

1
Synthesis of Separation Processes

Petros Proios, Michael C. Georgiadis, and Efstratios N. Pistikopoulos

1.1
Introduction

Process synthesis has received considerable attention over the last 30 years and it continues to be an active research area in chemical engineering, with significant advances achieved in terms of developing synthesis methods for subsystems (reactor networks, separation systems, heat exchange networks, and mass exchange networks) and for total flow sheets. By definition, process synthesis is the determination of the topology of process units, as well as the type and design of the units within the flow sheet that will convert specified inputs into desired products. The synthesis task is usually driven by the optimization of a specific objective, typically based on economics. Systematic techniques for the synthesis and design of flow sheets are represented by two different approaches: hierarchical decomposition and mathematical programming. Reviews on early developments can be found in Hendry et al. (1973), Westerberg (1980), and Nishida et al. (1981). An overview of synthesis techniques is also available in the book by Biegler et al. (1997) and recent advances are presented in the excellent review article by Westerberg (2004).

Early work on process synthesis appeared on developing insights into finding better separation sequences (using distillation) for separating mixtures of n components. The emphasis on investigating techniques for the synthesis of complex distillation networks can be mainly attributed to the role that distillation plays in the economy of the overall plant. Distillation is a highly utilized and at the same time one of the most energy intensive unit operations in the chemical process industry. Mix indicated in 1978 that distillation accounted for about 3% of the total US energy consumption and that a 10% savings in distillation energy could amount to a savings of about $500 million in national energy costs (Mix et al. 1978). Today, the expense of distillation-related energy consumption has reached even higher levels, considering the expansion of the use of distillation in industry and the higher cost of utilities. These economic reasons have imposed energy efficiency as the main design target in distillation.

Computer Aided Process and Product Engineering. Edited by Luis Puigjaner and Georges Heyen

ISBN: 3-527-30804-0

Due to its importance, distillation has received particular attention in the field of chemical engineering, with publications about the operation and design of countercurrent separation cascades dating as early as 1889 (Sorel 1889). Moreover, since multicomponent separations require the use of sequences of distillation columns, significant research efforts have concentrated on the synthesis of these systems aiming at energy efficiency. Research on this subject has been further powered by the fact that extensive energy savings can be achieved through the selection of the most energy efficient sequence, amongst a large number of available candidates. This is an explicit consequence of the dependence of the distillation systems' energy consumption on the feed mixture and on the order in which its components are separated.

Technological breakthroughs are constantly called in to propose new techniques for energy efficiency that would compensate for the ever increasing energy-related distillation expenses. Two of the most promising techniques are heat integration and the thermal coupling of distillation columns. The former is based on the energy savings that can be achieved by heat integrating two distillation columns, that is, by using the heat generated in a column's condenser for the heat required in another column's reboiler, while satisfying appropriate temperature difference conditions. This technique can lead to substantial energy savings that can reach the order of 50% when compared to nonheat-integrated arrangements. Similar energy savings have been reported through the use of thermal coupling techniques in distillation, where heat units and their associated utilities are eliminated through the use of two-way liquid and vapor interconnections between columns, the latter being characterized as complex columns. These energy savings are the direct result of the elimination of heat units and the increase of thermodynamic efficiency, due to the minimization of remixing effects, which are generally associated with nonthermally-coupled arrangements.

However, in order to apply the aforementioned synthesis techniques for energy efficiency, certain complicating issues need to be addressed, which are mainly of structural and physical nature. The structural complications are related to the large number of alternative arrangements that need to be considered. Even in the simplest case from a structural perspective, where sequences of simple columns are examined (columns with a single feed and two products), the extensive connectivity possibilities between columns lead to the generation of a large number of alternative column sequences, which increase with the number of components to be separated. Moreover, these structural complications become even more intense through the incorporation of structural possibilities associated with heat integration and thermal coupling.

The physical complications are related to the complexity of the underlying physical phenomena, which involve simultaneous mass and heat exchange between liquid and vapor streams at the tray cascades. Furthermore, the physics of the problem are such that the choice of the optimal configuration is largely dependent on the feed mixture to be separated (its components' relative volatilities and composition). It has been reported (Tedder and Rudd 1978; Agrawal and Fidkowski 1998) that for a particular separation, column configurations that are generally regarded as highly energy efficient (for instance, fully thermally coupled columns), can, in fact, have

larger energy consumptions than sequences of more conventional columns. Consequently, in order to evaluate efficiently the energy consumption of a particular column sequence and the energy savings that can potentially be achieved through its heat integration or thermal coupling. The aforementioned physical phenomena need to be accurately captured.

Summarizing, it is not an exaggeration to state that the economic importance and associated complications have made the distillation column sequencing problem for energy efficiency one of the most challenging synthesis problems in chemical engineering, with numerous approaches proposed for its solution. One of the earliest attempts was based on total enumeration. This approach is, however, limited to problems with only a few alternatives. Other main approaches are the heuristic and physical insight ones. The former relies on rules of thumb derived by engineering knowledge and/or by the use of shortcut models, while the latter is based on the exploitation of basic physical principles, which are also based, to a certain extent, on simplified models and on graphical representations of the problem. These approaches generally enable quick and inexpensive calculations for the alternatives' physical evaluation. However, the fact that they are derived based on simplifying assumptions, which are valid only for certain cases, places a major limitation on their accuracy, validity, and applicability. Furthermore, more complications arise when the developed heuristics are conflicting, suggest more than one possible solution, or do not cover the details of the examined problem.

The most recent approach addressing this problem is the mathematical programming (algorithmic) approach, where the synthesis of column sequences is formulated as an optimization problem. Based on mathematical programming, one of the most important systematic approaches that has been receiving increased attention over the last years is superstructure optimization. Superstructures are, in general, superset flow sheets incorporating every feasible realization of the process in question. The generation and evaluation of each alternative realization takes place with the solution of an optimization problem, which usually involves the use of continuous and binary (0-1) variables, rendering the problem a mixed-integer programming (MIP) problem. However, most of these methods either use simplifying assumptions, limiting the validity and accuracy of the results, or treat the problem rigorously, but at an expense of computational effort.

Section 1.2 will provide an overview of techniques for the synthesis of simple column sequences. The subsequent section will describe in a comprehensive way the synthesis problem of heat-integrated distillation trains. State-of-the-art methodologies and algorithmic frameworks for the synthesis of complex distillation sequencing are critically discussed in Section 1.4. Finally, concluding remarks will be made in Section 1.5.

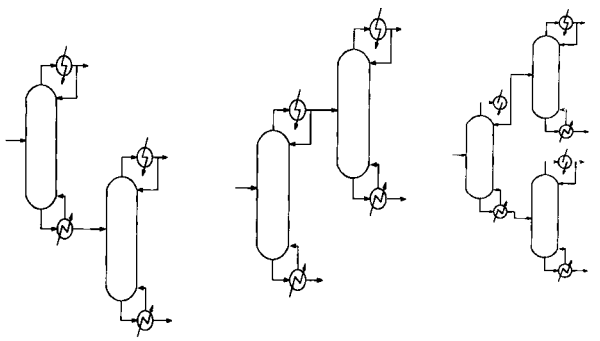
1.2
Synthesis of Simple Distillation Column Sequences

1.2.1
Simple Distillation Column Sequencing

As already mentioned, in order to separate multicomponent mixtures into pure or multicomponent product streams using distillation, more than one column needs to be employed, generating sequences of distillation columns. From chemical engineering knowledge it is known that for the same mixture separation, different distillation column sequences have different energy consumption levels, which can, in fact, be quite different from each other. Since distillation is an energy-intensive process widely used in the chemical industry, there is a substantial economic incentive in selecting the appropriate distillation column sequence for a particular separation. However, as already mentioned, two main complications make the distillation column sequencing problem one of the most challenging synthesis problems in chemical engineering, namely the increasing number of structural alternatives and the complexity of the underlying physical phenomena.

From a structural point of view, developing a method that could incorporate all the alternatives of interest, without simplifying assumptions, such as sharp splits or product streams enriched in a particular component produced once in a column sequence, is not a trivial task after the first member of multicomponent separations. For the latter only three possible simple column sequences exist (Fig. 1.1). However, an illustration of the difficulty of the problem is realized when the next problem is considered, namely the quaternary separation. For this problem, if sharp split assumptions are used, only five different structures are possible (Thompson and King 1972). However, if the simplifying assumptions are removed then 22 possible alternative sequences have been identified (as will be shown later). It must be noted that these alternatives may include more sections than the minimum number required, however, this is desirable since when general design targets are optimized, such as the total annualized cost (TAC), these structures may potentially exhibit an optimal tradeoff between operating and capital cost in their *additional* sections. Therefore, a proposed sequencing method must also be able to incorporate and generate the structural alternatives systematically and automatically.

