Matrix based method for synthesis of main intensified and integrated distillation sequences

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Abstract−The objective of many studies in this area has involved access to a column-sequencing algorithm enabling designers and researchers alike to generate a wide range of sequences in a broad search space, and be as mathematically and as automated as possible for programing purposes and with good generality. In the present work an algorithm previously developed by the authors, called the matrix method, has been developed much further. The new version of the algorithm includes thermally coupled, thermodynamically equivalent, intensified, simultaneous heat and mass integrated and divided-wall column sequences which are of gross application and provide vast saving potential both on capital investment, operating costs and energy usage in industrial applications. To demonstrate the much wider searchable space now accessible, a three component separation has been thoroughly examined as a case study, always resulting in an integrated sequence being proposed as the optimum.

Keywords: Distillation Sequences, Process Synthesis, Multicomponent Distillation, Search Space

INTRODUCTION

Distillation is the most important and common separation technique in chemical, petrochemical, oil and gas industries, but at times with very high energy consumption [1]. Industrial mixtures commonly containing more than two components may not be separated efficiently in a single column. Thus, in a multicomponent separation, several columns ought to be employed in a sequence for the separation of mixtures to the number of desired products. This leads to numerous possible configurations (sequences) for separating a multicomponent mixture into relatively pure products (sharp split) or several multicomponent product streams (non-sharp or sloppy split). As a result, it is important to know different kinds of sequence classifications:

- Distillation sequences for separating an n-component feed could be classified in accordance with the number of distillation columns: having less than (n-1) columns (intensified or reduced), exactly (n-1) columns (complete), or more than (n-1) columns.

- Basic distillation configurations are those with n-1 columns to produce n product streams with each column using one reboiler and one condenser and produce n product streams. In these schemes, each product is collected from only one location in the sequence; so the number of product streams in each flow-sheet is equal to the number of components in the feed mixtures. Furthermore, there are non-basic configurations which have more than n-1 distillation columns.

Process Intensification principles help to achieve intensified and optimum distillation systems to save both energy and capital costs. To achieve an intensified and optimum configuration with not only energy saving, but also savings of capital cost (without imposing increased operational and control complexities), the first and the most important step is to predefine the search space as complete as possible.

The way to acquire a complete search space is a subject of debate with different approaches having been proposed in the literature. One important development was the superstructure flowsheet proposed by Sargent and Gaminibandara [2], which was then further developed by the state task network (STN) by Sargent in 1998 [3]. The flowsheet was realized to include all the schemes, known till 1996 before the presentation of satellite configurations by Agrawal [4]. Then, Agrawal presented a method to systematically generate basic sequences which classified configurations based on column products which could be distillates, side streams or bottoms products [5,6].

Fidkowski and Rong et al. proposed a combinatorial search which could generate a combination of basic and non-basic sequences [7]. These schemes have more operating and capital cost (due to employment of more columns, reboilers and condensers) as compared to basic configurations [6]. According to Giridhar and Agrawal the operating cost for non-basic configurations in terms of total heat duty is likely to be higher than that of optimal basic configurations in the investigated case studies [6]. Non-basic configurations are not considered in the search space of the current work. By specifying the basic configurations, other kinds of sequences could be easily generated from them [6].

Based on STN, Caballero and Grossmann developed a superstructure for the generation of the possible configurations for the separation of an n-component mixture [8-10]. They presented a

new algorithm containing two levels, one for generating basic sequences and another for different thermal states and feed compositions [11]. Errico et al. introduced a simple, four step synthesis method for the systematic generation of a complete search space based on maintaining the information about generation from one configuration to another. The benefit of saving the information between the families of configurations is that it could lead to a smaller number of alternatives to be compared to in order to find the optimum configuration [12]. The method later developed by Rong and Errico [13] and Ericco et al. [14] was named sequential synthesis methodology. Ivakpour and Kasiri submitted an algorithm to generate possible sequences by the introduction of a separation matrix. In the suggested algorithm, each sequence can include between one and n-1 simple and/or complex distillation columns and bypass streams [15]. Shah and Agrawal and Shenvi et al. presented a method to generate the search space using the concept of the separation matrix for sequences with maximum n-1 columns [16,17].

Shah and Kokossis [18,19], Kim and Wankat [20], Rong et al. [21-27], Kim [28,29], Kim et al. [30,31] Wang et al. [32], Yoo et al. [33] are other valuable research on generating and design of different basic configurations and their different thermal states as well as many more which are of less relevance to the present work and are therefore not cited here for brevity.

Among the algorithms proposed so far, some are based on the theories (e.g., graph theory) like Agrawal's [4] or Sargent's [3], which makes them difficult to convert to computer codes and programs to be utilized in synthesizing distillation flow sheets. Some others like Agrawal [5] or the step by step algorithm proposed by Errico et al. [12,14] have a systematic procedure based on network synthesis, which makes generation of sequences much easier and could cover most of the search space, but still do not have a mathematical background making them difficult to use for computer programming. Some others have a mathematical background which may be divided in two groups. The first group is based on MILP/MINLP as the procedures developed by Caballero and Grossmann [8,10,11] or Shah and Kokossis [18,19], which have difficulty in compatibility by rigorous simulations. The second group contains those based on a separation matrix like the works done by Ivakpour and Kasiri [15] or Shah and Agrawal [16] and Shenvi et al. [17]. As the present work lies in this category and in some ways is a further development of this type of approach, these are analyzed in more detail.

The present work illustrates that by representing each sequence as a certain matrix, it is possible to systematically generate all possible basic distillation column structures for a sharp and non-sharp separation of n-components, including intensified processes or those with further intensification potential. This method is based on the former algorithm developed by Ivakpour and Kasiri [15]. The proposed algorithm could generate every basic, simple, complex, thermally coupled and thermodynamically equivalent sequences automatically and systematically. Besides, the separation matrix method could generate sequences with less than n-1 distillation columns, which are generally referred to in the field as intensified sequences and also simultaneous heat and mass integrated sequences and divided-wall columns. According to process intensification

principles, these configurations have fewer column sections and fewer heat exchangers compared to the sequence from which they are derived. Therefore, the automatic and algorithmic generation of the intensified processes proposed here could be the main step in the process intensification of distillation systems and would help researchers and designers to have a complete search space, which could cover different types of sequences leading to more effective process proposals so far as intensification purposes are concerned. The proposed algorithm is comprehensive and could generate a search space, including different categories of sequences. The method could generate different sequences automatically and systematically. The mathematical base of the matrices used is such that the algorithm is speedy to use, may be readily programmed and could also be easily combined with self-developed and commercial software. As indicated in our previously published paper [15], it complies well with rigorous simulation methods.

SYNTHESIS ALGORITHM

Separation matrix is used for generating a nearly complete search space of basic distillation sequences for separating any n-component mixture (A, B, C… etc. sorted according to their relative volatility). Actually, the separation matrix is another form of STN representation, which makes the synthesis of basic distillation sequences much simpler [15]. The separation matrix is an upper triangular matrix comprised of distillation sequence characteristics like the number of distillation columns and interconnections between them. As stated in the STN algorithm, each distinct stream appears only once in the sequence. In the state task network, the nodes represent the mixtures and the lines connecting them represent the separation tasks which must be performed in the distillation column sections [2]. A column section is defined according to Hohmann et al. as a part of a column that is not interfered with entering or leaving mass streams or heat flows [34]. The separation is performed in two (rectifying and stripping) sections of a simple distillation column.

The main assumptions of the present work are the same as those considered in previous work mentioned above [15]. Fig. 1 demonstrates the proposed separation matrix for any three and four component feed mixture. As shown, the (φ or Φ) option of each stream is a member of the separation matrix and its position is fixed. φ is the sign of final products and could be assigned the values {I, II, S} and Φ is the symbol of sub-mixtures and could be assigned the values {0, I, II, III, S}. In the separation matrix:

1. The top product of the columns (from a condenser) is demonstrated by (φ or Φ={I}),
2. The bottom product of the columns (from a reboiler) is represented by (φ or Φ={II}),
3. The omitted mixture in crossover complete sequences is represented by (Φ={III}),
4. The mixtures produced as a side stream of distillation columns are represented by (φ or Φ={S}),

Consequently, using a matrix notation, φ or Φ option for each stream could be demonstrated using the two indices (in the form of row and column indices). Note that mixtures located in the same row have a common lightest component. Also, any mixture
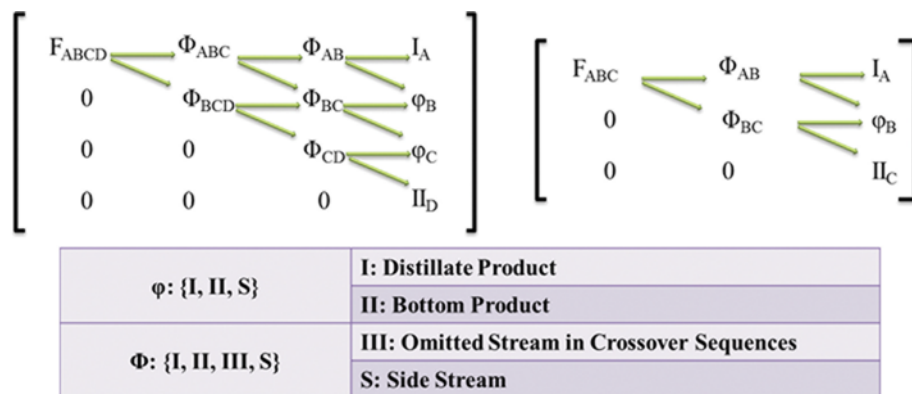
$$\begin{bmatrix} F_{ABCD} & \Phi_{ABC} & \Phi_{AB} & I_A \\ 0 & \Phi_{BCD} & \Phi_{BC} & \varphi_B \\ 0 & 0 & \Phi_{CD} & \varphi_C \\ 0 & 0 & 0 & II_D \end{bmatrix} \qquad \begin{bmatrix} F_{ABC} & \Phi_{AB} & I_A \\ 0 & \Phi_{BC} & \varphi_B \\ 0 & 0 & II_C \end{bmatrix}$$

φ: {I, II, S}	**I: Distillate Product**
	II: Bottom Product
Φ: {I, II, III, S}	**III: Omitted Stream in Crossover Sequences**
	S: Side Stream

Fig. 1. Proposed separation matrix for the three and four final product sequences.

located in the preceding column would consist of the two subsequent mixtures of the next column. For example, in Fig. 1, stream BC in a four component separation matrix, (located at (2, 3)) consists of B (located at (2, 4)) and C (located at (3, 4)). The mixture located in the first column is composed of all final products and is equivalent to the original feed. Likewise, the mixtures located on the same diagonal of the separation matrix have their heaviest components in common. As a consequence, by selecting the mixture (φ or Φ) options in the separation matrix the structure of the distillation sequence could be easily fixed. Despite this, for clarification purposes for each mixture the components are indicated as

a subscript in lower right of each array.

1. Distillation Sequences

1-1. Complete Sequences (Simple and Complex)

Complete sequences are those sequences that use exactly n-1 columns (each distillation column uses one reboiler and one condenser) to separate a mixture to n products which could be used in sharp and non-sharp separations [15].

