure for the generation of the partially thermally coupled scheme and the associated alternatives that contained a lower number of thermal couplings. The underlying principle used in their approach can be employed for the generation of each of the functionally distinct thermally coupled schemes from its counterpart in the functionally distinct separation sequences. First, the reboilers and condensers associated with submixtures of binary or more components in the simple column configuration can be removed by using thermal coupling streams. The combination of the simple columns can then be done (Petlyuk et al.[2]). That is, the individual two-section columns are combined in such a way that each product is obtained at a single point. This guarantees that the minimum number of column units is used in a functionally distinct thermally coupled configuration for a multicomponent distillation (e.g., $n - 1$ column units). The corresponding functionally distinct thermally coupled network configurations of Figure 1 are redrawn in schematic form in Figure 2.

Among all of the functionally distinct thermally coupled configurations of Figure 2, there are five schemes (a, b, and d−f) that use only sharp splits in the separations. These five schemes are produced from the well-known conventional simple column configurations. They constitute a unique subspace of thermally coupled configurations with only side stripper(s) and/or side rectifier(s) for any *n*-component mixture.[21] There are four schemes (j, m, p, and r) with only one condenser and one reboiler in each scheme. Scheme r is the well-known Petlyuk-type fully thermally coupled scheme as in Sargent and Gaminibandara,[16] while the other three are called satellite column fully coupled configurations.[18] The schemes c, g−i, k, l, n, and q shown in Figure 2 can be distinguished by the fact that each of them has totally three condenser(s) and reboiler(s). There are 18 configurations of Figure 2a−r; each of these has three column units. It is interesting to note that there is a unique feature in the schemes s−v. Each of them can produce another intermediate volatility product with one more column unit in the scheme. Schemes s and t produce another intermediate volatility product (B), while schemes u and v produce another (C). They are feasible and useful configurations, especially in the situations where products with different purities are required.[27] Moreover, these schemes cannot be derived from the prior superstructures of Sargent and Gaminibandara[16] and Agrawal.[18] As in Figure 1, there is another configuration for each of the schemes t and v shown in Figure 2, corresponding to the network representation in Figure 1t′,v′, that is shown in Figure 2t′,v′, respectively. Another interesting scheme is that shown in Figure 2o; even though it has a total of four heat exchangers, it might be attractive for some specific

feed mixtures. For example, if the splits A/B and C/D are easy ones and with approximately the same relative volatilities and the split B/C is a difficult one with a significant amount of BC in the feed, then the scheme might be more economically attractive than those schemes with four heat exchangers and containing only sharp splits.

4. Discussion

4.1. Structural Features of the Configurations Shown in Figure 2. The structural arrangements of the column units of the functionally distinct thermally coupled schemes shown in Figure 2 are determined based on the intended individual splits in the distinct separation sequences. The column sections of each configuration shown in Figure 2 are numbered based on the sequence of the intended individual splits of the corresponding distinct separation sequence given in Table 3. Each of the odd numbers 1, 3, 5, 7, 9, and 11 designates a rectifying column section, and each of the even numbers 2, 4, 6, 8, 10, and 12 designates a stripping column section. These structural arrangements are similar to the simple column configurations in which each simple column performs one specific separation of the intended individual splits. Specifically, each of the five thermally coupled configurations a, b, and d−f with only sharp splits shown in Figure 2 has exactly the same structural arrangement of the three columns as its counterpart in the simple column configurations. Each of the remaining thermally coupled configurations shown in Figure 2 has one or two column units in which more than two column sections are used and contains one or more sloppy splits in the separation sequence. The column unit with more than two column sections is obtained by the combinations of the individual two-section columns which produce the same product(s). It is interesting to note that the first column unit in each of the functionally distinct thermally coupled configurations shown in Figure 2 performs the first split of the feed mixture, i.e., the first split shown in Table 2. We define the functionally distinct thermally coupled configuration, shown in Figure 2, as *the original thermally coupled configuration* with regard to the intended individual splits in its corresponding functionally distinct separation sequence, which distinguishes it from the other possible thermodynamically equivalent arrangements. Usually, one sloppy split in the thermally coupled configurations will require two more column sections than configurations with only sharp splits in which the minimum number ($2(n - 1)$) of column sections are used. However, each of the three configurations p, s, and u shown in Figure 2 increases by four column sections when only one sloppy split is included, and each of the configurations t and v increases by six column sections when two sloppy splits are included.