From a physical representation point of view, the proposed method must be accompanied by a physical model that can capture the underlying phenomena accurately. Due to the complexity of the physical phenomena taking place within each distillation column, rigorous physical models are required for an accurate physical representation. However, the incorporation of rigorous models leads, by default, to the generation of nonconvex mathematical problems whose solution is quite involved and usually computationally expensive. In order to obtain easy and fast solutions, numerous methods have been proposed approximating the physical behavior of distillation columns with models based on a number of simplifying assumptions, thus trading accuracy and applicability for ease of calculation.



(a) Direct Sequence (b) Indirect Sequence (c) 3 Columns

Figure 1.1 Ternary simple column sequencing alternatives.

Finally, due to the aforementioned complexities, an efficient sequencing method must also be accompanied by an appropriate solution procedure. For the case of three or five structural alternatives, an implicit enumeration solution procedure is acceptable. However, even for the quaternary case including nonsharp separations, implicit enumeration is not the most efficient solution procedure, especially if rigorous models are used, due to the computational effort required.

Due to the aforementioned importance and associated difficulties of the simple column sequencing problem, a number of methods have been proposed over the years for its solution, based on different approaches for process synthesis. These approaches involved heuristic methods (Seader and Westerberg 1977), evolutionary techniques (Stephanopoulos and Westerberg 1976), hierarchical (Douglas 1988), implicit enumeration (Fraga and McKinon 1995) and thermodynamic insights (Bek-Pedersen 2003; Bek-Pedersen and Gani 2004), to name but a few. However, one approach that has received a lot of attention recently, is the superstructure optimization approach. In this approach a superstructure of the problem is generated that, according to Westerberg (Andrecovich and Westerberg 1985a,b), *"Should contain all feasible distillation sequences and all feasible operating conditions for any column within the superstructure."* Due to the importance of the superstructure optimization approach, particular attention will be given to the various superstructure optimization methods proposed for the synthesis of simple distillation column sequences.

1.2.2
Superstructure Methods for Simple Column Sequencing

An early systematic superstructure method for the simple column sequencing problem was proposed by Andrecovich and Westerberg (1985a,b). The proposed method addressed the separation problem of a multicomponent feed into pure product streams, generating a superstructure according to the separation tasks taking place in each column and to the column connectivities. Using the assumption of sharp splits in each distillation column, the generation of the superstructure was based on

the list splitting technique of Hendry and Hughes (1972), ranking components in decreasing order of relative volatilities. The authors proposed two algorithms for generating systematically the column sequences. The synthesis problem was formulated as an MILP, with binary variables introduced for the presence of columns and with simple models based on total mass balances and feed split fractions. This work was further extended in the work of Wehe and Westerberg (1987), for the incorporation of bypass possibilities, addressing the more general problem, namely of distillation separation of multicomponent feed streams into multicomponent product streams. Simple sharp split column models were employed, which were generally linear, except for those of the superstructure splitters, where bilinearities were introduced (due to the absence of information about the composition of the splitter feed and the actual values of the splits obtained). In order to overcome this complication, the resulting nonlinear problem for each selected structure was relaxed through linearizations, generating a lower bound to the solution. For the sequence with the best lower bound, the nonlinear problem was solved to obtain an upper bound on the global optimum. Optimal column sequences were considered those that had similar upper and lower bounds, while the ones with lower bounds above the best upper bound were discarded.

The general separation problem using superstructure optimization was also addressed by Floudas (1987). A superstructure method was developed for the sequencing of separators, without explicitly specifying the actual type of separators used. Distillation columns were also included as potential separator types. The objective was the minimization of a function related to the separation difficulty, which was calculated based on relative volatilities, for assuming distillation as the separation task. The method generated the superstructures based on the assumption of sharp (perfect) splits obtained in each separator. The number of separators in the superstructure was assumed fixed, thus eliminating the need for the introduction of binary variables. The optimal column sequences were derived by the selection of the column interconnections. In this method each separator was modeled using simple models of total and component mass balances, resulting in an NLP problem.

Floudas and Anastasiadis (1988) addressed explicitly the synthesis of simple distillation column sequences for the general multicomponent feed and product problem. Their method, as the one of Floudas (1987), generated a superstructure containing series and/or parallel arrangements of distillation columns, along with stream splitting, mixing and bypassing. In order to construct the superstructure, systematic stream mixing and splitting rules were provided, based on the assumption of sharp split separations performed in each distillation column. Simple distillation column physical models were employed based on assumptions of isothermal and isobaric columns with equal condenser and reboiler heat duties and general total and component mass balances, where the component compositions did not participate as variables but as parameters derived a priori over a number of shortcut simulations. The objective to be minimized was the system's total annualized cost (TAC), which was modeled as a function of the column feed flow rate. This was derived based on a linear approximation of the six-tenths factor rule used to scale equipment cost. The necessary coefficients for the cost functions were also based on simulations of shortcut

distillation models at different feed flow rates. The problem was posed as an MILP with binary variables denoting the existence or not of distillation columns, to be determined by the optimization along with their continuous interconnections, thus generating the optimal sequence.

In Aggarwal and Floudas (1990) the simple distillation column sequencing problem for general separations was revisited, relaxing the assumption of sharp separators. The latter were modeled based on the assumption of nondistributed nonkey components. The construction of the superstructures, and therefore the generation of the alternatives, was based on the assumption that in each column exist two adjacent (with respect to their volatility) key components, which are allowed to distribute between the column distillate and bottoms (whose recoveries were considered optimization variables). All other nonkey components were only allowed to appear in the distillate or bottoms. Based on the fact that each column performs a separation of adjacent key components, a maximum of $n-1$ columns was set up for an n component feed. Binary variables were introduced for the presence of each potential distillation column. In the structural model of the method, possibilities of mixing, splitting and bypassing were explicitly incorporated. The objective function for the optimization problem was the minimization of the system's TAC. Cost models were generated through regression analysis, based on the solution of numerous shortcut models over a range of flow rates, compositions and key component recoveries, and the problem was modeled as an MINLP. Finally, the method was extended to incorporate cases of nonadjacent key components, with intermediate components allowed to distribute between the column product streams.

The simple column sequencing problem of single feed to pure product streams was addressed in Novak et al. (1996) based on the generation of a network and a compact superstructure, which were viewed as combinations of interconnection nodes (mixers and splitters) and process units (distillation columns). The former were approximated using special linear constraints and the latter were based on the assumption of sharp splits. The compact superstructure was viewed as a simplification of the tree superstructure of Hendry and Hughes (1972) and of the network superstructure of Andrecovich and Westerberg (1985a,b) for sharp separations and was a modification of the superstructure provided by Floudas and Anastasiadis (1988), using less distillation columns. In the compact superstructure the number of columns was assumed fixed and binary variables were assigned only to the stream connectors. For an n component feed, the number of distinct sharp distillation sequences S (for all superstructure types employed) was equal to (Thompson and King 1972):

$$S = \frac{S(n-1)!}{n!(n-1)!} \tag{1}$$

The number of columns in the network and compact superstructures S^n and S^c, respectively, was found equal to:

$$S^n = \frac{n^3 - n}{6}, \quad S^n = n - 1 \tag{2}$$

The distillation columns were modeled based on the Gilliland/Fenske/Underwood method using assumptions of uniform relative volatilities per column and specifying minimum recoveries of light and heavy key components. The objective to be minimized was set as the system's TAC, employing the fixed charge model of Grossmann (1985) for the capital cost calculations. The structural (pure integer) constraints were based on the topology of the superstructure. The generated MINLP problem was solved using the modified OA/ER algorithm (Kravanja and Grossmann 1994), implemented in the computerized synthesizer PROSYN-MINLP (Kravanja and Grossmann 1993).