There are demonstrations of complete sequences of a three product separation in Fig. 2. According to the state task representation [15]:

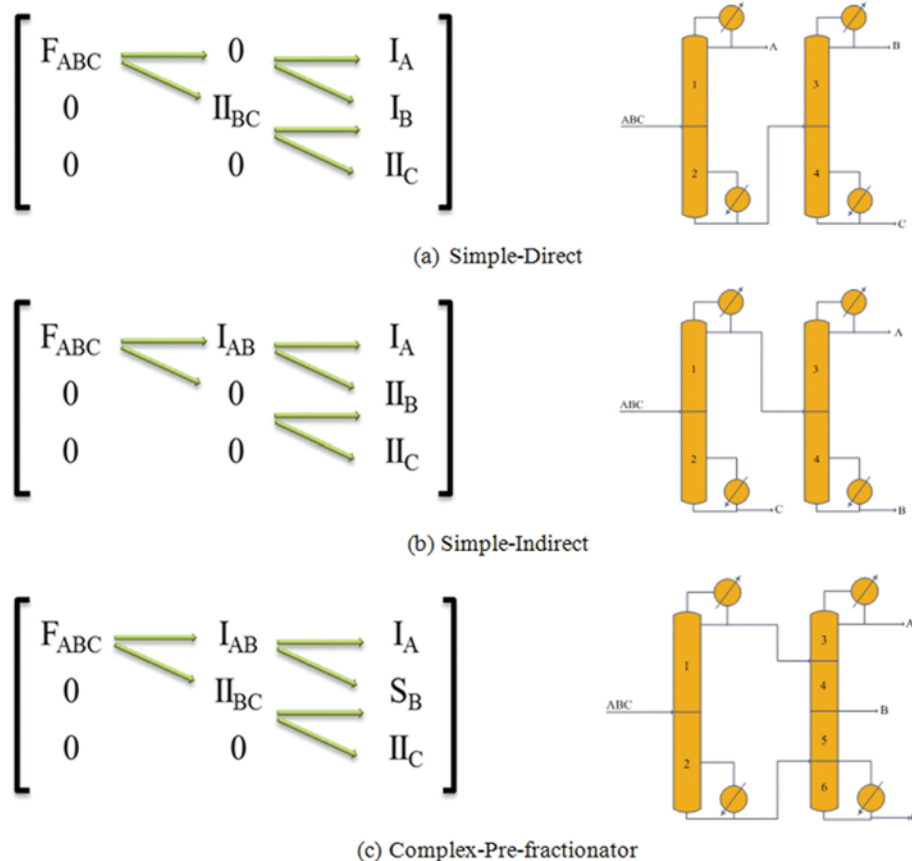1. When a mixture is produced from top of the column (distil-

$$\begin{bmatrix} F_{ABC} & 0 & I_A \\ 0 & II_{BC} & I_B \\ 0 & 0 & II_C \end{bmatrix}$$

(a) Simple-Direct

$$\begin{bmatrix} F_{ABC} & I_{AB} & I_A \\ 0 & 0 & II_B \\ 0 & 0 & II_C \end{bmatrix}$$

(b) Simple-Indirect

$$\begin{bmatrix} F_{ABC} & I_{AB} & I_A \\ 0 & II_{BC} & S_B \\ 0 & 0 & II_C \end{bmatrix}$$

(c) Complex-Pre-fractionator

Fig. 2. Separation matrices for the complete sequences of a three components mixture feed.

late) (φ or $\Phi=\{I\}$), all mixtures belonging to the same diagonal but in the previous columns must be eliminated from the separation matrix.

2. In a similar manner, when a mixture is a bottom product (φ or $\Phi=\{II\}$), all mixtures containing it as the lightest part in the previous columns must be eliminated from the separation matrix.

3. When a mixture is a side stream (φ or $\Phi=\{S\}$), no elimination is required.

4. In the last column, the lightest product must be produced from a condenser ($\varphi=\{I\}$) and the heaviest part must be produced from a reboiler ($\varphi=\{II\}$).

5. Note that the sub-mixture arrays in the first row, containing the lightest components, may only be recovered from a condenser in any of the sequences and their values must be $\{I\}$.

6. Also, the sub-mixture arrays in the main diagonal of the matrix, which contain heavy components, may only be recovered from a reboiler and their value becomes $\{II\}$.

The operation could be performed to generate all complete

Table 1. Number of simple and complex sequences for different number of products

N (number of components)	2	3	4	5	6	7	8
Simple seq.	1	2	5	14	42	132	429
Complex seq.	0	1	13	189	4331	185289	15766778

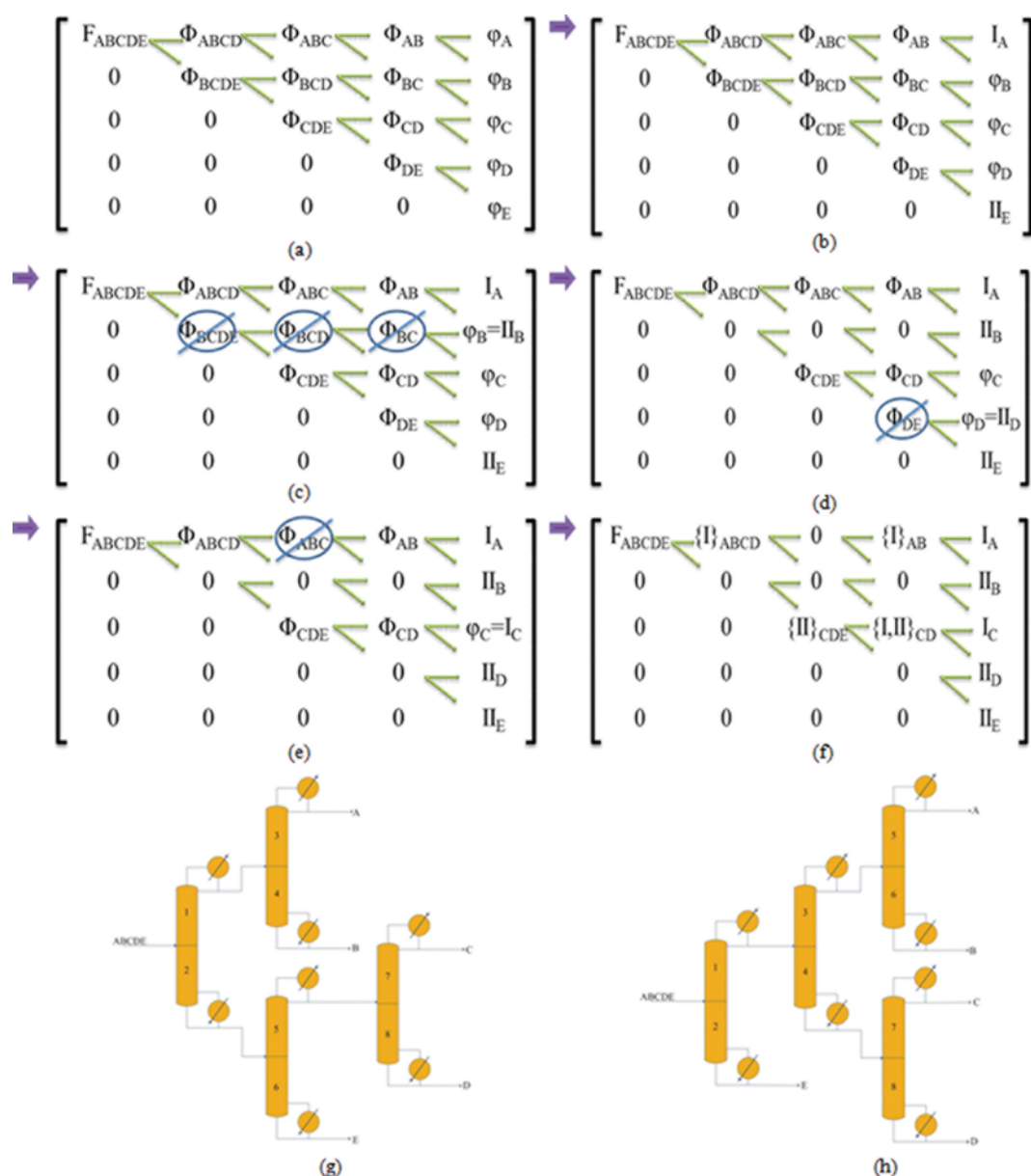
Fig. 3. Procedure of determination of the sequence's separation matrix.

sequence separation matrices by taking into account all possible φ or Φ option choices. The number of simple and complex sequences that could be generated is illustrated in Table 1. At each sub-mixtures selection step, three Φ option choices are possible and three different separation matrices will be generated consequently for three component mixtures. It is clear that because all sub-mixture possible choices are investigated for each φ or Φ, all possible sequences could be generated by this algorithm.

In Fig. 3, the proposed algorithm has been applied to a sample case with five final products (ABCDE). At the beginning, the general form of the separation matrix has been assembled (Fig. 3(a)). Then the φ sign in the last column is specified. A is the lightest part and must be collected from a condenser, while E is the heaviest part and must be collected from a reboiler (Fig. 3(b)). For the other three products different options are available ($\varphi = \{I, II, S\}$). For example, the collection of B and D from reboiler and C from a condenser ($\varphi_B = \{II_B\}$, $\varphi_C = \{I_C\}$, $\varphi_D = \{II_D\}$) is represented here. According to laws 1-6 presented above, by collecting B as a bottom product, all sub-mixtures containing B as a lightest part (Φ_{BC}, Φ_{BCD}, Φ_{BCDE}) in previous columns must be omitted from the separation matrix (Fig. 3(c)). The same must be implemented in sub-mixtures containing D (Φ_{DE}) (Fig. 3(d)).

Also, C is designated to be collected as distillate (i.e., $\varphi_C = \{I_C\}$), so all sub-mixtures belonging to the same diagonal, but in previous columns (Φ_{BC}, Φ_{ABC}), must be removed (Fig. 3(e)). Afterwards, by moving to the previous columns and choosing the remaining Φ options, the entire separation matrix would be determined (Fig. 3(f)). As shown, there are different options for the remaining arrays, each of which could lead to different configurations, two of which are illustrated in Figs. 3(g) and 3(h). If $\Phi_{CDE} = \{II_{CDE}\}$ and $\Phi_{CD} = \{I_{CD}\}$ this means that the first column is being used as a pre-fractionator (Fig. 3(g)) and if $\Phi_{CDE} = \{0\}$ followed by $\Phi_{CD} = \{II_{CD}\}$ (Fig. 3(h)) represents E being separated as a bottom product in the first column.

