Design and Optimization of Thermally Coupled Distillation Schemes for the Separations of Multi-Component Mixtures

5 AUTHORS, INCLUDING:

Juan Gabriel Segovia-Hernandez
Universidad de Guanajuato
142 PUBLICATIONS **1,038** CITATIONS

Design and Optimization of Thermally Coupled Distillation Schemes for the Separation of Multicomponent Mixtures

Christopher Jorge Calzon-McConville,[†] **Ma. Bibiana Rosales-Zamora,**[†]
Juan Gabriel Segovia-Hernández,[†] **Salvador Hernández,**[*,†] **and Vicente Rico-Ramírez**[‡]

Facultad de Química, Universidad de Guanajuato, Noria Alta s/n, Guanajuato, Gto., 36050, México, and Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Avenida Tecnológico y García Cubas s/n, Celaya, Gto., 38010, México

The design of thermally coupled distillation sequences for the separation of multicomponent mixtures is complex because of the greater number of degrees of freedom in comparison to distillation sequences based on conventional columns. The energy-efficient design procedure for thermally coupled distillation sequences for the separation of ternary and quaternary mixtures is extended to the separation of five or more component mixtures [Blancarte-Palacios, J. L.; Bautista-Valdés, M. N.; Hernández, S.; Rico-Ramírez, V.; Jiménez, A. Energy-Efficient Designs of Thermally Coupled Distillation Sequences for Four-Component Mixture. *Ind. Eng. Chem. Res.* **2003**, *42*, 5157]. The schemes analyzed (five fully thermally coupled sequences and two partially thermally coupled sequences) include side rectifiers, side strippers, or both types of side columns. The procedure uses initial designs for thermally coupled distillation sequences obtained from the distribution of tray sections of conventional distillation sequences and then optimized for energy consumption using the interconnecting flows as search variables. The methodology provides a robust tool for the design of multicomponent thermally coupled distillation schemes. The proposed design strategy results in thermally coupled sequences that not only achieve the specified separation but also require lower energy consumptions and better thermodynamic efficiencies than conventional distillation schemes.

1. Introduction

Distillation is the most widespread separation method in industry, but it is highly inefficient in the use of energy. For decades, the purpose of some research groups has been to develop tools for the design of separation schemes as simple and profitable as possible. Several strategies have been adopted to improve the energy performance of distillation systems. Nonconventional distillation sequences involve the use of thermal couplings in which heat transfer is accomplished by direct contact of material flows between the columns of the system. In the case of ternary mixtures, these thermally coupled arrangements include the side stripper, the side rectifier, and the fully thermally (Petlyuk scheme) coupled column, among others. As examples, the side stripper has been widely used in the processing of crude oil[1] and the side rectifier has been used in the cryogenic separation of air into oxygen, nitrogen, and argon.[2] Recently, the Petlyuk column has gained acceptance in the process industries[3] because it can be implemented through the use of a divided-wall distillation column. There is a considerable amount of literature on the analysis of the relative advantages of the thermally coupled distillation schemes (TCDS) for ternary separations.[4−8] In these studies, it has been reported that thermally coupled configurations are capable of achieving energy savings of up to 30% in contrast to the conventional direct and indirect distillation sequences for the separation of feeds with low or high content of the intermediate component, and that the energy savings depend on the amount of the intermediate component. When the energy savings of integrated schemes are calculated, it has been found that the Petlyuk system offers better savings than the systems with side columns. These

results have promoted the development of design methods for integrated systems.[9−11]

There are few works on extensions toward the design of integrated systems for mixtures of more than three components.[12−14] The lack of design strategies is due to the combinatorial problem of the possible configurations for multicomponent mixtures and the lack of experience and knowledge on the separation of four or more components by using thermally coupled schemes.[15] Optimal synthesis and design of multicomponent distillation processes are usually performed in a search space that excludes the considerations of complex thermally coupled distillation schemes. Recently, a shortcut design procedure has been reported for the design of multicomponent thermally coupled distillation columns.[16] Also, effective computational strategies based on disjunctive programming and proper thermodynamic initialization are emerging. An optimal synthesis of complex distillation columns using rigorous models has been reported;[17] the synthesis involves several mathematical programming approaches including NLP, MINLP, and generalized disjunctive programming models.

In this work, we present an energy-efficient design procedure for thermally coupled distillation sequences for the separation of five-component mixtures. Although several arrangements can be conceptually obtained for five-component mixtures,[18] we have focused our attention on seven schemes: five fully thermally coupled sequences (Figures 1−5) and two partially thermally coupled sequences (Figures 6 and 7). Such sequences were selected because of their potential for energy savings and for industrial implementation. In general, the most used thermally coupled column is the Petlyuk column, which can be implemented through the dividing-wall column proposed by Kaibel and Schoenmakers.[19] This thermally coupled distillation column can offer savings in both capital and energy consumption. Also, for the case of the separation of three or more component mixtures, Halvorsen and Skogestad[20−23] have used

* To whom correspondence should be addressed. E-mail: hernasa@quijote.ugto.mx.
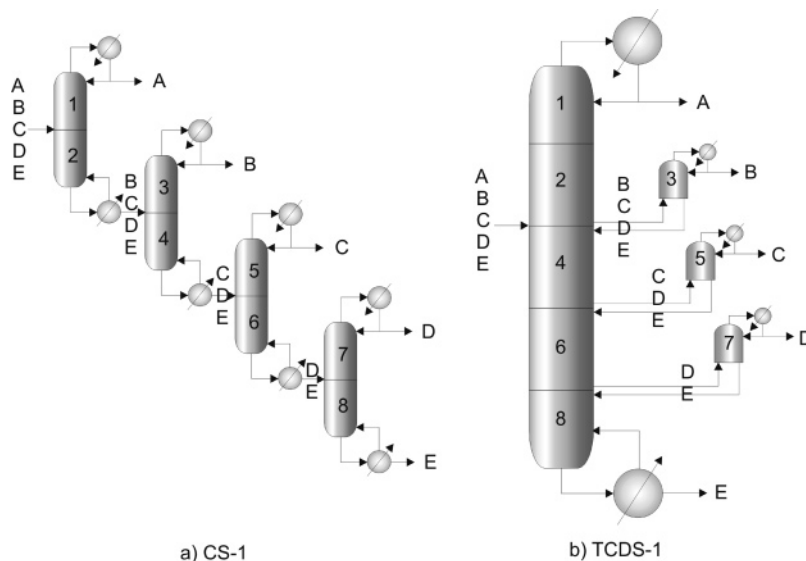† Universidad de Guanajuato.
‡ Instituto Tecnológico de Celaya.