Smith (1996) addressed the simple column sequencing problem generating a superstructure for the structural alternatives using the state operator network (SON) representation. In this representation the separation tasks and equipment were defined while the assignment of tasks to the equipment had to be determined. Stream mixers and splitters were included before and after each distillation column to arrange all possible interconnections. The distillation columns were modeled using a slightly modified version of the rigorous tray-by-tray *MESH* distillation column model of Viswanathan and Grossmann (1993). The method did not employ any simplifying assumptions such as sharp splits or equimolar flow rates. Binary variables were used in order to determine the number of trays within each column (reflux tray location). In the SON method the number of columns was rationally fixed according to the number of components in the feed. The feed tray location and the column interconnections, defining the column sequences, were continuous decisions, determined by their flow rate values. The generated MINLP problems were solved in GAMS using the DICOPT MINLP solver (Kocis and Grossmann 1989). The solution procedure included the solution of the relaxed MINLP problem and then a branch-and-bound search over the nonzero relaxed binary variables. This procedure was followed since, as reported, the full MINLP problem failed to converge in DICOPT, due to scaling and domain errors in the set-up of the NLP subproblems.

To overcome the implicit assignment of processing tasks to processing units, Papalexandri and Pistikopoulos (1996) developed a general synthesis framework based on a mass and heat transfer representation. Utilizing fundamental mass/heat transfer principles within a superstructure environment, this building block synthesis method exploits modeling concepts from the well defined heat exchanger network (HEN) and mass exchange network (MEN) problem. Synthesis alternatives are not prepostulated, but instead embedded within a network of mass and heat exchanging modules that allow nonconventional hybrid systems to be revealed. In terms of total process flow sheet alternatives, the potential of this approach has been illustrated through application to ideal systems including separation, reaction, and heat integration operations. The approach has also been applied to the synthesis of flexible heat and mass exchange networks (Papalexandri and Pistikopoulos 1994). Ismail et al. (1999) modified and extended the mass/heat transfer module to general multicomponent nonideal systems and reactive distillation systems (Ismail et al. 2001).

Yeomans and Grossmann (1999a) proposed a systematic modeling framework based on superstructure optimization in which the sequencing of simple distillation

columns was also addressed. The superstructures were obtained using the state task network (Sargent 1998) and the state equipment (operator) network representations (Smith 1996; Smith and Pantelides 1995). These two representations can be regarded as complimentary to each other. In the STN, tasks and states are defined while the equipment assignment is unknown, while in the SEN, as indicated above, the tasks and equipment are defined and the assignment of tasks to equipment must be determined. The synthesis problem was modeled with the generalized disjunctive programming (GDP) (Raman and Grossmann 1994). In order to use GDP, conditional constraints had to be identified from permanent ones, that is, constraints that held in all structural alternatives. Having identified the conditional constraints, these were then represented with disjunctions and assigned to Boolean (logical) variables representing their existence. For a Boolean variable of value equal to true, the conditional constraints (corresponding to a column physical model) became activated, otherwise all variables participating in these constraints were set to zero. The GDP models were then transformed to MILP problems using the convex hull formulation of the disjunctions (Balas 1985). The generation of the superstructures for the examined problem was based on sharp separations performed in the distillation columns, which were modeled using simple mass balances and recoveries, generating linear physical models. The above modeling framework was also implemented in Yeomans and Grossmann (1999b) for the synthesis of simple distillation column sequences employing nonlinear shortcut distillation column physical models. The latter were based on assumptions of sharp splits, where only the distribution of adjacent key components was allowed along with high recovery of the key components. The Fenske/Underwood/Gilliland method was used for the calculation of the minimum number of trays and of the minimum reflux.

The simple column sequencing problem using GDP was also addressed in Caballero and Grossmann (1999). The column superstructures were generated using the STN, SON and an intermediate representation. The latter was proposed based on the STN representation, however, allowing the columns the possibility of performing multiple tasks. The distillation column models were aggregated using mass transfer feasibility constraints at the section boundaries. These models bore many similarities with the ones used for the representation of simple distillation columns in the generalized modular framework (Papalexandri and Pistikopoulos 1996). However, the two models have many structural and physical modeling differences. Structurally, the building blocks of the superstructure are different. In Caballero and Grossmann (1999) each building block consisted of a set of two aggregated column sections with their heat units and a feed position mixer (with predefined interconnections between them). In the GMF each Mass/Heat (M/H) module and each Heat Exchange (He) module constitutes different building blocks. Moreover, as shown in Papalexandri and Pistikopoulos (1996), the GMF building blocks by definition have more extensive interconnection possibilities. From a physical modeling point of view, in Caballero and Grossmann (1999) simplifying assumptions of equimolar flow rates, isothermal operation and sharp splits were employed. Moreover, in order to provide valid mass transfer feasibility constraints, the mass transfer direction had to be known and postulated, which depended on the separation task taking place in

a particular column section. The GMF mass transfer is arranged through driving force constraints, which are formulated in such a way that the mass transfer direction does not need to be prepostulated or known a priori. However, both models provide a lower bound on the energy consumption of distillation columns. In the proposed method the generated GDP problems were transformed into MINLP problems by assigning a binary variable to each Boolean variable and by transforming the disjunctions into big-*M* constraints.

The most recent superstructure method for the simple column sequencing problem was proposed in Yeomans and Grossmann (2000a), using rigorous *MESH* models for the physical representation of distillation columns. The superstructure for the problem was generated using the SON representation, as implemented in Yeomans and Grossmann (1999a). The computational difficulties of the rigorous *MESH* models, associated with equations becoming singular, the solution of redundant equations, the need for good initialization procedures and the convergence difficulties due to nonexisting columns or flows were overcome using a GDP adaptation of the Viswanathan and Grossmann (1993) distillation column model. In the GDP model the feed, the condenser and reboiler stages were modeled as permanent and all the other stages as conditional, assigned to a Boolean variable. The disjunctions were modeled so that for existing stages (whose Boolean variables had a value of true), phase equilibrium constraints were enforced along with other *MESH* constraints, thus allowing mass and heat exchange between the contacting phases. For the opposite case, of nonexisting stages, the *MESH* constraints were applied without the phase equilibrium constraints and the input stream properties of the stage were set equal to those of the output stream, thus making the nonexisting stage a simple input-output stage. The translation of the GDP problems into MINLP problems was also done by transforming the disjunctions into big-*M* constraints. Moreover, appropriate initialization schemes were provided based on relaxed purity and recovery constraints. Table 1.1 presents an overview of superstructure methods for simple column sequencing.

The synthesis of azeotropic separation processes has also received significant attention in the literature. Table 1.2 summarizes most of the developed approaches for the analysis, design, and synthesis of homogeneous azeotropic separation systems.

Recently, Proios (2004) addressed the simple distillation column sequencing problem through the GMF synthesis model. From a structural point of view, a GMF structural model has been developed that can generate the feasible structural alternatives for the examined problems, aiming at addressing efficiently the first complication of the column sequencing problem. In the proposed GMF sequencing method the accompanying physical model is based on the GMF physical model originally introduced by Papalexandri and Pistikopoulos (1996) and extended by Ismail et al. (1999, 2001). This model, which is based on aggregation, can be viewed as an intermediate between the simplified and the rigorous models. On one hand it avoids potentially limiting simplifying assumptions, such as equimolar flow rates, isothermal operation, sharp splits, etc., thus increasing the accuracy of the physical representation. On the other hand, due to aggregation it generates problems of smaller

Table 1.1 Summary of superstructure methods for simple column sequencing.

Authors	Features
Simplified methods (sharp splits)	
Andrecovich and Westerberg (1985)	Network superstructure, simple mass balances
Wehe and Westerberg (1987)	General separation, nondistr/nonkey, mass balances
Floudas (1987)	General separation, mass balances
Floudas and Anastasiadis (1988)	General separation, mass balances
Aggarwal and Floudas (1990)	General separation, nondistr/nonkey, mass balances
Novak et al. (1996)	Network & compact superstructures, mass balances
Yeomans and Grossmann (1999a)	STN & SON superstructures, GDP, mass balances
Yeomans and Grossmann (1999b)	STN & SON superstructures, GDP, nonlinear shortcut models
Caballero and Grossmann (1999)	STN, SON & intermediate superstructures, aggregated models
Rigorous methods (MESH model, Viswanathan and Grossmann (1993))	
Smith (1996)	SON superstructure, MESH modified model
Yeomans and Grossmann (2000)	SON superstructure, GDP

size, which are easier to solve. Finally, the GMF was accompanied by a solution procedure, using formal MINLP solution techniques that find the optimal sequence without having to evaluate all structural alternatives. The overall synthesis framework and solution approach was demonstrated in several case studies (Proios 2004).