4.2. Thermodynamically Equivalent Structures and Side-Column Arrangements. It is well-known that, in a thermally coupled configuration, one can generate thermodynamically equivalent structures by rearrangements of some of the column sections among the column units. For example, the generation of thermodynamically equivalent structures from the original thermally coupled configurations for ternary mixtures was illustrated by Rong and Kraslawski.[21] *A thermodynamically equivalent structure* is defined as a thermally coupled configuration that has the same individual splits and the same thermal couplings for the

same submixtures, while it contains different structural arrangements of the column sections among the column units from the original thermally coupled configuration. It is possible to generate different thermodynamically equivalent structures for four or more component mixtures. For example, starting from the FC shown as Figure 2r, Agrawal[19] illustrated the generation of the more operable thermodynamically equivalent structures, which avoided the difficulties of vapor transfers among the column units. However, there might be other considerations when generating the possible thermodynamically equivalent structures from the original thermally coupled configurations, such as heat-transfer issues as well as other equipment design issues. A very interesting subspace of the thermodynamically equivalent structures for the original thermally coupled configurations shown in Figure 2 is presented in Figure 3. Each of the functionally distinct thermally coupled configurations shown in Figure 2 can produce a thermodynamically equivalent side-column arrangement of the column units as shown in Figure 3.

Each thermodynamically equivalent side-column configuration shown in Figure 3 has the following features:

(i) A main column with feed is used to produce the most volatile component (A) at the top and the least volatile component (D) at the bottom.

(ii) Each side column is used to produce a product of the intermediate volatility component.

(iii) There is a main condenser at the top end and a main reboiler at the bottom end in the main column. The other heat exchanger(s) are associated with the side columns.

The two thermodynamically equivalent side-column arrangements shown in Figure 3p,r have coincidentally the same structural arrangements of their three column units. However, they are functionally distinct thermally coupled configurations with inherently different intended individual splits produced from the two different original thermally coupled configurations shown in Figure 2p,r. In an earlier work on the synthesis of the FCs with the minimum number of $4n - 6$ column sections for multicomponent mixtures, Agrawal[18] observed that the satellite column fully coupled configuration (shown in Figure 3p) cannot be derived from the superstructure of Sargent and Gaminibandara's[16] sequentially fully coupled scheme (shown in Figure 2r) but can be derived from his new superstructure of the satellite column fully coupled scheme (shown in Figure 3r). Note that the two fully thermally coupled superstructures shown as Figures 2r and 3r are functionally the same thermodynamically equivalent structures with inherently the same intended individual splits, while the two configurations shown in Figure 3p,r with coincidentally similar structures are functionally distinct thermally coupled configurations with inherently different intended individual splits. This observation can explain why the thermodynamically equivalent side-column arrangement shown in Figure 3p cannot be derived from Sargent and Gaminibandara's[16] sequentially fully coupled superstructure (Figure 2r) but can be derived from Agrawal's[18] satellite column fully coupled superstructure (Figure 3r) for quaternary mixtures.

We also expect that the other possible thermodynamically equivalent schemes for quaternary mixtures can be derived from the functionally distinct thermally coupled configurations shown in Figure 2.

5. Conclusions

For multicomponent separation, thermally coupled distillation systems have the potential to significantly reduce both the operating and capital costs when compared to the traditional simple column configurations. An a priori knowledge of all possible configuration alternatives is of paramount importance in the synthesis of the optimal separation systems, given a specific multicomponent feed/separation. This paper presented the synthesis of all of the functionally distinct thermally coupled distillation schemes for quaternary mixtures. By identification of the possible individual splits for a multicomponent mixture, all of the inherently distinct separation sequences can be generated for a multicomponent distillation. It was shown that a set of intended individual splits of a feasible separation sequence uniquely defined a functionally distinct thermally coupled scheme for a multicomponent distillation.

Twenty-two functionally distinct thermally coupled configurations have been identified for the quaternary distillation separation scheme. These include the possible thermally coupled schemes incorporated in the available superstructures. Moreover, some new feasible thermally coupled distillation configurations have been derived which are not included in the known superstructures. These functionally distinct thermally coupled configurations constitute a unique space with which the other possible thermally coupled schemes can be generated, such as thermodynamically equivalent structures, the dividing-wall columns, and alternatives with a lower number of thermal couplings. This, together with the subspace contained in the traditional simple column configurations, will contribute to a more complete search space for all of the possible alternatives when developing global optimal distillation systems for quaternary separations.

The ideas and concepts presented in this work for the generation of all of the functionally distinct thermally coupled configurations for quaternary mixtures can be extended to any *n*-component mixtures ($n \geq 4$). However, for a mixture of five or more components, the combinatorial problem results in a much more complex task in order to design all of the functionally distinct thermally coupled schemes. Currently, a general procedure is being developed with the aim of developing a general procedure for the synthesis of all of the functionally distinct thermally coupled configurations for a mixture of five or more components.

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