Figure 1. Preliminary design of the fully thermally coupled sequence (TCDS-1) from a conventional distillation sequence.
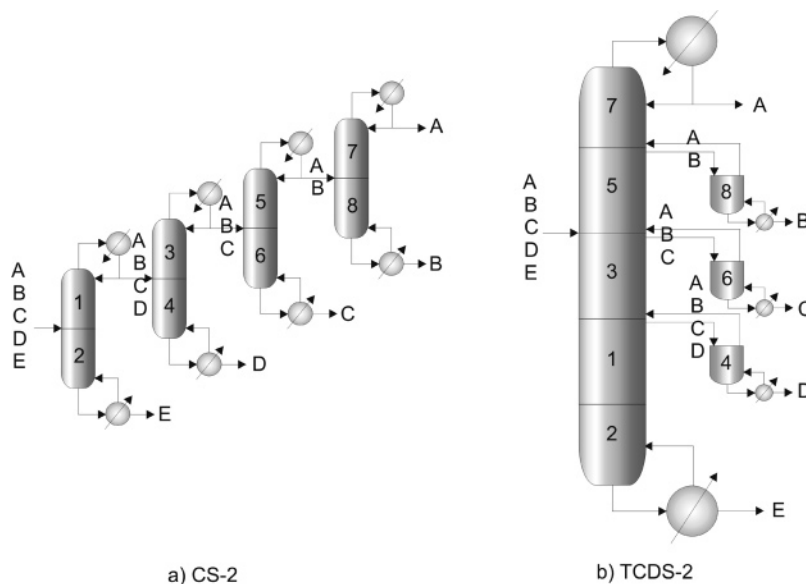

Figure 2. Preliminary design of the fully thermally coupled sequence (TCDS-2) from a conventional distillation sequence.

diagrams of the minimum vapor generated in the reboiler to achieve the separation at minimum reflux conditions and have found that Petlyuk-type schemes present the largest energy savings (around 40%). The Petlyuk-type option can reduce both energy and capital costs. Also, BASF has reported that most of the thermally coupled distillation schemes implemented in the new developments are Petlyuk-type column.

Finally, an analysis on thermodynamic efficiency (η) is included, since one could be reducing energy consumption only to use more expensive energy. Some works have reported that not all thermally coupled distillation schemes can have better thermodynamic efficiencies than the corresponding thermally coupled distillation sequences.[24] Also, some other options such as diabatic distillation columns can be attractive alternatives for reducing the energy consumption and improving the thermodynamic efficiency.[25,26]

2. Development of the Design and Optimization Strategies

It is well-known that the design of the thermally coupled distillation sequences can be modeled through superstructures suitable for optimization procedures with mathematical programming techniques. However, the task is complicated and is likely to fail due to numerical issues. Two efforts for the optimal design of TCDS schemes for separation of ternary mixtures in the area of mathematical programming are the work of Dünnebier and Pantelides[27] and the research of Caballero and Grossmann.[28] For a multicomponent mixture, the problem is clearly more complicated as the combinatorial nature of the system results in a superstructure that it is significantly more complex to solve.

In this work, to overcome the complexity of the simultaneous solution of the tray arrangement and energy consumption within a formal optimization algorithm, we have decoupled the design problem in two stages: (1) tray configuration; (2) energy-efficient design (optimal energy consumption).

In the first stage, our approach begins with the development of preliminary designs for the complex systems based on the designs of the conventional distillation sequences (see Figures 1−7). For the conventional sequences, it is assumed that each column performs its respective split (i.e., the separation of the light and heavy key components) with molar recoveries of 98%
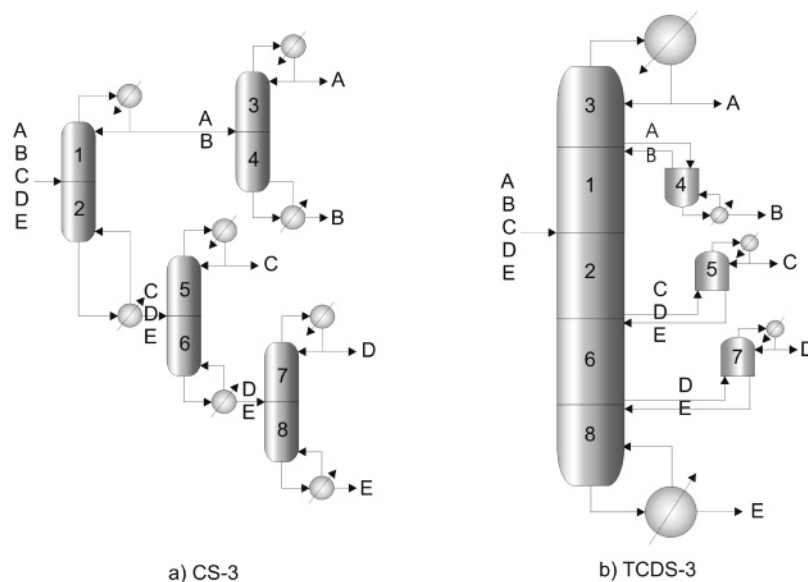
a) CS-3   b) TCDS-3

Figure 3. Preliminary design of the fully thermally coupled sequence (TCDS-3) from a conventional distillation sequence.

a) CS-4   b) TCDS-4

Figure 4. Preliminary design of the fully thermally coupled sequence (TCDS-4) from a conventional distillation sequence.