1.3 Synthesis of Heat-integrated Distillation Column Sequences

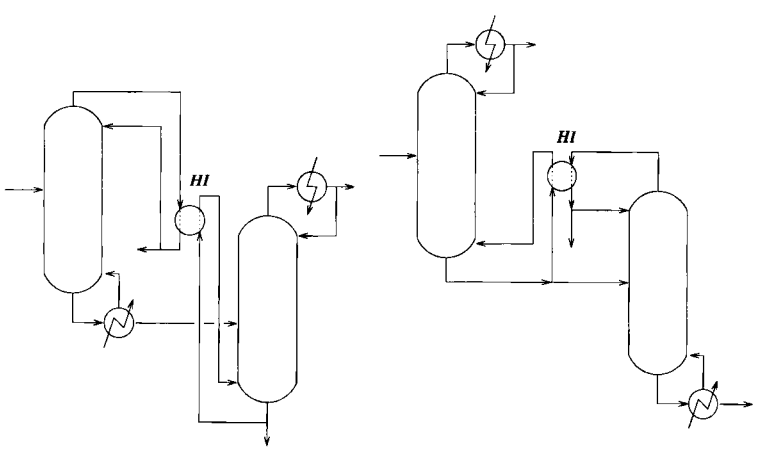
1.3.1 Heat-integrated Distillation Column Sequencing

As shown in the previous chapter, there is a substantial economic incentive for the development of methods for the simple distillation column sequencing problem, since significant energy savings can be achieved by finding the most energy efficient column sequence for a particular separation. However, even higher energy savings

can be achieved in distillation sequences by incorporating techniques such as heat integration (HI) and thermal coupling. In this chapter, the former technique is employed, while the latter is examined in the following chapter.

In general, distillation heat integration makes use of the heat generated in a column's condenser in order to provide the heat required in another column's reboiler (an illustration for the direct column sequence is shown in Fig. 1.2). The generated heat in the column's condenser is produced by the condensation of the vapor effluent of the column's top end, through heat exchange with a cold utility (cooling water) due to a heat gradient. On the contrary, in a column's reboiler, heat is required for the vaporization of the liquid effluent of a column's bottom end, through heat exchange with a hot utility (steam). Structurally, two process streams exist: one vapor (hot) from a column's top end that needs to be cooled and a liquid (cold) from a column's bottom end that needs to be heated. Provided there is a sufficient heat gradient between those two streams the latter can be made to exchange heat with each other. In order to achieve the necessary heat gradients the column pressures are shifted appropriately, since the column pressure has a direct effect on the column temperature levels (for nonazeotropic and nonreacting mixtures, raising the column pressure raises the column temperature). The operating cost savings achieved through HI have been reported to reach 50% as compared with non-HI column sequences (Hostrup et al. 2001). The obtained energy savings compensate for a potential increase in the capital expenditure due to the use of pumps, which is usually considered negligible when compared to the overall column investment cost (Novak et al. 1996).

Due to its economic importance, a large number of methods have been proposed for the synthesis of HI column sequences. Some characteristic methods proposed over the years included the dynamic programming algorithm of Rathore et al. (1974)



(a) Forward *HI* Match (b) Backward *HI* Match

Figure 1.2 Illustration of a ternary direct column sequence.

Table 1.2 Summary of design procedures for homogeneous azeotropic separation.

	Entrainer selection
Doherty and Caldarola (1985)	RCM, total reflux, ternary mixtures. Assumes linear distillation boundaries and no boundary crossing.
Stichlmair J., Fair, J.R., Bravo J.L. Chemical Engineering progress 85 (1989), p. 63	DLM, total reflux, linear distillation boundaries.
Foucher et al. (1991)	RCM, total reflux, ternary. Automatic procedure.
Laroche L., Bekiaris N., Andersen H.W., Morari M. AICHE Journal, 38 (1992), p. 1309	RCM, ternary. Analysis based on "equivolatility curves."
Column sequencing & bounding strategies	
Laroche et al. (19926)	RCM, all reflux, ternary. Separability in single feed columns.
Wahnschafft et al. (1992)	RCM, all reflux, ternary mixtures, single feed columns. Bounds by feed pinch point trajectories.
Fidkowski et al. (1993)	DLM, all reflux, ternary, single feed. Introduces "distillation limit," accounts for boundary crossing, algebraic-based.
Stichlmair and Herguijuela (1992)	DLM, all reflux, ternary, single feed. Accounts for curved distillation boundaries.
Jobson et al. (1995)	Achieves attainable product region based on simple distillation and mixing for ternary mixtures.
Safrit and Westerberg (1997)	RCM. Algorithm determining boundaries & distillation regions for n-component systems.
Rooks et al. (1998)	RCM. Equation-based approach to determine distillation region structures of multicomponent mixtures.
Design & optimization	
Boundary value design procedure	
Levy et al. (1985) Knight and Doherty (1986) Julka and Doherty (1990) Knapp and Doherty (1994) Fidkowski et al. (1991)	Ternary mixtures, single feed columns, CMO Ternary, single feed with heat effects. Multicomponent, single feed, CMO. Tracks fixed points ternary, double feed column, CMO. Calculates R_{min} and R_{max}.Up to four components, single feed, CMO. Algebraic continuation arc method to locate tangent pinch.
Stichlmair et al. (1993)	Ternary mixture, "pinch point" geometry.
Bauer and Stichlmair (1995)	Combines pinch point analysis with process MINLP optimization for ternary mixtures in single-feed columns.
Castillo et al. (1998a)	Introduces the concept of staged leaves for ternary mixtures in single feed.
Thong et al. (2004)	Two-stage synthesis procedure for separating multicomponent azeotropic mixtures.

the Branch-and-Bound techniques of Sophos et al. (1978) and Morari and Faith (1980), the thermodynamic insights (pinch) technique of Linnhoff et al. (1983), to mention but a few. However, focus will be, as elsewhere, on the superstructure optimization methods proposed for the solution of this problem. A distinct characteristic of the majority of these methods is that they are based on column sequencing methods, incorporating elements of heat exchanger network (HEN) synthesis. An overview of the superstructure HI column sequencing methods is provided next.

1.3.2
Superstructure Methods for HI Simple Column Sequencing

A number of superstructure methods have been reported in the open literature for the treatment of various facets of HI distillation sequencing problem. Andrecovich and Westerberg (1985a) incorporated HI possibilities in their MILP simple column sequencing method. This was realized by assuming instances of columns at different prespecified pressure levels. The pressure ranges were determined by the available hot and cold utility temperatures. The method constructed the HI sequencing schemes using two proposed algorithms. The hot and cold streams were the condenser, reboiler, and utility streams. Having specified the column pressures, the temperatures of the condensers and reboilers were also considered fixed. The heat duties of each condenser and reboiler at each column instance were assumed proportional to the feed flow rate. The HI possibilities were incorporated using HEN transportation (Cerda et al. 1983) and the transshipment (Papoulias and Grossmann 1983) problem formulations. However, in the above approach an invalid assumption was used, which assumed that the product of the column heat duty and the reboiler-condenser temperature difference was constant in each column. This essentially meant that the reboiler and condenser heat duties and their temperature difference were assumed independent of the column temperature (or pressure) levels. In order to rectify this, Andrecovich and Westerberg (1985b) removed this assumption. The results derived generated the same HI sequences as previously, but the calculated utility targets were improved.

The HI column sequencing superstructure method of Andrecovich and Westerberg (1985b) was also used in Kakhu and Flower (1988), incorporating three types of complex columns (Petlyuk, side stripper, and side rectifier) to be heat integrated with other simple column sequences. The HI problem was addressed through the transshipment/transportation formulations. The distillation columns were modeled assuming sharp separations and total mass balances, generating a MILP problem, solved for the minimization of the TAC. The capital cost functions were based on a fixed-charge part and on a feed-flow-rate-dependant part and the column heat duties were also given as simple functions of the feed-flow rate.