Under certain circumstances, some of the sub-mixtures within the separation matrix might be omitted and accordingly new sequences could be achieved. Sub-mixtures related to a reboiler or a condenser could not be omitted as their omission would bring about fewer reboilers or condensers, which contradicts the initial assumption of having an equal number of reboilers and condensers as the number of distillation columns in complex complete sequences. Final products could not be omitted since the separation is aimed at their production. As a result, the sub-mixtures designated by $\Phi = \{S\}$ in complex complete sequences could be removed under special conditions ($\Phi = \{III\}$). These are referred to as cross-
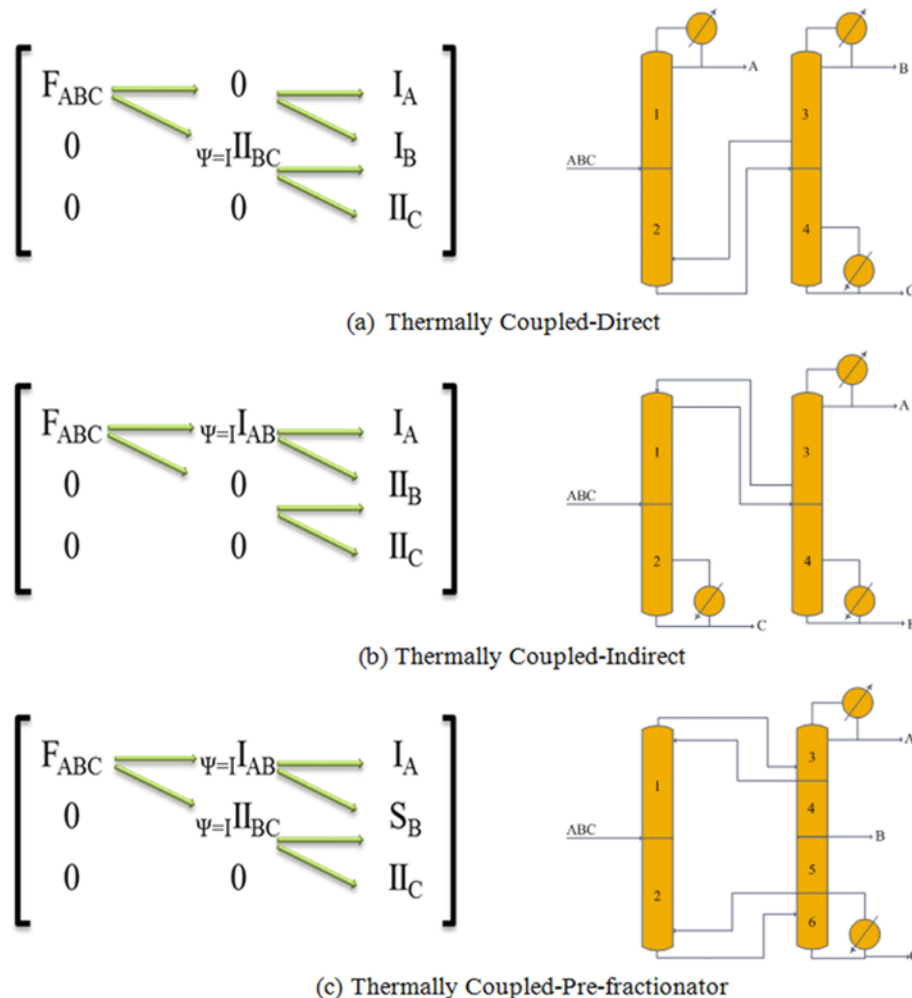

(a) Thermally Coupled-Direct

(b) Thermally Coupled-Indirect

(c) Thermally Coupled-Pre-fractionator

Fig. 4. Separation matrices for thermally coupled sequences of three a component mixture feed.

$$\begin{bmatrix} F_{ABC} & 0 & I_A \\ 0 & \lambda{=}I \\ \Psi{=}I \; II_{BC} & I_B \\ 0 & 0 & II_C \end{bmatrix}$$

(a) Thermodynamically equivalent-Direct

$$\begin{bmatrix} F_{ABC} & \lambda{=}I \\ \Psi{=}I \; I_{AB} & I_A \\ 0 & 0 & II_B \\ 0 & 0 & II_C \end{bmatrix}$$

(b) Thermodynamically equivalent-Indirect

Fig. 5. Separation matrices for thermodynamically Equivalent of a three components mixture feed.

$$\begin{bmatrix} F_{ABC} & \lambda{=}I \\ \Psi{=}I \; I_{AB} & I_A \\ 0 & \lambda{=}0 \\ \Psi{=}I \; II_{BC} & S_B \\ 0 & 0 & II_C \end{bmatrix}$$

(a) Thermodynamically equivalent on AB sub-mixture for a Pre-fractionator structure

$$\begin{bmatrix} F_{ABC} & \lambda{=}0 \\ \Psi{=}I \; I_{AB} & I_A \\ 0 & \lambda{=}I \\ \Psi{=}I \; II_{BC} & S_B \\ 0 & 0 & II_C \end{bmatrix}$$

(a) Thermodynamically equivalent on BC sub-mixture for Pre-fractionator structure

$$\begin{bmatrix} F_{ABC} & \lambda{=}I \\ \Psi{=}I \; I_{AB} & I_A \\ 0 & \lambda{=}I \\ \Psi{=}I \; II_{BC} & S_B \\ 0 & 0 & II_C \end{bmatrix}$$

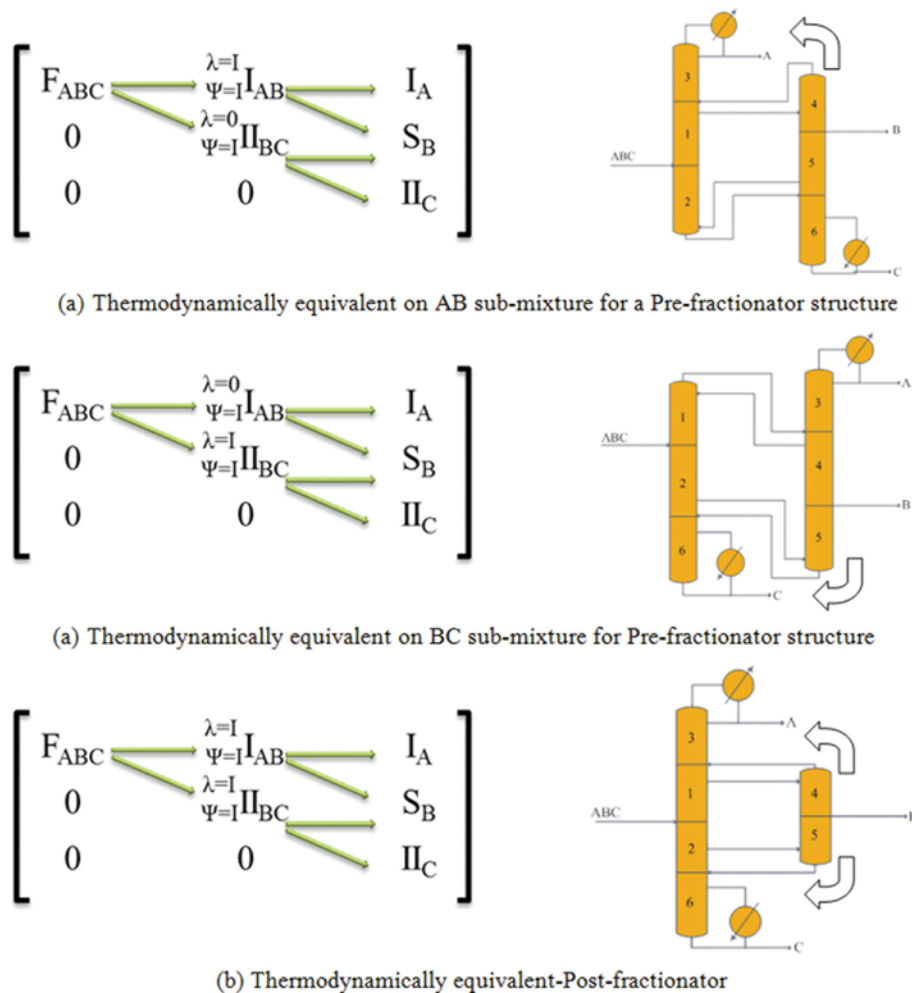(b) Thermodynamically equivalent-Post-fractionator

Fig. 6. Separation matrices for more operable thermodynamically equivalent sequences of a three components mixture feed.

over sequences due to the creation of cross points between indicating lines of different distillation columns in the locations of removing streams in their separation matrices. These are thoroughly explained by Ivakpour and Kasiri [15].

1-2. Thermally Coupled

A thermal coupling configuration could be generated by substitution of a condenser and/or a reboiler not associated with the final product streams with a bidirectional vapor-liquid connection. For sequences with more than one sub-mixture, it is possible to eliminate the corresponding heat exchangers one at a time or altogether. Also, it is possible to replace a one-directional side stream of no final product ($\Phi=\{S\}$) with a two-directional stream between two columns. Replacing a reboiler ($\Phi=\{II\}$) with a two way communication stream could lead to a side rectifier sequence, and replacing a condenser ($\Phi=\{I\}$) with a two way communication could result in the side stripper type configuration after finding the thermodynamically equivalent configuration.

In the presented method, for easier programing of these changes in the algorithm, an index is added to the sub-mixture arrays. Hence, each of the sub-mixture streams that could be a candidate for thermal coupling has an additional ψ sign in the lower left of the sub-mixture array associated with it ($_\psi\Phi_{rk}$). ψ could be "0" or "I", indicating absence or presence of thermal coupling, for its related reboiler or condenser, respectively.

Fig. 4 presents the thermally coupled structures generated from the simple and complex column configurations and its separation matrix. In this way, it is possible to present all thermally coupled sequences systematically:

1. Choose the sub-mixture that could be replaced by bidirectional streams (i.e., $\Phi=\{I, II, S\}$).

2. Change the value of ψ from 0 to I for each sub-mixture.

1-3. Thermodynamically Equivalent

The thermodynamically equivalent configurations could be generated from the thermally coupled sequences through moving one column section associated to a condenser and/or a reboiler, which provides the common reflux flow rate or the vapor boil up between two consecutive columns. In this case, with the omission of a condenser or a reboiler associated with a sub-mixture from a simple column in a distillation configuration makes the rectifying or the stripping section of the succeeding columns movable. For this reason the number of movable sections is equal to the number of thermal couplings in the considered sequence [25].

(a) Configuration with thermally coupled side stream between two consecutive columns

(b) Thermodynamically equivalent configuration that is created from (a) by moving more than one section at once
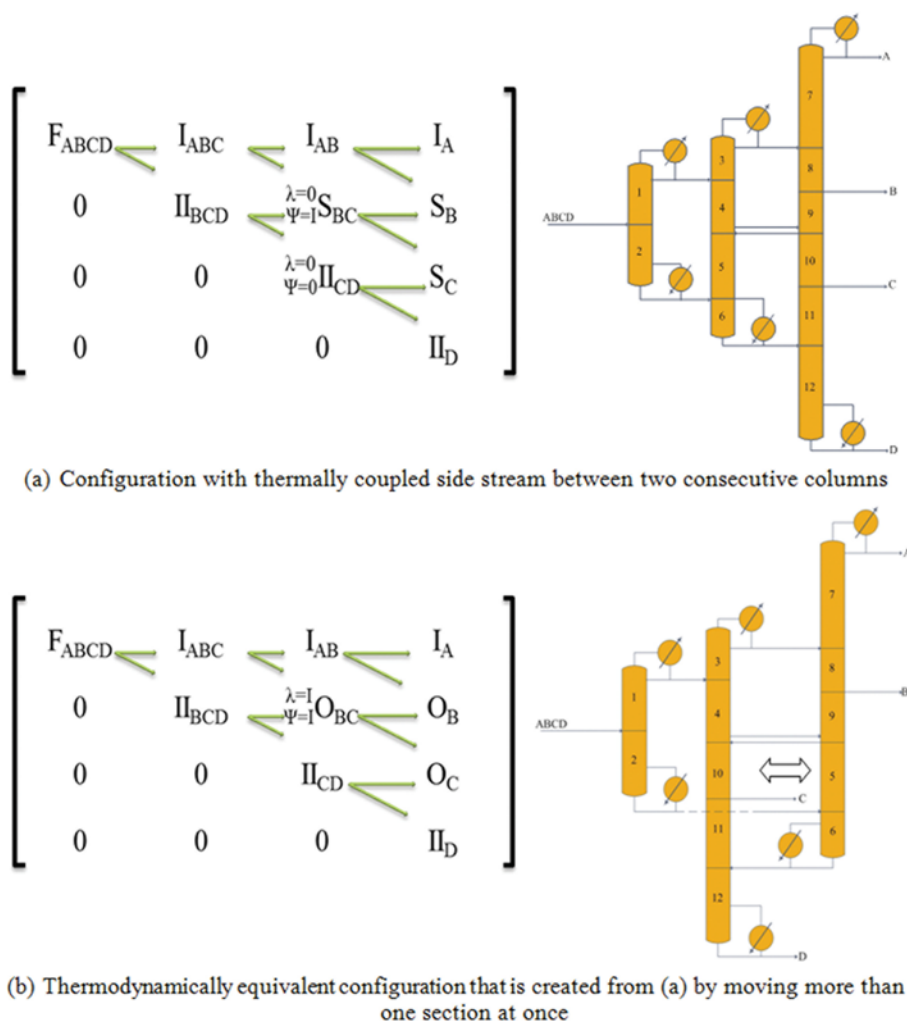
Fig. 7. Separation matrices for satellite configuration of a four components mixture feed.