a) CS-5   b) TCDS-5

Figure 5. Preliminary design of the fully thermally coupled sequence (TCDS-5) from a conventional distillation sequence.

respectively. Then, by use of the shortcut method of Fenske–Underwood–Gilliland, the tray structures of conventional distillation schemes are obtained. As an initial heuristic, the number of the trays in each conventional distillation column is obtained by considering a reflux ratio of 1.33 times the minimum reflux ratio.
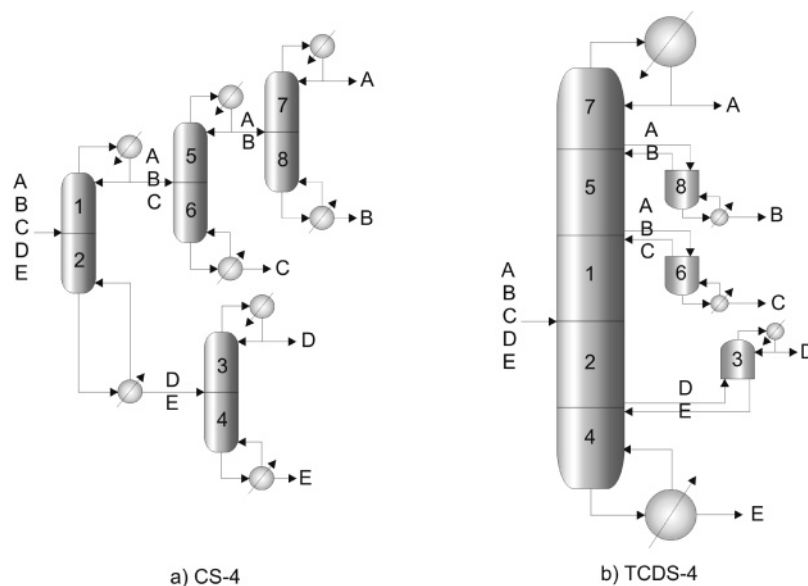
Figure 6. Preliminary design of the partially thermally coupled sequence (TCDS-6) from a conventional distillation sequence.

Figure 7. Preliminary design of the partially thermally coupled sequence (TCDS-7) from a conventional distillation sequence.
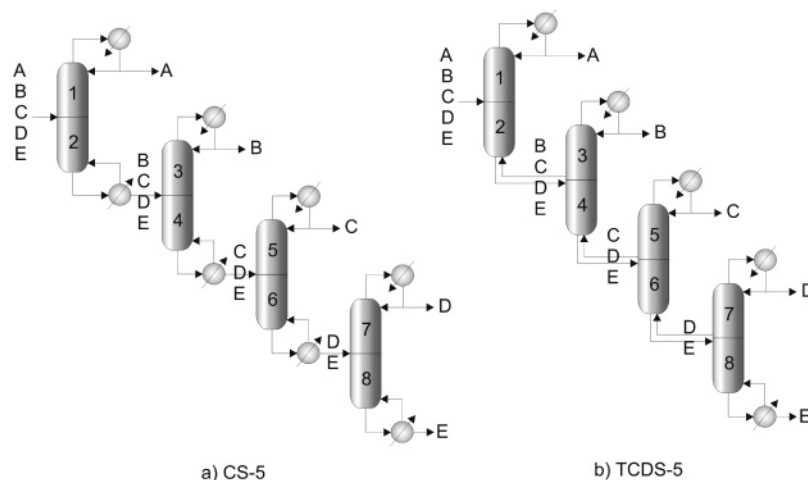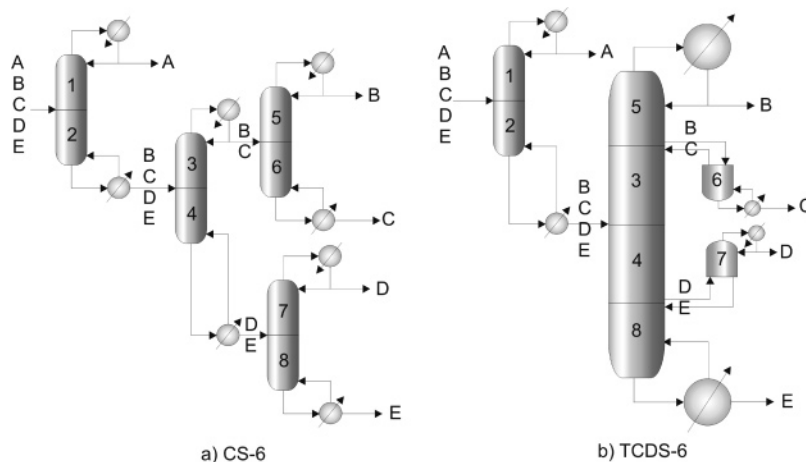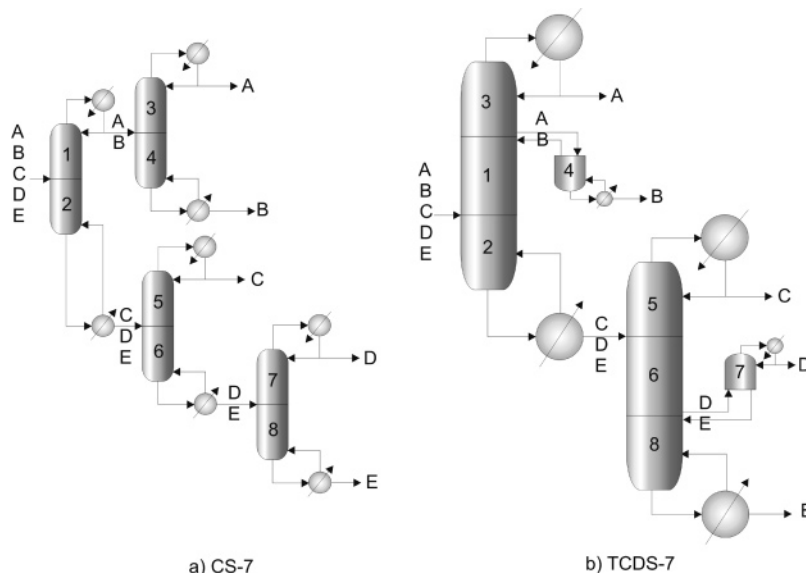
The conventional distillation sequences (Figures 1a–7a) show eight different tray sections. These sections are used as a basis for the arrangement of the tray structure of the coupled schemes through a section analogy procedure. For instance, in the main column of the integrated sequence of Figure 1b, the total number of trays is obtained by conceptually moving the stripper sections (sections 4, 6, and 8 from Figure 1a) from the second, third, and fourth columns of the conventional sequence to the bottom of the first column. The reboilers of the first, second, and third columns are replaced by vapor–liquid interconnections with side rectifiers. The number of trays in the side rectifiers of the complex scheme is equal to the number of trays in the rectifier section in the second, third, and fourth columns of the conventional arrangement, respectively (sections 3, 5, and 7 from Figure 1a). A similar procedure is applied to obtain the other thermally coupled schemes. See Figures 1–7.