Paules and Floudas (1988) addressed the HI simple column sequencing problem, generating a superstructure based on sharp split columns. The presence of each column was assigned to a binary variable, along with the HI possibilities between potential condenser and reboiler matches. In order to provide more realistic HI

schemes, the effects of pressure were taken into account *implicitly*, through relating the column pressure to the condenser temperature. The latter was included as a variable in the optimization problem. Through shortcut simulations at different pressure ranges and using regression analysis, the reboiler temperatures and the TAC expressions were formulated as functions of the condenser temperatures. The pressure ranges were determined by the available hot and cold utilities available. The overall problem was posed as an MINLP solved for the minimization of the TAC using the APROS methodology.

Raman and Grossmann (1993) developed a model for the synthesis of HI distillation column sequences, where the sequencing problem without HI was based on the MILP method of Andrecovich and Westerberg (1985a). In the HI sequencing problem, columns of sharp splits were incorporated, which were represented in the HI problem through the temperatures of reboilers and condensers. In contrast with the HI method of Andrecovich and Westerberg (1985a), the reboiler and condenser temperatures were not considered constant, but were incorporated as variables. The columns were modeled operating at arbitrary pressures, since the authors did not incorporate pressure explicitly as a variable in their HI method. The columns' capital cost was expressed in the fixed charge-variable charge (feed-flow-rate-dependant) model. In the operating cost model the heat loads of the reboilers and condensers were calculated by simple functions of the feed flow rate. The generated problem was solved using a proposed incorporation of logic in the branch-and-bound scheme.

The simple column sequencing method of Novak et al. (1996) was also extended for the incorporation of HI possibilities, combining the compact and network column sequencing superstructures with the multistage HEN superstructure of Yee at al. (1990) (NLP) or Yee and Grossmann (1990) (MINLP in which binary variables were used for every potential heat match). The columns were modeled assuming sharp splits and using the Fenske-Gilliland-Underwood shortcut model. The investment cost of pumps was found to be small compared to that of the columns and was therefore neglected. In the case studies, the MINLP form of the HEN problem was employed, along with a simple initialization and linearization scheme for overcoming convergence problems.

In Grossmann et al. (1998) the above column sequencing superstructure method was coupled to the Duran and Grossmann (1986) HEN model and its disjunctive MILP reformulation. The latter was proposed in order to overcome difficulties experienced with the above model handling isothermal streams (due to its convergence to suboptimal solutions). In a revisited HI column sequencing problem from Novak et al. (1996), the Duran and Grossmann (1986) model and its disjunctive reformulation-generated HI structures were characterized by the same column sequencing, but with different HI schemes. The Duran and Grossmann (1986) model produced the worst solution, while its disjunctive reformulation and the Novak et al. (1996) solution produced the best results, which were quite similar.

The HI column sequencing problem was also addressed as an extension of the simple column sequencing problem of Yeomans and Grossmann (1999a). However in order to produce more realistic HI results, energy balances were added in the simple mass balance models employed for the physical representation of the distillation

columns. The HI synthesis procedure was based on the Raman and Grossmann (1993) model. The convex hull formulation was applied to the generated GDP problem for its translation to an MILP problem. For the incorporation of HI possibilities, the Raman and Grossmann (1993) HI model was also implemented in Yeomans and Grossmann (1999b), coupled to the proposed nonlinear GDP simple column sequencing model (involving nonlinear shortcut distillation column physical models).

In the distillation column sequencing method of Caballero and Grossmann (1999) HI possibilities were incorporated based on the heat integration models of Paules and Floudas (1988) and Raman and Grossmann (1993). The heat loads of the isothermal reboilers and condensers were calculated as a function of their vapor flow rates and heat of vaporization, while simplified energy balances were used for the incorporation of HI possibilities. Heat exchange feasibility constraints were enforced between condenser and reboiler temperatures for their potential HI matches, which were assigned to a binary variable. The authors did not consider the incorporation of pressure in the proposed method. An objective function was used for the minimization of the sequences' operating cost, which enabled the method to derive valid lower bounds of the represented systems' energy consumption.

Finally, a superstructure optimization method was proposed by Hostrup et al. (2001), incorporating thermodynamic insight principles. The main principle in this method was the use of thermodynamic insight techniques (Jaksland et al. 1995) in order to generate a superstructure of alternatives, to be further optimized using formal superstructure MINLP techniques. Three main steps were defined in this method: the problem formulation (identification of tasks and techniques), the flow sheet optimization, and the validation/analysis. A general separation problem posed in Aggarwal and Floudas (1990) was revisited also incorporating HI possibilities. In the first step of the method having provided the feed mixture to the ICAS synthesis toolbox (CAPEC 1999), based on thermodynamic insights two feasible separation techniques were identified (flash and distillation), which were eventually presented as a single technique, thus reducing the size of the generated MINLP problem. In the structural optimization step the compact superstructure of Novak et al. (1996) was employed and extended for the general separation case. HI was implemented in this model using the Yee and Grossmann (1990) HEN model. The columns were modeled using the Fenske/Gilliland/Underwood shortcut model and the HI results indicated 50% lower operating costs than those of the non-HI case. Recently, Proios (2004) extended the GMF model for the simple column sequencing problem to account for heat integration opportunities. To this end, an HI block has been introduced, along with its structural and physical model components. A summary of superstructure-based methods for HI simple column sequencing is presented in Table 1.3.

Table 1.3 Summary of superstructure methods for HI simple column sequencing.

Authors	Features
Simplified methods (sharp splits)	
Andrecovich and Westerberg (1985)	HEN transportation/transshipment, fixed P columns
Kakhu and Flower (1988)	Andrecovich and Westerberg (1985b) – three complex columns
Paules and Floudas (1988)	P via condenser temperature, regression analysis
Raman and Grossmann (1993)	Andrecovich and Westerberg/Paules and Floudas, Logic BB
Novak et al. (1996)	HEN of Yee and Grossmann (1990)
Grossmann et al. (1998)	HEN of Duran and Grossmann (1986) and its GDP MILP
Yeomans and Grossmann (1999a,b)	HI of Raman and Grossmann (1993), GDP
Caballero and Grossmann (1999)	HI of Raman and Grossmann (1993), GDP
Hostrup et al. (2001)	Thermodynamic insights and Novak et al. (1996)
Proios (2004)	Extension of the GMF to account for heat integration opportunities

1.4 Synthesis of Complex Distillation Column Sequences

1.4.1 Complex Distillation Column Sequencing

In Section 1.2 it was illustrated that choosing the most appropriate simple column sequence out of a set of possible alternatives can lead to substantial energy savings. In Section 1.3 these energy savings were extended by applying heat integration techniques on these simple column sequences. However, it has been reported, as will be shown below, that high energy savings can also be achieved through the incorporation of thermal coupling in complex columns (columns with multiple feeds and side streams). In this section, an overview of techniques for the complex distillation column sequencing problem (that is, the sequencing problem where both simple and complex columns are considered) is critically presented.

An illustration of the complex distillation sequencing problem is given here for the ternary separation problem (the first member of the multicomponent separation).

The alternative sequences for ternary distillation are shown in Fig. 1.3. From those alternatives, the most common in both literature and industrial practice are those consisting of simple distillation columns, which are shown in Figs. 1.3a–c. However, the number of alternatives increases considerably when complex columns are considered (Figs. 1.3d–k). All these complex columns are either partially or fully ther-