A thermodynamically equivalent sequence consumes as much energy as the corresponding thermally coupled structure. However, by improving liquid and vapor flow rate redistribution between sections, the capital cost saving [12] and better controllability of the system [35] could be attained.

Fig. 5 represents thermodynamically equivalent structures generated from the thermally coupled configurations for a three product separation system. These configurations, as can be seen, are reproduced by moving sections between columns. In the current work, a new index has been used to indicate the possibility of moving these sections. This index has been added to the upper left part of the Φ array (λ). This superscript could be assigned the value "I" or "0". To make a section movable in a distillation column, the condenser or the reboiler associated with the sub-mixture must be omitted, initially. Therefore, in the separation matrix, the related array of the sub-mixture of moving sections should have (ψ=I). Therefore, in a systematic programming practice in order to generate all possible thermodynamically equivalent configurations, ψ should be checked to be I before changing the λ for each sub-mixture. As a result, the arrays representing moving sections will have two I values for both indices ψ and λ. An example for more clarification of this is presented in a three-component mixture in Fig. 5. In Fig. 5(a), which is the thermodynamic equivalent sequence produced from the configuration presented in Fig. 4(a), section 4 is moved from the second column to the first, and in Fig. 5(b), which could be created from the sequence illustrated in Fig. 4(b), section 3 is moved from the second column to the first.

A more operable thermally coupled configuration presented by Agrawal and Fidkowski [35] could also be completely generated by the separation matrix method proposed here. These configurations and their related separation matrix are illustrated in Fig. 6. These configurations are produced from pre-fractionators scheme (Fig. 4(c)) by moving sections 3 and 6 one by one or both at once. In Figs. 6(a) and 6(b) the indices of sub-mixture $\{^{\lambda=0}_{\psi=I}I_{AB}\}$ and $\{^{\lambda=0}_{\psi=I}II_{BC}\}$ change to $\{^{\lambda=I}_{\psi=I}I_{AB}\}$ and $\{^{\lambda=I}_{\psi=I}II_{BC}\}$, respectively.

Besides, in some cases, with a side stream of no final product (Φ={S}) with a two-directional stream between the two columns, it is possible to move more than one connected section at the same time. For example, in Fig. 7(a), a configuration with one thermally coupled side stream is illustrated. By replacing sections in the lower part of the bidirectional side stream in two consecutive columns (sections 5 and 6 in the second column and sections 10, 11 and 12 in the third) new thermodynamic equivalent scheme could be generated, which is presented in Fig. 7(b). The same may be stated about sections 3 and 4 in the second column and sections 7, 8 and 9 in the third in the upper part of the two directional side stream.

1-4. Intensified Sequences

Commonly, in non-sharp separation not aimed at producing pure products, it is possible to do the separation with fewer distillation columns. When a distillation column or a section of it is omitted, its products will not be produced. As a result, these products must be deleted from the separation matrices.

The only possible intensified states in the sequence of a three component feed are demonstrated in Fig. 8. Fig. 8(a) is created by omitting the side rectifier (section 3) in Fig. 5(a) and obtaining product B as a side stream, and Fig. 8(b) is produced by deleting side stripper (section 4) in Fig. 5(b) and collecting B as a side stream.
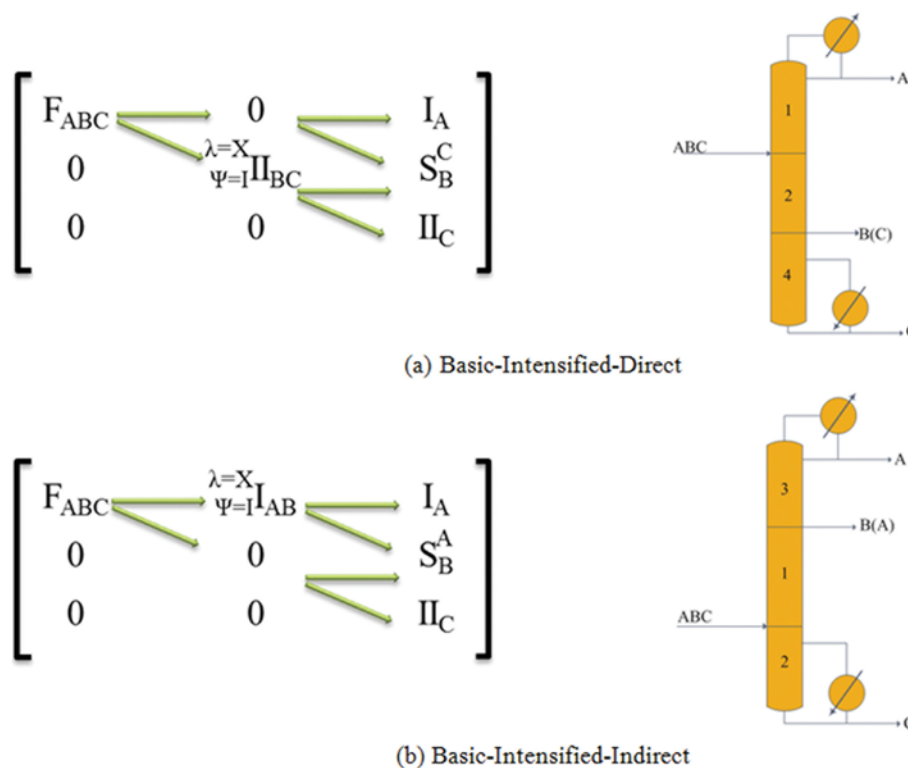

(a) Basic-Intensified-Direct

(b) Basic-Intensified-Indirect

Fig. 8. Separation matrices for intensified sequences of three components mixture feed.

(a) Side rectifier
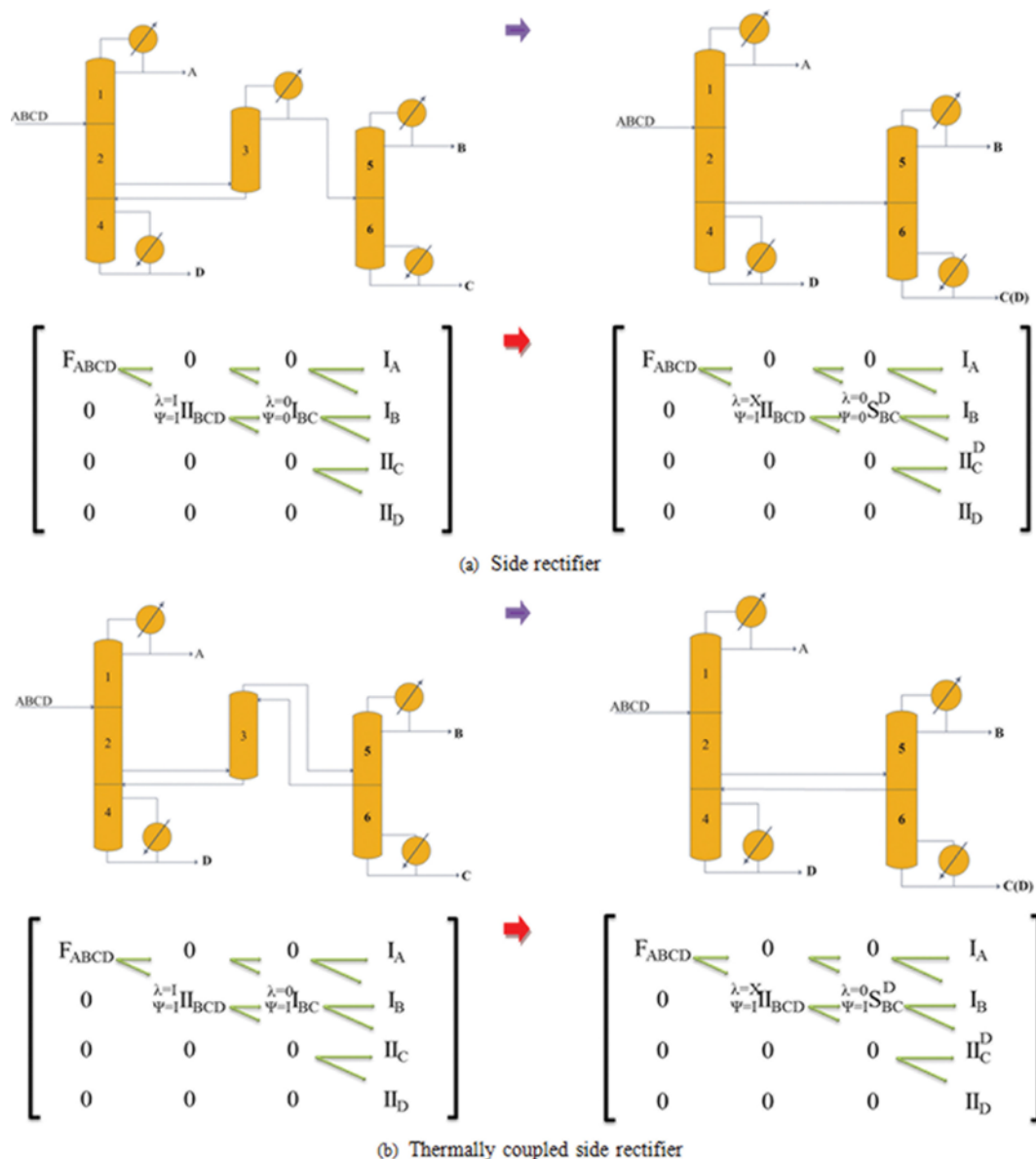

(b) Thermally coupled side rectifier

Fig. 9. Different kinds of side columns in thermodynamically equivalent sequences and respective intensified structures with their separation matrices.

The deleted products are illustrated by X in the separation matrix. λ is assigned X in the upper left of the array in these cases. In these sequences the separation could not take place completely and, for example, in Fig. 8(a) part of component C is leaked into product B. The same is true for Fig. 8(b) in which part of A is leaked into product B. These components are called suspended components and illustrated by an index on upper right of the arrays.

For configuration with more components (n>3), the intensified configurations which have fewer than n-1 columns could be generated simply, by omission of the side columns having only one section from the thermodynamically equivalent structures. Samples of these sequences with their separation matrices can be seen in Fig. 9. In these configurations if the side column is a side rectifier ($\{_{\psi=I}^{\lambda=I}II_{BCD}\}$ in Figs. 9(a) and (b)), then in the separation matrix of the intensified structure the array of bidirectional product stream

is omitted (changed from $\{_{\psi=I}^{\lambda=I}II_{BCD}\}$ to $\{_{\psi=I}^{\lambda=X}II_{BCD}\}$) and the first array related to the lightest components in the following columns of the matrix ($\{_{\psi=0}^{\lambda=0}II_{BC}\}$) is changed to {S} ($S_{BC}$). The heaviest component (D) here is leaked into the next column and can be seen in the heavy product as a suspended component.