After the tray arrangements for the integrated designs have been obtained, an optimization procedure is used to minimize the heat duty supplied to the reboilers of each coupled scheme, taking into account the constraints imposed by the required purities of the five product streams. Although the number of trays is not formally optimized, a parametric analysis is carried out to test different tray arrangements by changing the recoveries of the key components. The resulting sections serve as a basis for the tray arrangements of the complex scheme; such a

procedure allows the comparison of different designs to detect the design with superior performance in terms of energy consumption. In practice, the procedure is limited by the number of tray arrangements that the designer decides to consider.

The remaining degrees of freedom after design specifications and tray arrangement are used to obtain the proper values of the interconnecting vapor streams which provide minimum energy consumption. Three or two degrees of freedom (depending on the number of thermal links; see Figures 1–7) remain for each integrated sequence. Our selections for these degrees of freedom are the interconnecting flows (vapor or liquid, depending of the scheme). The search procedure provides the optimal values of the interconnecting flows to minimize the energy consumption for the separation. The design is successful if it meets the product specifications. The optimization procedure is described in Figure 8.

The optimization strategy can then be summarized as follows: (a) A base design for the complex schemes is obtained. (b) A value for each interconnecting flow (vapor or liquid) is assumed. (c) A rigorous model, based on the MESH equations, is used for the simulation of the coupled schemes with the proposed tray arrangement. In this work, the process simulator Aspen Plus 11.1 is used for this purpose. If the product compositions are obtained, then the design is kept; otherwise, proper adjustments must be made. (d) The value of intercon-
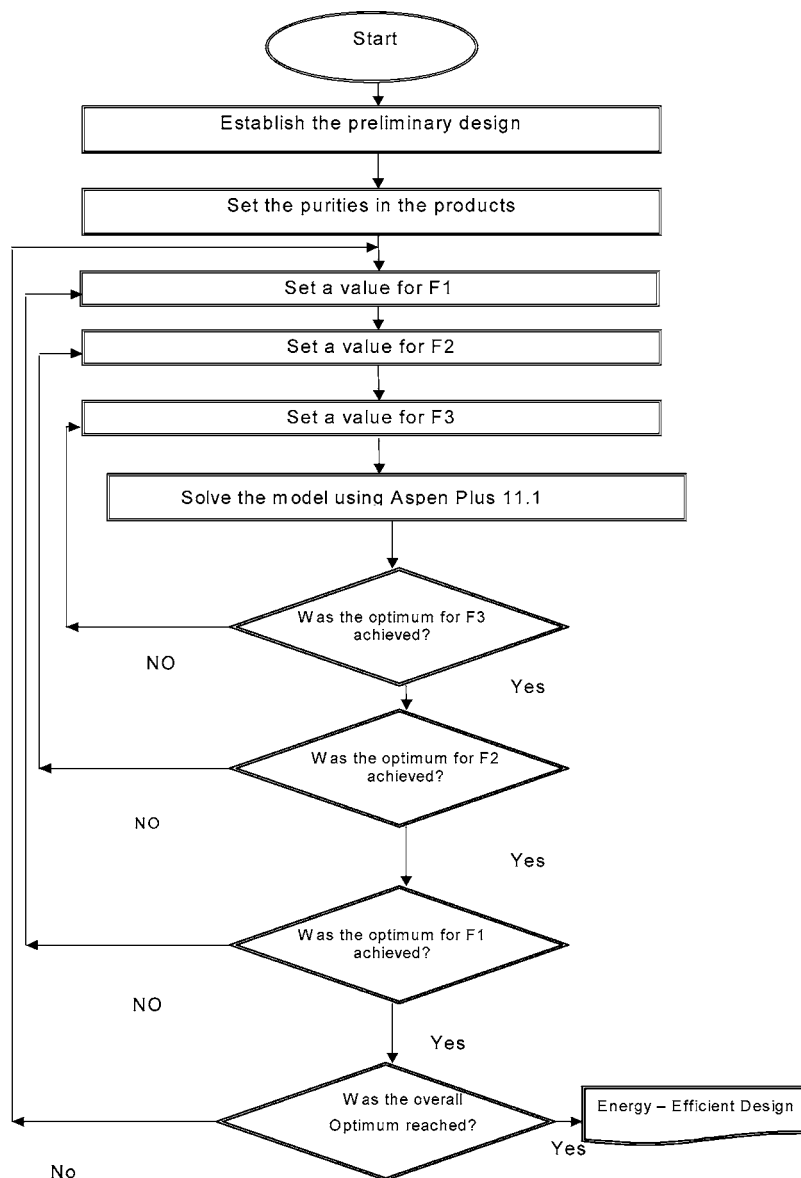
Figure 8. Optimization strategy.

necting flow (F3) is changed and the algorithm goes back to step c until a local minimum in energy consumption is determined for the assumed values of the other interconnecting flows (F1 and F2). A similar procedure is used for F2 and F1. (e) The value of F2 is modified (F1 is kept constant), going back to step c until the energy consumption is minimum. (f) The value of F1 is modified, going back to step c until the minimum energy consumption supplied to the reboilers is obtained. When the procedure ends, an optimum value has been detected for the design of the complex schemes. This methodology is valid for the optimization of the thermally coupled distillation schemes involving three interconnecting streams (Figures 1−5). Still, the algorithm can also be used when two interconnecting streams are presented (Figures 6 and 7).