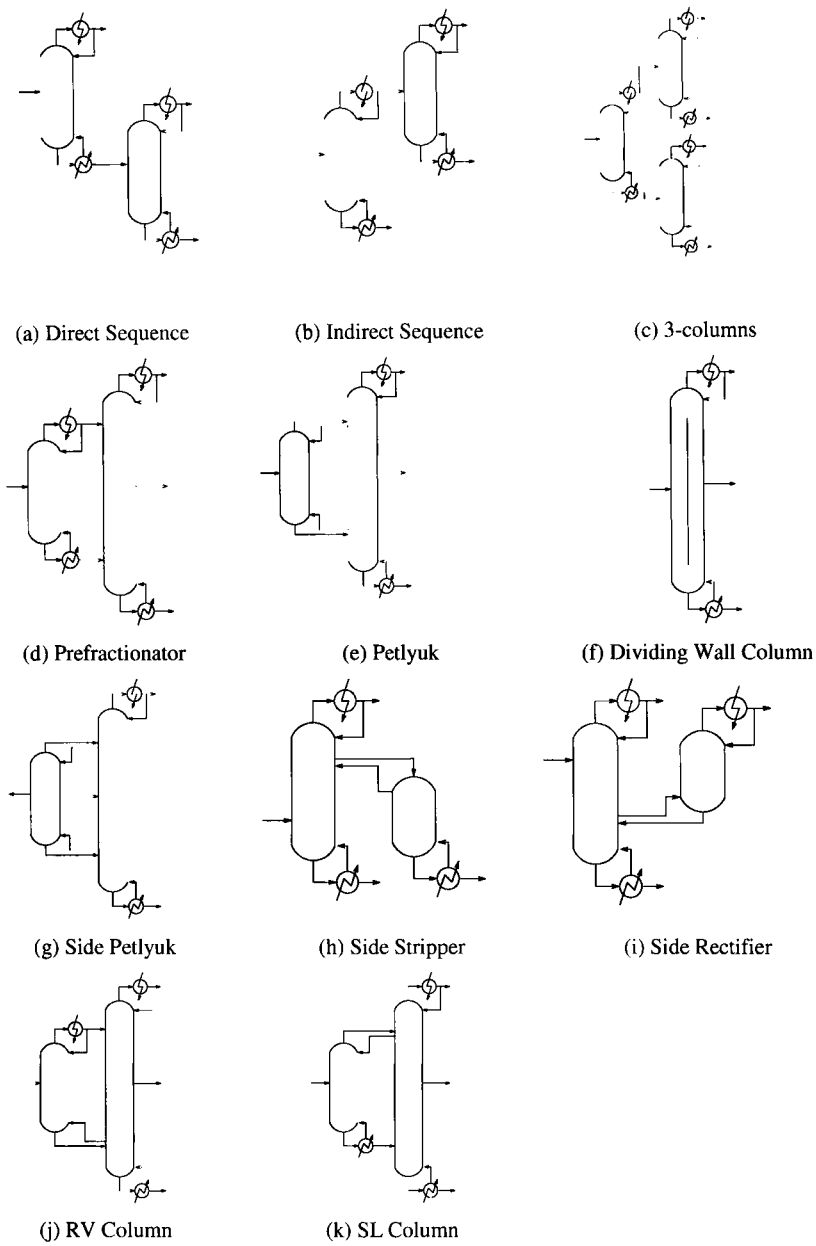


Figure 1.3 Alternative configurations for the distillation of a nonazeotropic ternary mixture.

mally coupled. From these, the fully thermally coupled (Petlyuk) column (Fig. 1.3e) has been receiving increasing attention, as it has been found that it can exhibit energy consumption reductions of up to 40% compared to conventional configura-

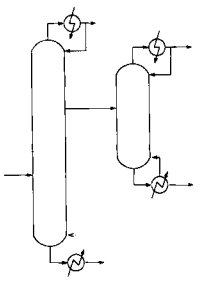
tions (Fidkowski and Krolikowski 1986; Glinos and Malone 1988; Triantafyllou and Smith 1992; Annakou and Mizsey 1996; Dunnebier and Pantelides 1999), which is due to its thermodynamic efficiency (minimization of losses due to unnecessary remixing). The dividing wall column (Fig. 1.3f) is considered thermally equivalent to the Petlyuk column under the assumption of no heat transfer through the vertical wall. It also provides capital cost savings by including the main and the prefractionation column of the Petlyuk arrangement in the same shell. The two final configurations (RV and SL) are essentially a side rectifier column with a direct vapor connection and a side stripper column with a direct liquid connection, respectively (Agrawal and Fidkowski 1999a).

However, some further column configurations have been reported in the literature (Fig. 1.4) (Agrawal 2000b). As indicated in Fig. 1.4, these configurations are modifications of some of the complex columns, aiming at the improvement of the latter's controllability. According to Agrawal (2000b), control difficulties can be encountered in complex columns, the source of which the author traced to the columns' vapor interconnections. In the alternatives to Fig. 1.4, one or more "problematic" vapor interconnection streams have been replaced with additional rectifying sections and condensers or with stripping sections and reboilers. These configurations, which are assumed to be thermally equivalent to their "parent" configurations, increase the number of structural alternatives for ternary distillation to 18 versus the eight reported by Tedder and Rudd (1978). Therefore, the issue that needs to be formally addressed is to provide a method that systematically incorporates the complex structural possibilities of thermally coupled columns in a unified way with simple column sequences, while capturing accurately the underlying physical phenomena in order to obtain the most energy efficient distillation sequences.

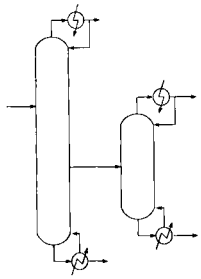
1.4.2
Superstructure Methods for Complex Distillation Sequencing

The first systematic superstructure method for generating distillation column sequences, including complex arrangements, was the sequential column superstructure presented initially by Sargent and Gaminibandara (1976) and extended in Eliceche and Sargent (1981) (see also Fig. 1.5). The authors proposed a rigorous tray-by-tray model for the design of distillation columns with multiple feeds and side streams. The number of stages and the optimal feed and side stream locations in each column required the introduction of a large number of discrete variables, rendering the problem a large scale MINLP. The combinatorial complications were handled by treating the integers as continuous variables rounded off each time to the nearest integer variable, eventually reducing the problem to a nonlinear programming (NLP) problem.

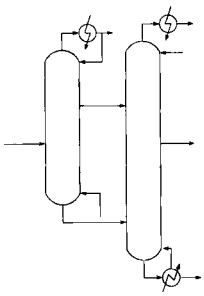
The work on the sequential column superstructure was continued in Mei (1995), by investigating the possibilities of aggregation and size reduction, by using as superstructure building blocks column segments (aggregations of trays) and connecting units, whose existence was denoted by binary variables. Using the fact that trays do not operate at equilibrium, their number in each column segment was not



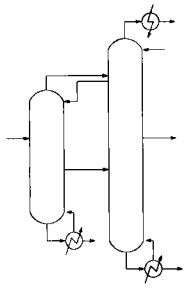
(a) Modified Side Stripper



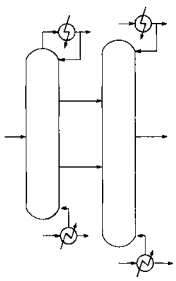
(b) Modified Side Rectifier



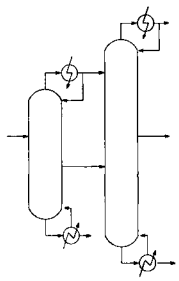
(c) Modified Petlyuk 1



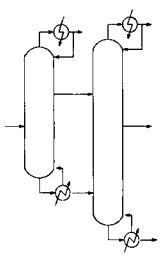
(d) Modified Petlyuk 2



(e) Modified Petlyuk 3



(f) Modified Petlyuk 4



(g) Modified Petlyuk 5

Figure 1.4 Modified configurations for operability targets.

specified as an integer variable. Moreover, each building block was modeled as a modular simulator using as inputs a guess of the number of trays, the flow rates, and the intensive variables characterizing each input stream and generating outputs of the calculated flow rates and intensive variables of each output stream to be included in the optimization. The case studies demonstrated the effect of the modular treatment of the problem, which led to mathematical models of less than 100 variables and equations, respectively.

Agrawal (1996) proposed a satellite column superstructure method for the separation of near-ideal mixtures of four and more components (n) into pure (or near pure) products, generating more than one fully thermally coupled distillation column sequences, with a single reboiler and condenser. This superstructure involved $n-2$ columns as satellites around a central column, while generating an overall smaller minimum number of column sections than the sequential column superstructure (Sargent and Gaminibandara 1976) for $n \geq 4$. The method was also extended to the generation of all the other feasible partially or nonthermally coupled column sequences for the examined separations through the addition of reboilers and condensers at the appropriate end of each column section of the satellite superstructure. A step-wise procedure was provided for the generation of all the FC structural alternatives. It was shown that although for $n-3$ the satellite and the sequential column superstructures are equivalent, for $n \geq 4$ the former is more complete than the latter. However, no formal structural optimization model was provided by the authors for the automated generation of all the alternatives. The proposed satellite superstructure representation was extended in Agrawal (2000a), providing a systematic method to draw more alternative FC column sequences, which are topologically different and allegedly more operable than those presented in the previous publication. From a thermodynamic point of view, the additional structures were equivalent to those of the 1996 publication.