Also, if the side column is a side stripper ($\{_{\psi=I}^{\lambda=I}I_{ABC}\}$ in Figs. 9(c) & (d)), then in the separation matrix of the intensified structure the array of bidirectional product stream is omitted (changed from $\{_{\psi=I}^{\lambda=I}I_{ABC}\}$ to $\{_{\psi=I}^{\lambda=X}I_{ABC}\}$) and the first array related to the heaviest components in the following columns of the matrix ($\{_{\psi=0}^{\lambda=0}II_{BC}\}$) is changed to {S} ($S_{BC}$). The lightest component (A) here is leaked into the next column and can be seen in the light product as a suspended component.

In total, the following rules could be concluded for generating intensified structures from basic ones:
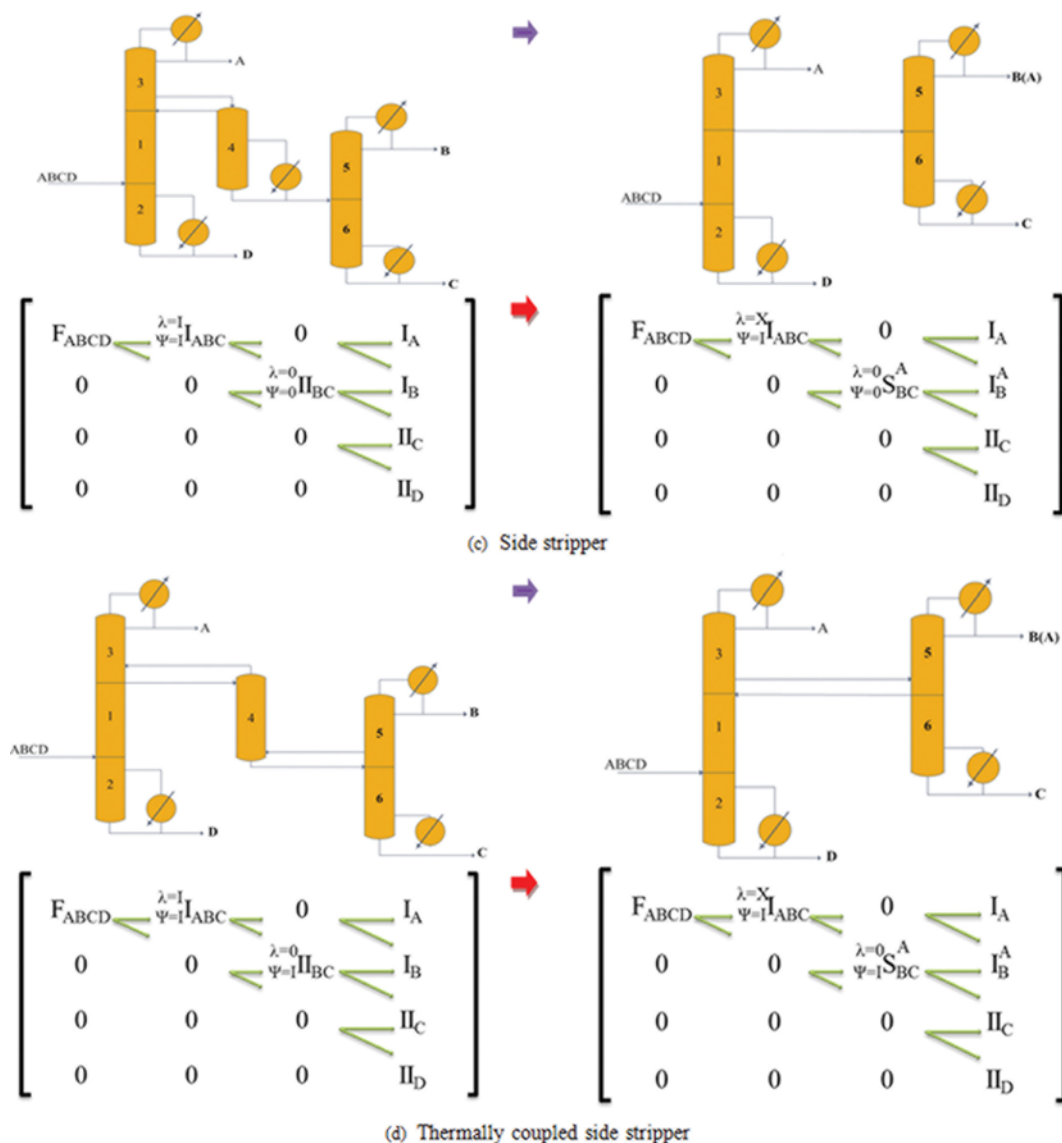
(c) Side stripper

(d) Thermally coupled side stripper

Fig. 9. Continued.

1. Sections in some thermodynamic equivalent structures could be omitted if:

a. The section is the remainder of a column with some parts moved to produce a thermodynamic equivalent structure.

b. The array next to the moving section's product ($\Phi=\{^{\lambda=I}_{\psi=1}\Phi\}$), on the same row, is $\Phi=\{I\}$ and in the diagonal direction is $\Phi=\{II\}$.

2. In these configurations if the remainder column is a side rectifier ($\Phi=\{I\}$), then in the separation matrix of the intensified structure the array of bidirectional product stream is omitted ($\Phi=\{^{\lambda=X}_{\psi=1}II\}$), and the first array related to the lightest components in the following columns of the matrix is changed to $\{S\}$. As a result, the heavier components are leaked to this side product and can be seen in the heavy products of the following columns and are illustrated by an index on upper right of the arrays as suspended components.

3. If the remainder column is a side stripper ($\Phi=\{II\}$), then in the separation matrix of the intensified structure the array of bidi-

rectional product stream is omitted ($\Phi=\{^{\lambda=X}_{\psi=1}I\}$), and the first array related to the heaviest components in the following columns of the matrix is changed to $\{S\}$. So, the lightest components are leaked into this side product and can be seen in light products of the following columns and are illustrated by an index on upper right of the arrays as suspended components.

4. In case 2 the suspended components are heavier components in the side rectifier feed, the number of which is equal to the difference between feed and product column numbers.

5. In case 3 the suspended components are lighter components in the side stripper feed, the number of which is equal to the difference between feed and product row numbers.

In recent years, some of the intensified structures have been studied (like Kim and Wankat [20]), but these are limited to four component separations with sequences only composed of one simple column and one complex column. In the present work new configurations as well as the intensified structures studied in previ-

ous works have been taken into consideration and could be generated systematically. These configurations are very important in non-sharp separations and are rarely investigated.

1-5. Simultaneous Heat and Mass Integrated Sequences

Simultaneous heat and mass integrated sequences (SHMI) are the new group of intensified or reduced sequences which were illustrated for the first time by Shenvi et al. in 2013, but it seems that there is no synthesis method claiming to generate them all systematically [36]. These intensified sequences are created by combining the reboiler of a light component mixture of a column by a condenser of a heavy component mixture of another column. According to Shenvi et al. [36], these are categorized as below:

1) Columns producing

a. The same final products

b. Different final products

2) Columns producing sub-mixtures

a. Sub-mixtures with the same components

b. Sub-mixtures with common components (overlapping components) between two sub-mixtures

c. Sub-mixtures with no overlapping components

3) Two columns of which one produces a final product and the other a sub-mixture.

In groups 1a and 2a when the reboiler and the condenser are omitted no new section needs to be added to the new column, but when the reboiler and the condenser are omitted in groups 1b, 2b, 2c and 3, a new section with adequate number of stages is required (to guarantee smooth passage in composition profile along the new section) to be added to the integrated column [36].

For generating groups 1a and 2a, like intensified configurations as mentioned in the former section, the arrays of the separation matrix φ or Φ are assigned the value of {S}. But groups 1b, 2b, 2c and 3 could be generated by giving the value of X to the ψ index in the lower left of the array. As mentioned by Shenvi et al. [36], there could be situations in which more than one possible integration opportunity exists in the configuration. In these situations the values of ψ get the value of X1, X2… for clarification.
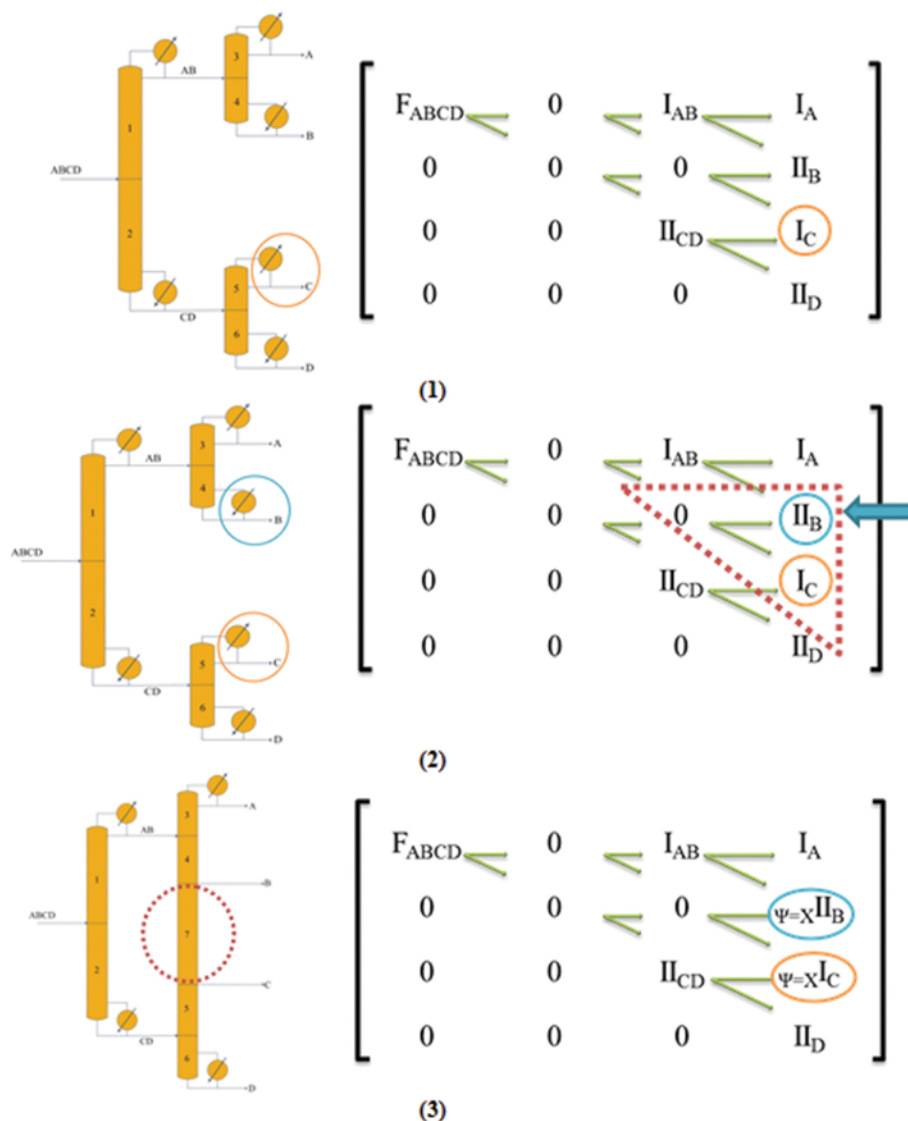