3. Case Study

The analysis presented in this work is based on the separations of two different five-component mixtures. The components of the mixtures considered are n-butane, n-pentane, n-hexane, n-heptane, and n-hexane for mixture 1, and n-butane, isopentane, n-pentane, n-hexane, and n-heptane for mixture 2. Two molar compositions F1 (A = 0.35, B = 0.1, C = 0.1, D = 0.1, E =

0.35) and F2 (A = 0.125, B = 0.25, C = 0.25, D = 0.25, E = 0.125) for each mixture are analyzed. Molar recoveries of 98, 94, 94, 94, and 97 are assumed for each component in the products. A feed flow rate of 45.5 kmol/h as saturated liquid is used. The operational pressure for each column is chosen to guarantee the use of cooling water in the condensers. The pressure drop for a single tray is given based on the heuristics of Kister.[28]

4. Results

The resulting designs and their performances with respect to energy consumption and thermodynamic efficiency are discussed in the following sections.

4.1. Sequences with Three Thermal Couplings (Fully Thermally Coupled). The design and energy optimization of fully thermally coupled sequences for each feed mixture were carried out. Typical optimization surfaces for the TCDS-1, mixture 1 and feed F1, are shown in Figure 9, where the combination of interconnecting flow rates that provides the minimum energy consumption was determined. The tray arrangements and some important design variables for that sequence after the optimization task are given in Table 1. The
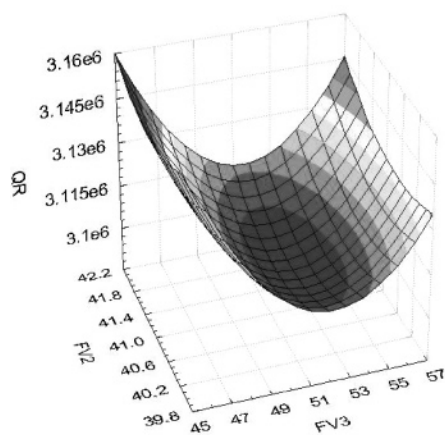
a) FV1=13.65 kmol/h. Total reboiler heat duty = 905.4 kW.
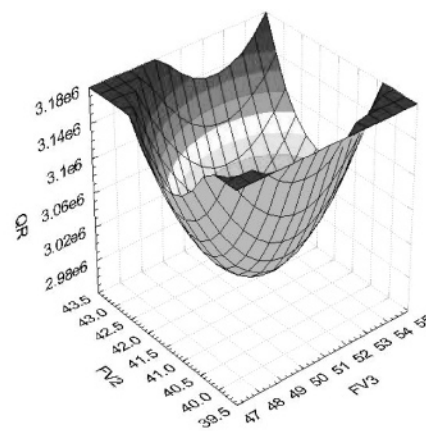
b) FV1=15 kmol/h. Total reboiler heat duty = 867 kW.
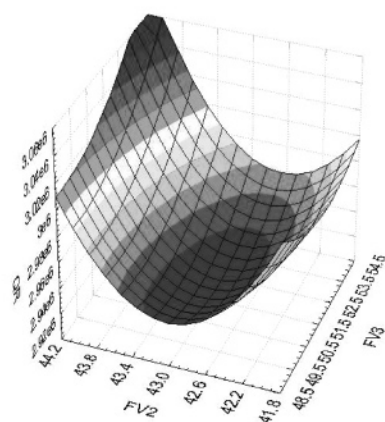
c) FV1=15.5 kmol/h. Total reboiler heat duty = 841.1 kW (optimum).

d) FV1=16.8 kmol/h. Total reboiler heat duty = 853.5 kW.

Figure 9. Search for the energy-efficient design of the TCDS-1, mixture 1, composition F1.

Table 1. Design Variables for the TCDS-1, Mixture 1, Feed F1

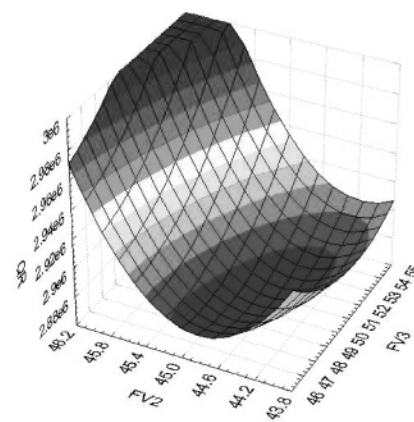| column	variables
main column	stages = 41
	feed stage = 9
	reflux ratio = 1.72
	FV1 = 15.5 kmol/h
	FV2 = 43.2 kmol/h
	FV3 = 51.5 kmol/h
	pressure = 4.52 atm
side rectifier 1	stages = 10
(where component B is purified)	
	distillate flow rate = 4.47 kmol/h
side rectifier 2	stages = 11
(where component C is purified)	
	distillate flow rate = 4.41 kmol/h
side rectifier 3	stages = 11
(where component D is purified)	
	distillate flow rate = 4.39 kmol/h