A method was also proposed for the generation of feasible distillation column sequences was the state task network (Sargent 1998), which was analyzed more thoroughly in Doherty and Malone (2001). The method initially identified the network states (mixtures created by all the feasible separations) and then the separation tasks, which were assigned to a distillation column or, in the case of complex distillation columns, to a section of a distillation column. Having identified the possible states and tasks, a superstructure could be generated linking a distillation task between two consecutive states and by using logical constraints for the feasible sequencing of tasks. Since the STN is a one-to-one approach (one unit carries out only one task), this method generated a problem with a large number of units (contrary to the SON, which considered only a small number of multi-task units).

The complex distillation column sequencing problem was also examined in Dunnebier and Pantelides (1999), based on the state operator network (SON) method (Smith 1996). In the proposed method the distillation column operators were physically modeled based on the rigorous tray-by-tray model of Viswanathan and Grossmann (1993). Binary variables denoted the existence of column operators, number of trays (reflux return tray location), and side stream locations (see Fig. 1.6). The authors included some very useful comments regarding the convergence complexities of the exam-

ined problem, while stressing the importance of complex arrangements for energy efficiency and the use of accurate models for their representation.

Yeomans and Grossmann extended their disjunctive model for the rigorous design of simple distillation columns (Yeomans and Grossmann 2000a) to the incorporation of complex arrangements (Yeomans and Grossmann 2000b) based on the sequential column superstructure representation of Sargent and Gaminibandara (1976). In both studies, once the superstructure for the column sequence had been postulated, the representation was translated into a GDP mathematical problem, which was then transformed into an MINLP problem. The column trays were arranged as permanent and conditional ones. The former were fixed in the superstructure and corresponded to the feed, reflux, and boil-up trays. The conditional trays were assigned to a Boolean variable, which when false, turned these trays into simple input-output trays with no mass transfer. The authors concluded that their method avoided the numerical difficulties associated with including redundant equations and with singularities due to liquid and vapor flows taking a value of zero and improving the model's robustness.

Caballero and Grossmann (2001) provided a superstructure method on the STN formalism of Yeomans and Grossmann (1999a) for the generation of all FC column sequences for n components from the satellite superstructure (Agrawal 1996). In conjunction with the guidelines provided in the latter publication, the superstructure was modified for the generation of all the partially and nonthermally coupled column sequences. The superstructure was modeled structurally using repositional logic expressions (Raman and Grossmann 1991) and each column was modeled physically

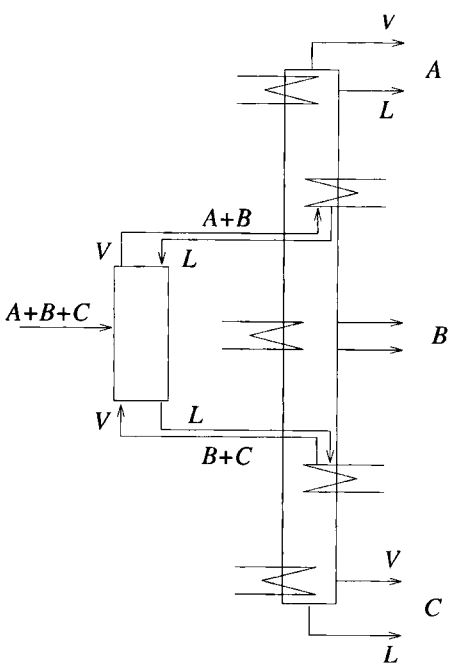


Figure 1.5 Sequential column superstructure (Eliceche and Sargent 1981).

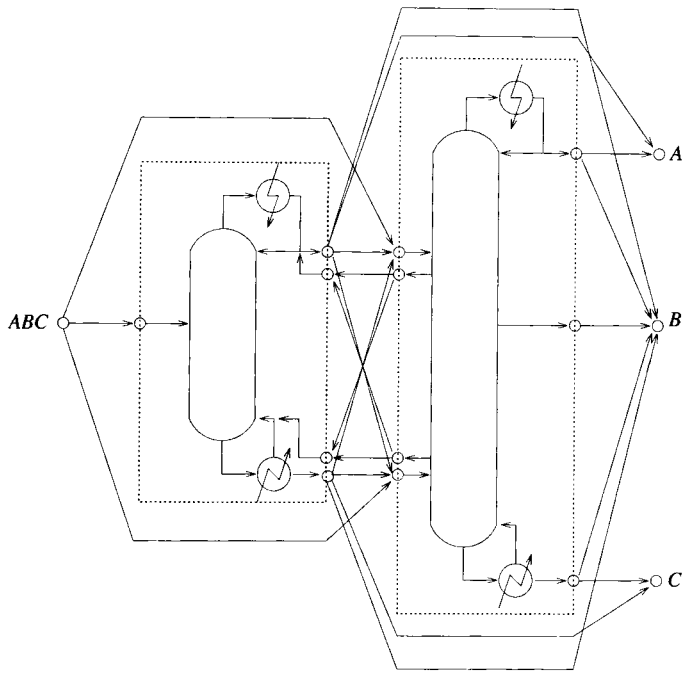


Figure 1.6 Superstructure for ternary distillation (Dunnebier and Pantelides 1999).

using a simple shortcut distillation column models based on a modified version of Underwood's equations (Carlberg and Westerberg 1989a,b) and using fixed costs for the heat units and column sections. The complete synthesis problem was modeled using GDP and solved using a modified version of the logic-based outer approximation algorithm.

In a recent paper Agrawal (2003) proposed an improved systematic procedure for the generation of basic and thermally coupled column sequences. In both types of column sequences it was imposed that a product stream enriched in a particular component was produced only once. A systematic procedure including useful guidelines was provided initially for generating all the basic column sequences, followed by a procedure for the thermally coupled column case. The latter was based on the generation of thermally coupled columns by replacing reboilers and condensers of basic sequences with two-way interconnections between columns. The method that could be readily modified in order to incorporate other structural possibilities regarding the transfer of streams between columns can be viewed as a useful tool for the construction of a systematic superstructure optimization method for the automatic generation of the reported and of other "unknown" column sequences. Coupled to an efficient and appropriately designed physical model and solution procedure, solutions can be generated providing optimal designs from an energy and/or operability point of view.

Table 1.4 Summary of superstructure methods for complex column sequencing.

Authors	Features
Sargent and Gaminibandara (1976)	Sequential column superstructure, *MESH* model
Eliceche and Sargent (1981)	Sequential column superstructure, *MESH* Model
Mei (1995)	Sequential column superstructure, pseudo-aggregated model
Agrawal (1996, 2000, 2003)	Satellite column superstructure
Sargent (1998)	STN (Doherty and Malone (2001))
Dunnebier and Pantelides (1999)	SON superstructure, MESH (Smith 1996)
Yeomans and Grossmann (2000b)	Sequential column superstructure, MESH
Caballero and Grossmann (2001)	Satellite column superstructure, GDP, shortcut model
Shah and Kokossis (2002)	Synthesis of complex distillation sequences
Proios (2004)	Extension of the GMF for synthesis of complex column sequencing

Shah and Kokossis (2002) proposed a new representation for the synthesis and optimization of complex separation systems. This representation is based on tasks instead of units. The problem is formulated as an MILP and its efficiency was illustrated in several problems based on the literature as well as industrial problems.

1.5 Conclusions

A comprehensive review of state-of-the-art techniques for the synthesis of energy efficient simple, heat integrated, and complex distillation column sequences, has been presented is this chapter. Emphasis was placed on systematic and rigorous approaches focusing on the systematic generation and evaluation of the alternative designs in a compact and unified way. The problem of significant economic and scientific interest required the tackling of underlying structural and physical complicating issues. These were inherently related to increasing the number of structural alternatives and the complexity of the underlying mass and heat exchange physical phenomena. The economic potential in conjunction with these complications has "compelled" virtually all major research groups, both in academia and industry, to propose methods for the distillation column sequencing problem, addressing it in its entirety or just certain components of it.

The presented superstructure methods have contributed significantly to the efficient treatment of the distillation sequencing problem. It has been shown that the nonconvexities and discontinuities of the generated large scale MINLP problems, which have imposed a limitation of many rigorous approaches, have been overcome

through the use of techniques such as disjunctive modeling and its associated solution procedures. These limitations can be treated through the use of aggregated models, like the GMF, by easing the computational effort due to the reductions in the size of the generated MINLP problems, achieved without compromising the accuracy of the results.