Fig. 10. Procedure of determination of the heat and mass integration structures.
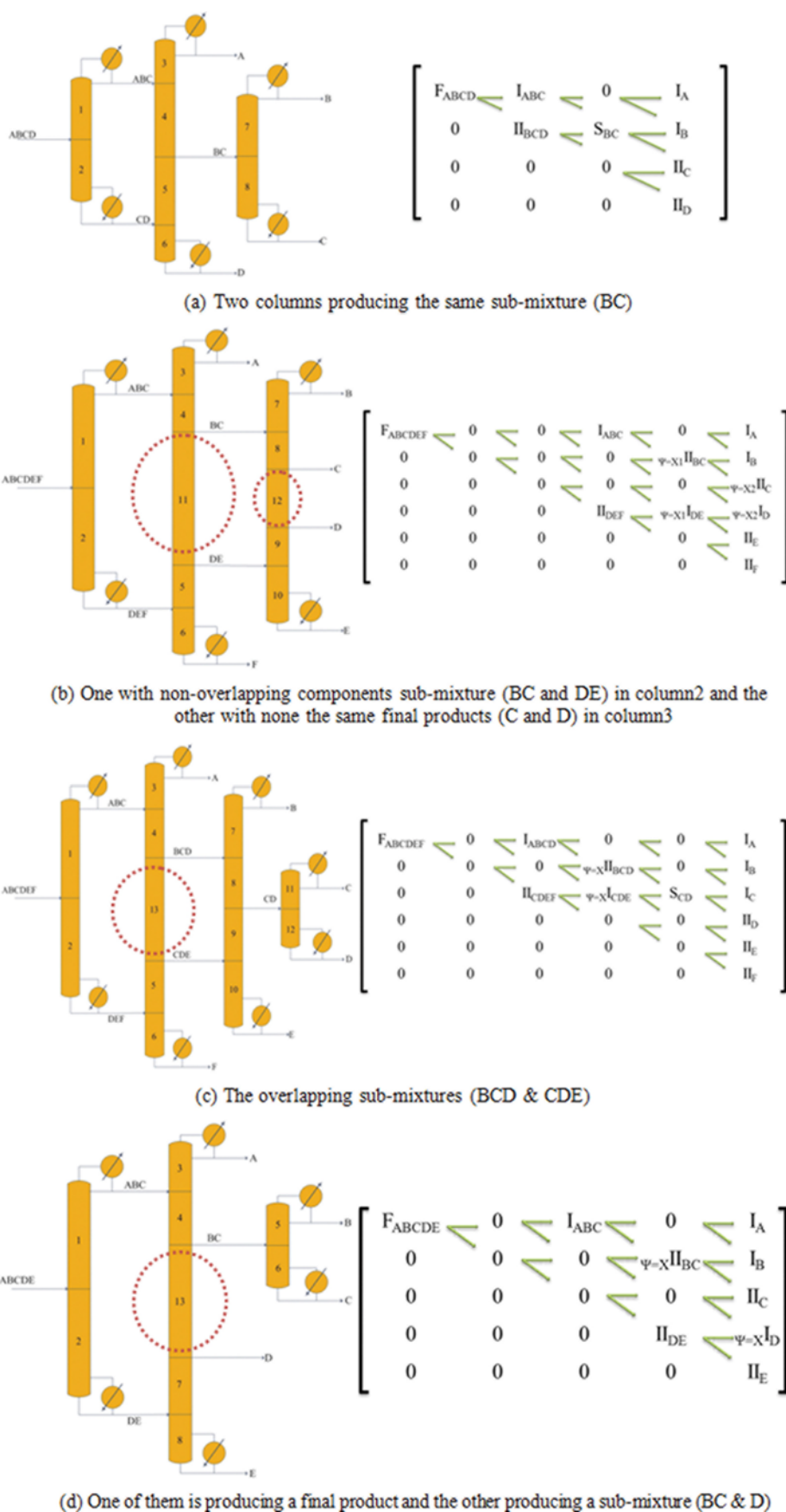
(a) Two columns producing the same sub-mixture (BC)

(b) One with non-overlapping components sub-mixture (BC and DE) in column2 and the
other with none the same final products (C and D) in column3

(c) The overlapping sub-mixtures (BCD & CDE)

(d) One of them is producing a final product and the other producing a sub-mixture (BC & D)

Fig. 11. Different examples of heat and mass integrated configurations and their related separation matrix.

For generating these configurations (1b, 2b, 2c and 3) from basic schemes:

1. First search for a heavy sub-mixture or a final heavy product drawn from a condenser.

2. Then create a triangle of the array found in step 1 and two other arrays of the second line of the separation matrix (one in the same column and the other in the same diagonal).

3. If there is a reboiler in this triangle producing mixtures with lighter components, then the integration is possible.

4. Change the value of ψ ($_\psi\Phi_{ik}$) to "X" for the found heavy sub-mixture ($\Phi=\{_{\psi=X}I\}$) or final heavy product ($\varphi=\{_{\psi=X}I\}$) and the sub-mixture with lighter components drawn from the reboiler ($\Phi=\{_{\psi=X}II\}$).

The procedure for a configuration of group 1b is presented in Fig. 10.

Here are some other examples of these configurations (presented by Shenvi et al. [36]) and their related separation matrices. Fig. 11(a) illustrates a configuration with a combined column (column 2) being made of two columns producing the same sub-mixture (BC); the array in the third column and the second line is changed to $\{S_{BC}\}$. No new section is added to the new combined column other than the reboiler and condenser of the related omitted columns. In Fig. 11(b), another scheme is presented which

offers two possibilities for heat and mass integration: One with non-overlapping sub-mixtures (BC & DE) and the other with two final product streams (C & D). In the related separation matrix, the first combination is represented by X1 ($\{_{\psi=X1}II_{BC}\}$ and $\{_{\psi=X1}I_{DE}\}$) and the other by X2 ($\{_{\psi=X2}II_C\}$ and $\{_{\psi=X2}I_D\}$). As a result, the configuration with five columns for a separation of a six component mixture is reduced to a three column structure and a new section is added to each new combined column, sections 11 in column 2 and section 12 in column 3. An example of a combination of columns which produce sub-mixtures with overlapping components (BCD & CDE) ($\{_{\psi=X}II_{BCD}\}$ and $\{_{\psi=X}I_{CDE}\}$) is demonstrated in Fig. 11(c). Here again after combination a new section is needed and section 13 is added to the combined column. Finally, an example from group 3 for a five component mixture is illustrated in Fig. 11(d). Here the column producing D as the final product is combined with the column producing BC as a bottom product. Section 13 is added to the new column producing D as a side stream, ($\{_{\psi=X}II_{BC}\}$ and $\{_{\psi=X}I_D\}$).

1-6. Divided-wall Columns

Divided-wall column sequences are other categories which are usually considered in order to save investment [37-40]. These configurations consist of two columns arranged in a single shell and divided by an internal wall. These sequences could be easily gener-
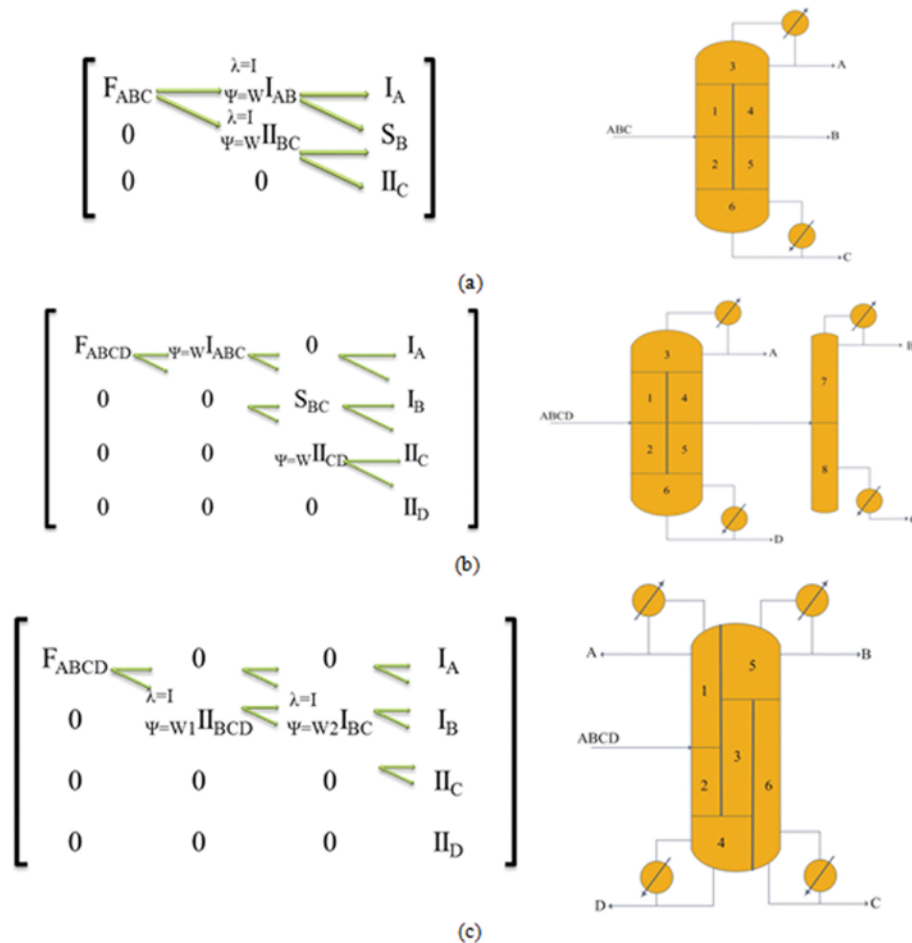

Fig. 12. Sequences with divided-wall columns.

ated from thermally coupled or thermodynamically equivalent structures (post fractionator, pre fractionator or side columns).

In these sequences, there is one to n-1 common components among product streams. So in their separation matrices, there are {I} and {II} arrays in one column or in consecutive columns with common components, and there are no arrays between them (in other rows and columns). These sequences could also be generated from some simultaneous heat and mass integrated sequences in which there are two consecutive arrays with $\psi = \{X\}$.

For presenting the divided-wall columns, the value of ψ is changed to W (Fig. 12(a), (b)). So in separation matrices in which both ψ and λ have the value I ($\{^{\lambda=I}_{\psi=I}\Phi\}$), which is the sign of a side column in the sequence, the value of ψ is changed and the separation matrix for the divided-wall column is generated. For more tedious sequences with more divided-wall columns, the value of ψ accepts W1, W2… for more clarification (Fig. 12(c)).

DISCUSSION

The modified method enables the matrix based algorithm, first reported by Ivakpour and Kasiri in 2009, of generating basic thermally coupled, thermodynamically equivalent and reduced (both intensified and simultaneous heat and mass integrated) structures for n-component separation systems.