Table 2. Optimum Energy Requirements (kW) and Thermodynamic Efficiencies for Fully Thermally Coupled Sequences, Mixture 1

feed	sequence	total reboiler duty (kW)	η (%)
F1	CS-1	1090.2	15.65
	TCDS-1	841.1	26.67
	CS-2	1181.5	20.60
	TCDS-2	793.7	29.67
	CS-3	1062.8	17.8
	TCDS-3	931.6	24.9
	CS-4	1168.0	18.0
	TCDS-4	708.0	33.5
	CS-5	1092.2	15.65
	TCDS-5	841	26.67
F2	CS-1	2032.8	5.47
	TCDS-1	1246.7	14.40
	CS-2	2039.5	11.62
	TCDS-2	1471.8	12.61
	CS-3	1213.5	15.4
	TCDS-3	1123.0	16.9
	CS-4	1332.5	16.8
	TCDS-4	960.5	19.4
	CS-5	2032.8	5.47
	TCDS-5	1246.6	14.40

results obtained for energy consumption and thermodynamic efficiency (computed through standard expressions as explained in Seader and Henley;[29] see the Appendix) for the five fully thermally coupled sequences for each case study are summarized in Tables 2 and 3. In general, the TCDS presented energy savings in the range between 10 and 38% in contrast to conventional distillation sequences (Table 4). It can be noted that the energy requirements are lower for feed F1 than for feed F2 for each TCDS analyzed (Tables 2 and 3). Similar behavior is shown for the thermodynamic efficiencies: they are higher in feed F1 than in feed F2. For most of the cases studied here, the second-law efficiency of the TCDS is higher than that of the corresponding conventional distillation option. The inefficiency of conventional sequences has been reported as a consequence of remixing.[30,31] Therefore, proper optimization of fully thermally coupled sequences should avoid such a

Table 3. Optimum Energy Requirements (kW) and Thermodynamic Efficiencies for Fully Thermally Coupled Sequences, Mixture 2

feed	sequence	total reboiler duty (kW)	η (%)
F1	CS-1	1363.5	26.84
	TCDS-1	1027.2	23.70
	CS-2	2921.2	6.62
	TCDS-2	2185.8	9.29
	CS-3	1070.8	16.7
	TCDS-3	837.1	23.8
	CS-4	1196.6	17.4
	TCDS-4	827.41	27.7
	CS-1	1363.5	26.84
	TCDS-1	1027.3	23.70
F2	CS-1	2390.3	9.76
	TCDS-1	1560.7	13.02
	CS-2	3998.6	4.14
	TCDS-2	2964.1	5.71
	CS-3	1551.6	13.1
	TCDS-3	1428.7	11.5
	CS-4	1652.1	14.9
	TCDS-4	1514.7	13.3
	CS-1	2390.3	9.76
	TCDS-1	1560.6	13.02

Table 4. Energy Savings of the Fully Thermally Coupled Sequences in Comparison with Their Corresponding Conventional Distillation Sequences

mixture	feed	sequence	% of energy savings[a]
mixture 1	F1	TCDS-1	22.8
		TCDS-2	32.8
		TCDS-3	12.3
		TCDS-4	39.4
		TCDS-5	22.8
mixture 1	F2	TCDS-1	38.7
		TCDS-2	27.8
		TCDS-3	7.5
		TCDS-4	27.9
		TCDS-5	38.7
mixture 2	F1	TCDS-1	24.6
		TCDS-2	25.2
		TCDS-3	21.8
		TCDS-4	30.8
		TCDS-5	24.6
mixture 2	F2	TCDS-1	34.7
		TCDS-2	25.9
		TCDS-3	7.9
		TCDS-4	8.3
		TCDS-5	34.7

[a] In comparison with its conventional sequence.

remixing problem. The methodology proposed generates designs where the effect of the remixing is eliminated. Three trends for fully thermally coupled sequences were obtained: (1) fully thermally coupled sequences always required less energy consumption to achieve the separation for both feed compositions considered; (2) energy savings were higher in the feed composition with low content of the intermediate components; (3) the second-law efficiencies calculated show that the introduction of optimized thermal links increased the thermodynamic efficiency. In general, the results show that the optimization of these thermal links causes significant energy savings and improves the values of second-law efficiencies.

Figure 9 displays the response surfaces for the optimization of the TCDS-1 option. The response surfaces show an interesting effect of the search variables. The design is sensitive, in terms of its energy consumption, to changes in the interconnecting flow rates (Figure 9b). On the other hand, there are combinations of interconnecting flow rates in which the energy consumption does not vary significantly (Figure 9c−d). An implication of this observation has to do with operational considerations. In some regions of interconnecting flow rates, minor changes in the operating conditions of the thermally coupled schemes can

Table 5. Optimum Energy Requirements (kW) and Thermodynamic Efficiencies for Partially Thermally Coupled Sequences, Mixture 1

feed	sequence	total reboiler duty (kW)	η (%)
F1	CS-6	1446.4	12.95
	TCDS-6	1157.7	25.80
	CS-7	1484.2	15.80
	TCDS-7	1096.5	22.21
F2	CS-6	1222.5	15.59
	TCDS-6	960	17.74
	CS-7	1482.7	9.29
	TCDS-7	1241.	15.62

Table 6. Energy Savings of the Partially Thermally Coupled Sequences in Comparison with Their Corresponding Conventional Distillation Sequences, Mixture 1

feed	sequence	% of energy savings[a]
F1	TCDS-6	19.95
	TCDS-7	26.11
F2	TCDS-6	21.47
	TCDS-7	16.3

[a] In comparison with its conventional sequence.

lead to a significant deterioration of its energy consumption. The control design of this system appears to be an important task to develop. In all cases analyzed, the results show that, in the optimal region of interconnection flow rates, the design is not very sensitive, in terms of its energy consumption, to changes in the interconnecting flow (Figure 9c).

One detail is worth highlighting: the TCDS-1 and TCDS-5 are thermodynamically equivalent schemes. A simple column has two sections, the rectifying and stripping sections. Based on the function of each of the column sections in a complex distillation scheme (i.e., either rectifying sections or stripping sections), a complex scheme can be converted into a sequence in which each unit has only one rectifying column section and one stripping column section. Then the connections of the units are determined according to the interconnections of their streams. Thus, for the TCDS-1 scheme, TCDS-5 could be obtained. That converted sequence[6] is a thermodynamically equivalent scheme of the corresponding TCDS-1. In this work, we show that both sequences have similar energy consumption and second-law efficiencies, therefore verifying their thermodynamic equivalence (Tables 2 and 3).

4.2. Sequences Partially Thermally Coupled. For the case of sequences partially thermally coupled (structures with reduction in thermal couplings), the results are presented in Tables 5 and 6. In Figure 10, the search for the optimal interconnection flow rate for TCDS-6 (mixture 1, composition F1) is shown. In all cases, TCDS-6 and TCDS-7 schemes show heat loads much lower than conventional sequences. The thermodynamic efficiency in the complex systems is higher in comparison to that of conventional arrangements. Similarly to fully thermally coupled schemes, the structures with a reduction in thermal couplings presented energy savings in the range between 15 and 25% in contrast to conventional distillation sequences (Table 6). When the optimization surface (Figure 10) for TCDS-6 sequence is analyzed, the shape of the response surface suggests a lower sensitivity of energy consumption to changes in operating conditions.

A remark on partially thermally coupled structures can be established. As expected, the schemes with a reduction in thermal couplings have total reboiler duty lower in comparison to conventional arrangements. However, for fully thermally coupled schemes, the energy savings were above those obtained for partially thermally coupled structures. The results show that the reduction in the number of interconnection streams increases
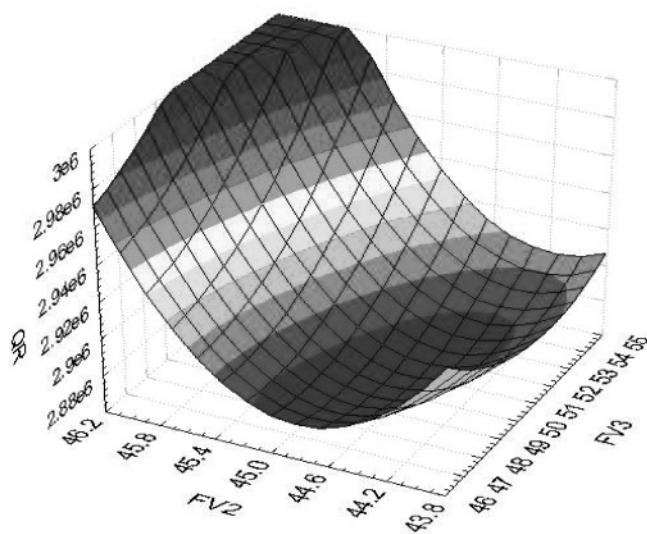
Figure 10. Minimum energy consumption for the TCDS-6, mixture 1, composition F1.

the total energy demand in the reboilers of complex schemes, for the same separation. This is an interesting situation because some authors[32,33] have claimed that the reduction of interconnection flows in complex arrangements might provide better operating properties. As a result, we would expect that the controllability properties could be improved at expenses of higher energy consumptions. This observation opens the field for the development of research of the effect of the number of thermal links in the control properties of TCDS systems.

5. Conclusions

The design and optimization of thermally coupled distillation sequences (fully or partially coupled) for the separation of five-component mixtures were studied. A general energy-efficient design procedure is developed for any type of the thermally coupled scheme. The method is based on a section analogy procedure with respect to the characteristics of a conventional distillation sequence. The methodology provides a robust tool for the design of multicomponent thermally coupled distillation schemes. The examples have shown that the design procedure can provide all of the operating parameters needed. Some trends were observed: (i) TCDS presented energy savings between 20 and 30% in contrast to the conventional schemes. (ii) Regarding thermodynamic efficiency, in all cases, the introduction of thermal links increased its value. (iii) The possibilities for the use of five-component thermally coupled distillation arrangements depend on the characteristics of the mixtures and the distribution of the feed compositions (amount of intermediate components). (iv) The reduction in the number of thermal links increases the total energy demand in the reboilers of complex schemes. (v) The optimization surfaces obtained for each design seem to indicate that the designs are sensitive, in terms of energy consumption, to changes in the interconnecting flow rates so that these structures are suitable candidates for analysis of their dynamic properties.

Appendix

With the optimized designs of the TCDS schemes, the thermodynamic efficiencies can be computed using the laws of thermodynamics. We used for this task the equations reported in the textbook by Seader and Henley.[29] The equations are as follows:

first law of thermodynamics

$$\sum_{\text{out of system}} (nh + Q + W_\text{s}) - \sum_{\text{into system}} (nh + Q + W_\text{s}) = 0 \quad (1)$$

second law of thermodynamics

$$\sum_{\text{out of system}} (ns + Q/T_\text{s}) - \sum_{\text{into system}} (ns + Q/T_\text{s}) = \Delta S_\text{irr} \quad (2)$$

exergy balance

$$\sum_{\text{into system}} \left[nb + Q\left(1 - \frac{T_0}{T_\text{s}}\right) + W_\text{s} \right] - $$
$$\sum_{\text{out of system}} \left[nb + Q\left(1 - \frac{T_0}{T_\text{s}}\right) + W_\text{s} \right] = \text{LW} \quad (3)$$

minimum work of separation

$$W_\text{min} = \sum_{\text{out of system}} nb - \sum_{\text{into system}} nb \quad (4)$$

second-law efficiency

$$\eta = \frac{W_\text{min}}{\text{LW} + W_\text{min}} \quad (5)$$

where $b = h - T_0 s$ is the exergy function, $\text{LW} = T_0 \Delta S_\text{irr}$ is the lost work in the system, and η is the thermodynamic efficiency. The thermodynamic properties such as enthalpies and entropies of the streams of the distillation sequences were evaluated through the use of the simulator of processes Aspen Plus 11.1.

Nomenclature

h = molar enthalpy
n = mole flow
Q = heat
s = molar entropy
T_0 = temperature of the surroundings
T_s = temperature of the system
W_min = minimum work for separation
W_s = shaft work
η = second-law efficiency

Literature Cited

(1) Watkins, R. N. *Petroleum Refinery Distillation*, 2nd ed.; Gulf Publishing: Houston, TX, 1979.

(2) Seidel, M. German Patent 610503, 1935.

(3) Hairston, D. The Divide in Distillation. *Chem Eng.* **1999**, April, 32.