One of the problems in the other reported matrix method [16,17] is that depending on the interpretation of separation matrix, the same matrix could match more than one configuration in different categories. For example, a case is presented in which a matrix can correspond to a basic configuration (with exactly n-1 columns) (Fig. 13(a)) as well as intensified configuration (with fewer than n-1 columns) (Fig. 13(b)) [17]. Such problems are overcome in the presented method by assigning a different value for each array of the matrix. Fig. 13(c) demonstrates both separation matrices of
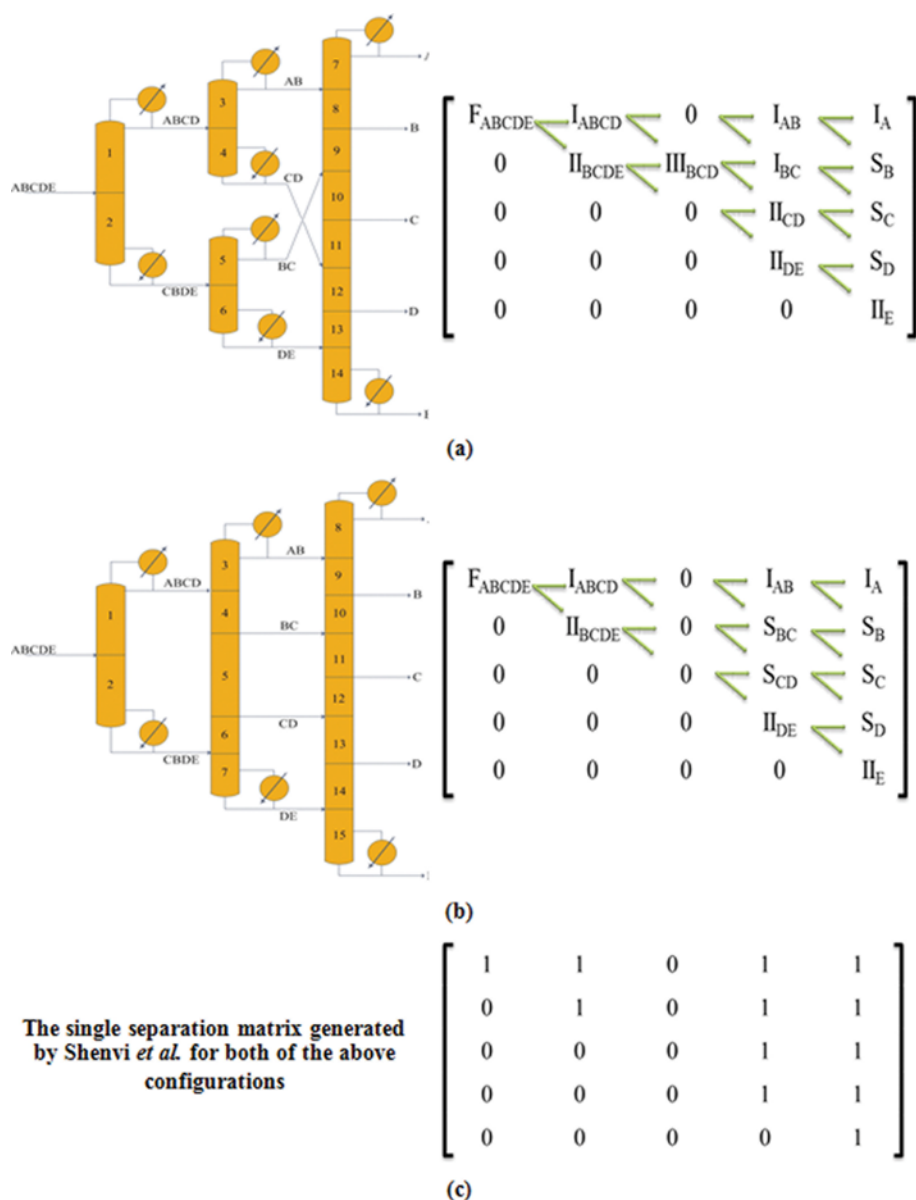

(a)

(b)

The single separation matrix generated by Shenvi et al. for both of the above configurations

$$\begin{bmatrix} 1 & 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

(c)

Fig. 13. Example of a candidate matrix for a five-component feed mixture illustrated in Shenvi et al. [17].

Table 2. Number of sequences derived from simple complete configurations

N (number of components)	2	3	4	5	6	7	8
Simple seq.	1	2	5	14	42	132	429
Thermally coupled seq.	0	2	15	112	882	9108	128700
Thermodynamically equivalent seq.	0	2	32	512	16384	1048576	134217728
Reduced seq.	0	2	31	127	511	2047	8191
Total	1	8	83	765	17819	1059863	134355048

Shenvi et al. and the present work for the above case.

The following table (Table 2) illustrates the number of possible sequences which could be generated from the simple complete configurations. Configurations are separated into subdivisions for more clarity (The number of simultaneous heat and mass integrated systems is not presented in the table). By growing number of products, the number of possible configurations increases in an exponential manner. For configurations with complex columns the number of sequences that could be generated is much greater. For example, for a four component feed mixture, the number of complete complex sequences is 13, thermally coupled configurations are 140 and thermodynamically equivalent structures are 511.

In comparison with other methods, the proposed algorithm could simply, automatically and systematically generate basic structures (simple, complex, thermally coupled, thermodynamically equivalent, intensified, simultaneous heat and mass integrated and divided-wall column sequences). It is not restricted to the number of components (as in Kim [28,29]; Kim and Wankat [20]). Additionally, Most of the synthesis methods presented earlier could not cover all parts of a complete search space, like Kim et al. [30,31], Wang et al. [32] and Yoo et al. [33], which did not consider the thermal states in their algorithm; or Shah and Agrawal [16] and Shenvi et al. [17], which do not present thermodynamically equivalent configurations presented in Agrawal and Fidkowski [35]; Kim and Wankat [20], which do not cover all types of reduced structures. Besides, the sequences with divided-wall column are not considered by these researchers.
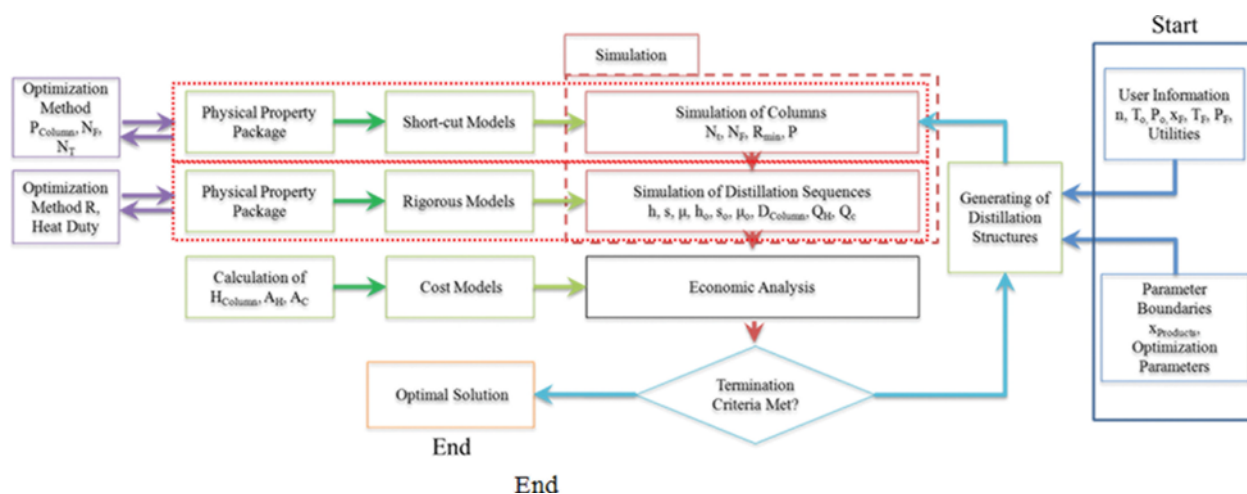
There is a step by step algorithm which was initially presented

by Errico et al. [12] and then developed further by Rong and Errico [13] and Errico et al. [14]. This could consider modifying structures introduced by Agrawal and Fidkowski [35] as well as complex structures introduced by Gridhar and Agrawal [6]. Their method could consider all basic, simple configurations (and their derivatives: thermally coupled, equivalent thermodynamic and intensified). Entailing a graphical approach the algorithm is more difficult to program. Being manual in generating initial configurations, if a configuration is missed initially, a phenomenon with quite a high possibility for more complex separations containing more components; it would lead to a loss of part of the search space in the subsequent stages of the procedure, which could have the potential of containing a global optimum. In the procedure proposed here, this could not happen due to the systematic and automatic nature of the procedure based on the separation matrix. Furthermore, this is the only systematic algorithm which could generate all simultaneous heat and mass integrated sequences to date.

In comparison to the methods like MILP/MINLP as in the works done by Caballero and Grossmann [8,10,11] or Shah and Kokossis [18,19], which have utilized short-cut or aggregated methods for simulating the sequences, the presented algorithm could be easily accompanied by a rigorous simulation method in finding the optimum distillation sequence and increase the accuracy of the calculations (as the work done by Ivakpour and Kasiri [15]).

SIMULATION AND OPTIMIZATION

The design strategy here is the same as in Ivakpour and Kasiri

Fig. 14. The procedure used for analysis of the configurations in the present study.

[15]. After considering the required configuration the next step would be defining the specification of the sequences. In this study, the authors used a self-developed program for simulation (shortcut (Winn-Underwood-Gilliland method) and rigorous (Inside-out method)) and optimization (Simulated annealing method) of the sequences. The required design parameters are first determined by shortcut method. The initial information (like number of trays, feed and side products trays, min reflux ratio, operating pressure) could be acquired in this step. This step goes through an optimization method in which the pressures of the columns are optimized. The objective is to reach as close as possible to atmospheric pressure, keeping the condenser boiling point above 35 °C (assuming 25 °C for inlet cooling water temperature). Due to the components used and temperature and pressure range of the case

Table 3. Different samples considered in this study

Vapor fraction	Pressure (atm)	ESI*	Components	Mixture
0	4.5	1.86	n-Butane, i-pentane, n-pentane	M1
0	1.44	1.04	n-Pentane, n-hexane, n-heptane	M2
0	1.44	0.47	i-Pentane, n-pentane, n-hexane	M3

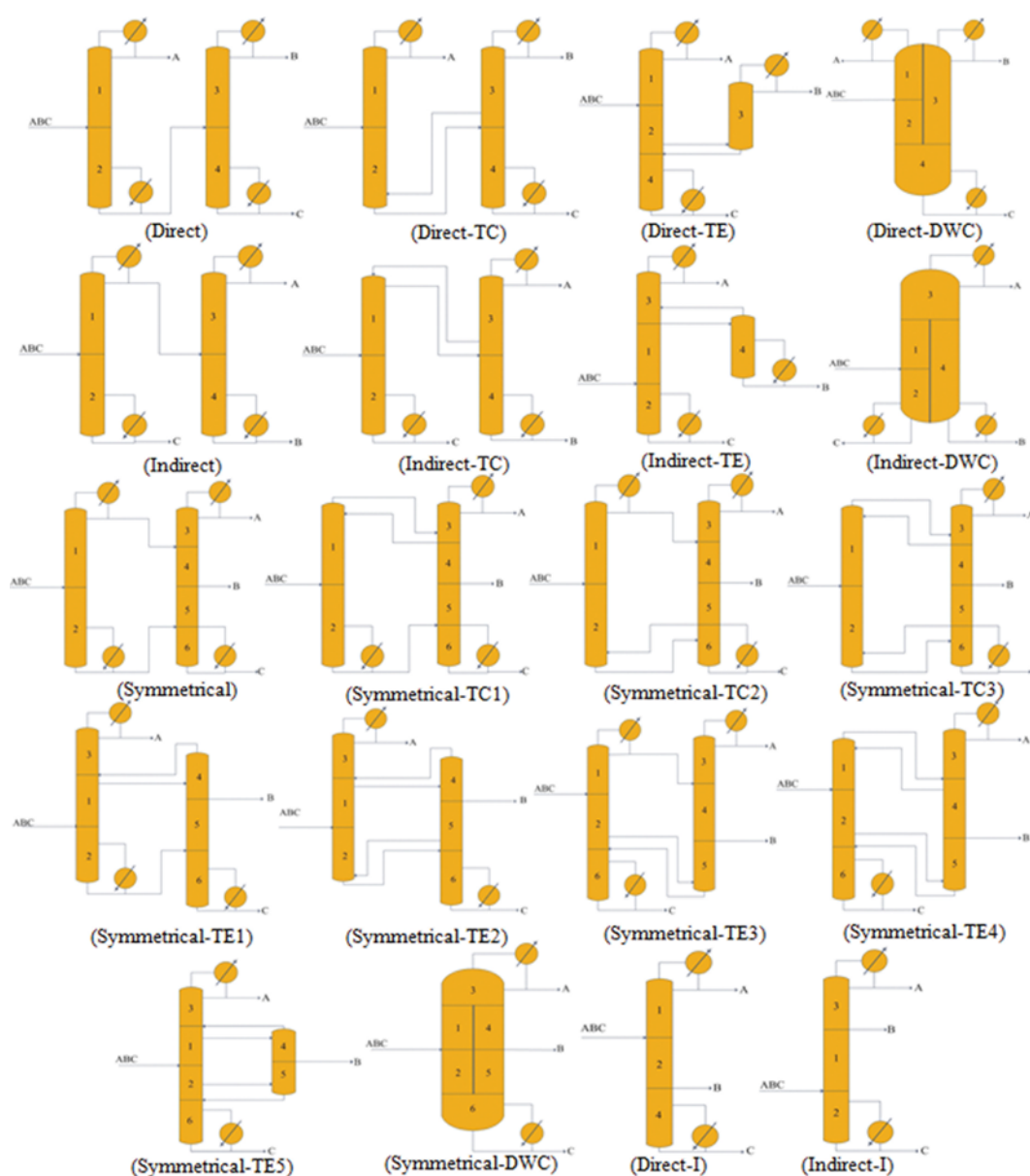*ESI $=\alpha_{AB}/\alpha_{BC}$ [5]