(4) Tedder, D.; Rudd, D. Parametric Studies in Industrial Distillation: Part I. Design Comparisons. *AIChE J.* **1978**, *24*, 303.

(5) Glinos, K.; Malone, M. F. Optimality Regions for Complex Column Alternatives in Distillation Systems. *Chem. Eng. Res. Des.* **1988**, *66*, 229.

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

(7) Yeomans, H.; Grossmann, I. Optimal Design of Complex Distillation Columns Using Rigorous Tray-by-Tray Disjunctive Programming Models. *Ind. Eng. Chem. Res.* **2000**, *39* (11), 4326.

(8) Rév, E.; Emtir, M.; Szitkai, Z.; Mizsey, P.; Fonyó, Z. Energy Savings of Integrated and Coupled Distillation Systems. *Comput. Chem. Eng.* **2001**, *25*, 119.

(9) Hernández, S.; Jiménez, A. Design of Energy-Efficient Petlyuk Systems. *Comput. Chem. Eng.* **1999**, *23* (8), 1005.

(10) Amminudin, K. A.; Smith, R.; Thong, D. Y.-C.; Towler, G. P. Design and Optimization of Fully Thermally Coupled Distillation Columns. Part I: Preliminary Design and Optimization Methodology. *Trans. Inst. Chem. Eng.* **2001**, *79*, 701.

(11) Muralikrishna, K.; Madhavan, K. P.; Shah, S. S. Development of Dividing Wall Distillation Column Design Space for a Specified Separation. *Trans. Inst. Chem. Eng.* **2002**, *80*, 155.

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

(13) Chrsitiansen, A.; Skogestad. S.; Lien, K. Complex Distillation Arrangements: Extending the Petlyuk Ideas. *Comput. Chem. Eng.* **1997**, *21*, S237.

(14) Blancarte-Palacios, J. L.; Bautista-Valdés, M. N.; Hernández, S.; Rico-Ramírez, V.; Jiménez, A. Energy-Efficient Designs of Thermally Coupled Distillation Sequences for Four-Component Mixture. *Ind. Eng. Chem. Res.* **2003**, *42*, 5157.

(15) Rong, B. G.; Kraslawski, A.; Nystrom, L. The Synthesis of Thermally Coupled Distillation Flowsheets for Separations of Five-Component Mixtures. *Comput. Chem. Eng.* **2000**, *24*, 247.

(16) Rong, B. G.; Kraslawski, A.; Nystrom, L. Design and Synthesis of Multicomponent Thermally Coupled Distillation Flowsheets. *Comput. Chem. Eng.* **2001**, *25*, 807.

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

(18) Rong, B. G.; Kraslawski, A. Partially Thermally Coupled Distillation Systems for Multicomponent Separations. *Ind. Eng. Chem. Res.* **2003**, *42* (6), 1204.

(19) Kaibel, G.; Schoenmarkers, H. Process Synthesis and Design in Industrial Practice. *Proceedings of ESCAPE-12*; Grievink, J., Schijndel, J. V., Eds.; Computer Aided Process Engineering 10; Elsevier: Amsterdam, 2002; p 9.

(20) Halvorsen, I. J.; Skogestad, S. Minimum Energy Consumption in Multicomponent Distillation. 1. V_{min} Diagram for Two-Product Column. *Ind. Eng. Chem. Res.* **2003**, *42*, 596.

(21) Halvorsen, I. J.; Skogestad, S. Minimum Energy Consumption in Multicomponent Distillation. 2. Three-Product Petlyuk Arrangements. *Ind. Eng. Chem. Res.* **2003**, *42*, 605.

(22) Halvorsen, I. J.; Skogestad, S. Minimum Energy Consumption in Multicomponent Distillation. 3. More Than Three Products and Generalized Petlyuk Arrangements. *Ind. Eng. Chem. Res.* **2003**, *42*, 616.

(23) Halvorsen, I. J.; Skogestad, S. Shortcut Analysis of Optimal Operation of Petlyuk Distillation. *Ind. Eng. Chem. Res.* **2004**, *43*, 3994.

(24) Flores, O. A.; Cárdenas, J. C.; Hernández, S.; Rico-Ramírez, V. Thermodynamic Analysis of Thermally Coupled Distillation Sequences. *Ind. Eng. Chem. Res.* **2003**, *42*, 5940.

(25) De Koeijer, G. M.; Rivero, R. Entropy Production and Exergy Loss in Experimental Distillation Columns. *Chem. Eng. Sci.* **2003**, *58*, 1587.

(26) Jiménez, E. S.; Salomon, P.; Rivero, R.; Rendon, C.; Hoffmann, K. H.; Schaller, M.; Andresen, B. Optimization of a Diabatic Distillation Column with Sequential Heat Exchangers. *Ind. Eng. Chem. Res.* **2004**, *43*, 7566.

(27) Dünnebier, G.; Pantelides, C. Optimal Design of Thermally Coupled Distillation Columns. *Ind. Eng. Chem. Res.* **1999**, *38*, 162.

(28) Caballero, J. A.; Grosmann, I. E. Generalized Disjunctive Programming Models for the Optimal Synthesis of Thermally Linked Distillation Columns. *Ind. Eng. Chem. Res.* **2001**, *40*, 2260.

(29) Kister, H. Z. *Distillation Design*; McGraw-Hill: New York, 1992.

(30) Seader, J. D.; Henley, E. *Separation Process Principles*; John Wiley and Sons: New York, 1998.

(31) Triantafyllou, C.; Smith, R. The Design and Optimization of Fully Thermally Coupled Distillation Columns. *Trans. Inst. Chem. Eng.* **1992**, *70*, 118.

(32) Hernández, S.; Pereira-Pech, S.; Jiménez, A.; Rico-Ramírez, V. Energy Efficiency of an Indirect Thermally Coupled Distillation Sequence. *Can. J. Chem. Eng.* **2003**, *81*, 1087.

(33) Agrawal, R.; Fidkowski, Z. More Operable Arrangements of Fully Thermally Coupled Distillation Columns. *AIChE J.* **1998**, *44*, 2565.

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