Fig. 15. Three component distillation sequences considered in this study.

studies, the Soave-Redlich-Kwong equation-of-state is selected for physical property and equilibrium calculations. The results of the shortcut method were used as the initial estimate in the rigorous simulations. The inside-out method according to Seader and Henley [41] was used as the rigorous simulation method. In this part the reflux ratio of the columns was optimized. The objective involves reaching the specified product purities utilizing minimum hot and cold utility in the reboiler and condenser, respectively. The simu-

lated annealing method was applied as an optimization method at both levels. The parameters were tuned for each case and the final parameters were applied in the optimization of the case studies. A detailed, thorough definition of the optimization procedure is beyond the scope of this article and will be presented in future works. The results of the rigorous calculations (column specification: height and diameter, heat of condenser and reboiler) were used for an economic study of the columns. For economic study, Guthrie's cost
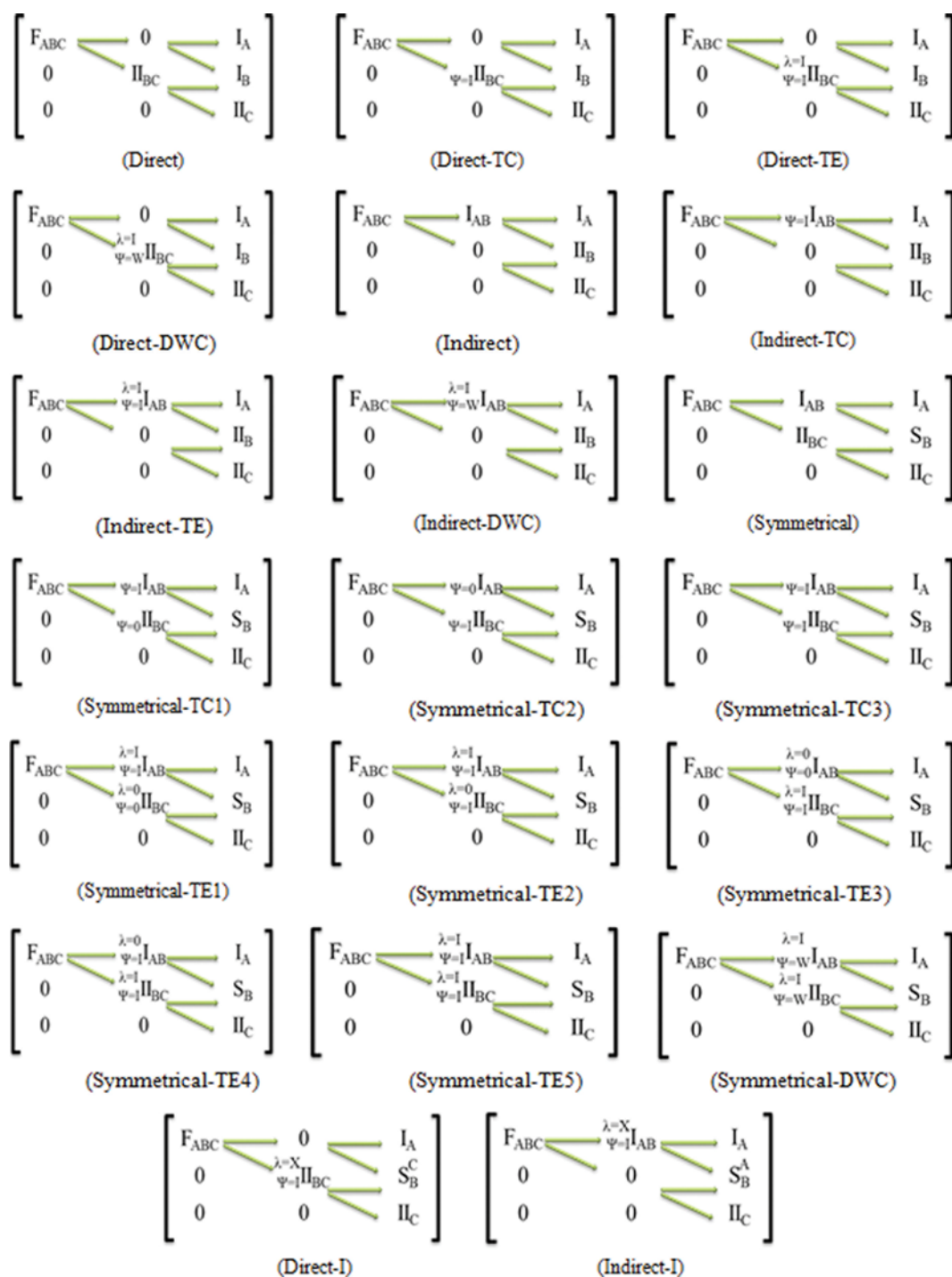

Fig. 16. Separation matrices for each distillation sequences presented in Fig. 15.

calculation method is applied as modified in Douglas [42]. The utility prices for calculating operating cost are as demonstrated in Seider et al. [43]. The schematic diagram of the procedure used for analysis of the sequences and finding the optimum configuration is presented in Fig. 14.

CASE STUDY

The algorithm was applied to mixtures containing three components with three different compositions (F1: [0.4, 0.2, 0.4], F2: [0.33, 0.34, 0.33] & F3: [0.15, 0.7, 0.15]) as presented in Table 3. The objective was to reach 98% purity in the final products. The execution time was about 1.32 h in a self-developed platform on a Core i7-4700MQ CPU at 2.4 GHz with 8 GB of RAM.

Fig. 15 presents the different categories of three component distillation sequences and Fig. 16 presents the related matrices generated by the proposed algorithm. A complete search space with three component feed mixture including simple, complex, thermally coupled, thermodynamically equivalent, intensified, and divided-wall column sequences was presented.

The proposed algorithm could generate all sequences and these

matrices could easily be translated within a self-developed programs or commercial software for simulation and optimization purposes. In Table 4 the economic study of the first three sequences under each condition is presented. Indirect-DWC sequence has the largest number of occurrences followed by Direct-DWC, Direct-TC, Indirect-TE and Direct-TE sequences, respectively. As presented, divided-wall column sequences have the largest and basic sequences have the smallest number of occurrences amongst the best configurations.

The algorithm could be used for sharp or non-sharp separations as presented here and in the former publication by Ivakpour and Kasiri [15]. By the proposed method a complete search space is generated that helps designers to consider the different categories of structures. The proposed algorithm is not limited by the number of components and could be applied to different case studies.

CONCLUSIONS

The optimum distillation sequence in separation of an n-component mixture could be achieved on condition that all possible configurations are generated via proper synthesis algorithm. This paper presents a matrix algorithm for generating all possible basic distillation column structures for sharp and non-sharp separation of n-component mixtures. This method is based on the former algorithm demonstrated by Ivakpour and Kasiri in 2009. By modifying the algorithm, every simple, thermally coupled, thermodynamically equivalent, intensified (configurations with less than n-1 distillation columns), simultaneous heat and mass integrated and divided-wall column sequences could be generated automatically and systematically. As stated, the new method has some features which may be listed as:

- No limitations in the number of components
- Coverage of nearly all parts of a complete search space
- Ease of programmability
- Independence from the initially guessed configurations (basic simple or complex)
- Ability to generate simultaneous heat and mass integrated and divided-wall column sequences

As the algorithm is mathematical, it could readily be programmed or utilized within any commercial software for simulation and optimization purposes for many separation case studies. Some special sequence categories like multi-effects, pump around, compressor aided separations and internal heat integrated distillation systems (HIDIC) is not included in this method. According to the nature of the algorithm, these sequences could be generated and would be considered in future work. The detailed optimization procedure is beyond the scope of this work and will be presented in future work.

Table 4. The result of total annual cost ($/y) for the best three sequences under different feed conditions

Mixture	Composition		Sequences	TAC ($/year)
M1	F_1	1st	**Indirect-DWC**	**293,472.592**
		2nd	Indirect-TE	296,297.113
		3rd	Symmetrical-DWC	303,743.586
	F_2	1st	**Direct-TC**	**340,502.266**
		2nd	Direct	367,942.217
		3rd	Indirect-TC	3778,841.474
	F_3	1st	**Indirect-DWC**	**508,593.831**
		2nd	Indirect-TE	512,115.351
		3rd	Indirect-TC	526,700.303
M2	F_1	1st	**Direct-TC**	**138,095.912**
		2nd	Direct-DWC	142,216.070
		3rd	Symmetrical-TC2	144,355.762
	F_2	1st	**Symmetrical-DWC**	**170,791.224**
		2nd	Symmetrical-TC3	172,106.681
		3rd	Direct-TC	175,504.430
	F_3	1st	**Symmetrical-TE2**	**196,042.597**
		2nd	Symmetrical-TC1	212,178.195
		3rd	Symmetrical-TE1	212,217.274
M3	F_1	1st	**Direct-DWC**	**278,968.356**
		2nd	Direct-TE	279,719.402
		3rd	Indirect-DWC	281,628.454
	F_2	1st	**Symmetrical-TE2**	**326,486.558**
		2nd	Direct-DWC	329,243.256
		3rd	Direct-TE	329,686.667
	F_3	1st	**Indirect-DWC**	**463,035.983**
		2nd	Symmetrical-TE2	469,954.929
		3rd	Indirect-TE	472,286.012

NOMENCLATURE

Symbols
Φ : all possible states for sub-mixtures
φ : all possible states for product type
S : side stream
I : top product

II   : bottom product
III   : eliminated mixture in crossover complete sequences

Superscripts

λ : sign of moving section or omitting section in related distillation columns
a, b   : presenting suspended components in each stream

Subscripts

ψ : sign of thermal coupling of the product in related distillation columns
r, k   : presenting components in each stream

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