It is important to note that lately we are seeing a growing discussion of constructing the process at a more fundamental level, that is, by thinking of the process as combinations of mass and heat exchanges (Westerberg 2004). The original work of Papalexandri and Pistikopoulos (1996), as extended by Ismail et al. (1999, 2001) and recently by Proios (2004), is a key step towards this direction. If these approaches successfully develop and are further applied, they will lead to designing and synthesizing not only the process, but also the unit operations themselves that should form the basis of these processes. Applications in synthesis of absorption, reactive absorption, and crystallization networks are clearly sought.

References

1 *Aggarwal, A., C. A. Floudas* (1990) Synthesis of General Distillation Sequences-Nonsharp Separations. *Comput. Chem. Eng.* 14(6), 631–653.

2 *Agrawal, R.* (1996) Synthesis of Distillation Column Configurations for a Multicomponent Separation. *Ind. Eng. Chem. Res.* 35, 1059–1071.

3 *Agrawal, R.* (2000a) A Method to Draw Fully Thermally Coupled Distillation Column Configurations for Multicomponent Distillation. *Trans IChemE Part A* 78, 454–464.

4 *Agrawal, R.* (2000b) Thermally Coupled Distillation with Reduced Number of Intercolumn Vapor Transfers. *AIChE J.* 46(11), 2198–2210.

5 *Agrawal, R.* (2003) Synthesis of Multicomponent Distillation Column Configurations. *AIChE J.* 49(2), 379–401.

6 *Agrawal, R., Z. T. Fidkowski* (1998) Are Thermally Coupled Distillation Columns Always Thermodynamically More Efficient for Ternary Distillations? *Ind. Eng. Chem. Res.* 37(8), 3444–3454.

7 *Agrawal, R., Z. T. Fidkowski* (1999a) New Thermally Coupled Schemes for Ternary Distillation. *AIChE J.* 45, 485–496.

8 *Andrecovich, M. J., A. W. Westerberg* (1985a) An MILP Formulation for Heat-Integrated Distillation Sequence Synthesis. *AIChE J.* 31(9), 1461–1474.

9 *Andrecovich, M. J., A. W. Westerberg* (1985b) A Simple Synthesis Method Based on Utility Bounding for Heat-Integrated Distillation Sequences. *AIChE J.* 31(9), 363–375.

10 *Annakou, O., P. Mizsey* (1996) Rigorous Comparative Study of Energy-Integrated Distillation Schemes. *AIChE J.* 35(6), 1877–1885.

11 *Balas, E.* (1985) Disjunctive Programming and a Hierarchy of Relaxations for Discrete Optimization Problems. *SIAM J. Alg. Discrete Methods* 6, 466–486.

12 *Bauer, M. H., J. Stichlmair* (1995) Synthesis and Optimization of Distillation Sequences for the Separation of Azeotropic Mixtures. *Comput Chem. Eng.* 19, S15–S20.

13 *Bek-Pedersen, E.* (2003) Synthesis and Design of Distillation Based Separation Schemes. Dissertation, Technical University of Denmark.

14 *Bek-Pedersen, E., R. Gani* (2004) Design and Synthesis of Distillation Systems Using a Driving-Force-Based Approach. *Chem. Eng. Process.* 43, 251–262.

15 *Biegler, L. T., I. E. Grossmann, A. W. Westerberg* (1997) *Systematic Methods of Chemical Process Design.* Prentice-Hall, New Jersey.

16 *Caballero, J. A., I. E. Grossmann* (1999) Aggregated Models for Integrated Distillation Systems. *Ind. Eng. Chem. Res.* 38, 2330–2344.

17 *Caballero, J. A., I. E. Grossmann* (2001) Generalized Disjunctive Programming Model for the Optimal Synthesis of Thermally Linked Distillation Columns. *Ind. Eng. Chem. Res.* 40, 2260–2274.

18 *CAPEC, Department of Chemical Engineering DTU* (1999) *ICAS Users Manual.* Lyngby, Denmark.

19 *Carlberg, N. A., A. W. Westerberg* (1989a) Temperature-Heat Diagrams for Complex Columns. 2. Underwood"s Method for Side Strippers and Enrichers. *Ind. Eng. Chem. Res.* 28, 1379–1386.

20 *Carlberg, N. A., A. W. Westerberg* (1989b) Temperature-Heat Diagrams for Complex Columns. 3. Underwood"s Method for the Petlyuk Configuration. *Ind. Eng. Chem. Res.* 28, 1386–1397.

21 *Castillo, F. J. L., D. Y. C. Thong, G. P. Towler* (1998a) Homogeneous Azeotropic Distillation. 1. Design Procedure for Single-Feed Columns at Nontotal Reflux. *Ind. Eng. Chem. Res.* 37, 987–997.

22 *Cerda, J., A. W. Westerberg, D. Mason, B. Linnhoff* (1983) Minimum Utility Usage in Heat Exchanger Network Synthesis. A Transportation Problem. *Chem. Eng. Sci.* 38(3), 373–383.

23 *Doherty, M. F., G. A. Caldarola* (1985) Design and Synthesis of Homogeneous Azeotropic Distillations. 3. Sequencing of Columns for Azeotropic and Extractive Distillations. *Ind. Eng. Chem. Fundam.* 24, 474–485.

24 *Doherty, M. F., M. F. Malone* (2001) *Conceptual Design of Distillation Systems.* McGraw-Hill, New York.

25 *Douglas, J. M.* (1988) *Conceptual Design of Chemical Processes.* McGraw-Hill, New York.

26 *Dunnebier, G., C. C. Pantelides* (1999) Optimal Design of Thermally Coupled Distillation Columns. *Ind. Eng. Chem. Res.* 38, 162–176.

27 *Duran, M. A., I. E. Grossmann* (1986) Simultaneous Optimization and Heat Integration of Chemical Processes. *AIChE J.* 32, 123–138.

28 *Eliceche, A. M., R. W. H. Sargent* (1981) Synthesis and Design of Distillation Systems. *IChemE Sytnp Ser* 61, 1–22.

29 *Fidkowski, Z. T., L. Krolikowski* (1986) Thermally Coupled System of Distillation Columns: Optimisation Procedure. *AIChE J.* 32, 537–546.

30 *Fidkowski, Z. T., M. Malone, M. F. Doherty* (1991) Nonideal Multicomponent Distillation: Use of Bifurcation Theory for Design. *AIChE J.* 37(12), 1761–1779.

31 *Fidkowski, Z. T., M. F. Doherty, M. Malone* (1993a) Computing Azeotropes in Multicomponent Mixtures. *Comput. Chem. Eng.* 17(12), 1141–1155.

32 *Floudas, C. A.* (1987) Separation Synthesis of Multicomponent Feed Streams into Multicomponent Product Streams. *AIChE J.* 33(4), 540–550.

33 *Floudas, C. A., S. H. Anastasiadis* (1988) Synthesis of Distillation Sequences With Several Multicomponent Feed and Product Streams. *Chem. Eng. Science* 43(9), 2407–2419.

34 *Fraga, E. S., K. I. M. McKinnon* (1995) Portable Code for Process Synthesis Using Workstation Clusters and Distributed Memory Multicomputers. *Comput. Chem. Eng.* 19, 759–773.

35 *Glinos, K., F. Malone* (1988) Optimality Regions for Complex Column Alternatives in Distillation Systems. *Chem. Eng. Res. Des.* 66, 229–240.

36 *Grossmann, I. E.* (1985) Mixed-Integer Programming Approach for the Synthesis of Integrated Process Flowsheets. *Comput. Chem. Eng.* 9, 463–482.

37 *Grossmann, I. E., H. Yeomans, Z. Kravanja* (1998) A Rigorous Disjunctive Optimization Model for Simultaneous Flowsheet Optimization and Heat Integration. *Comput. Chem. Eng.* 22, S157–S164.

38 *Hendry, J. E., R. R. Hughes* (1972) Generating Separation Process Flowsheets. *Chem. Eng. Prog.* 68, 71–76.

39 *Hendry, J. E., D. F. Rudd, J. D. Seader* (1973) Synthesis in the design of chemical processes. *AIChE Journal* 19, 1.

40 *Hostrup, M., R. Gani, Z. Kravanja, A. Sorsak, I. E. Grossmann* (2001) Integration of Thermodynamic Insights and MINLP Optimization for the Synthesis, Design and Analysis of Process Flowsheets. *Comput. Chem. Eng.* 25, 73–83.

41 *Ismail, S. R., E. N. Pistikopoulos, K. P. Papalexandri* (1999) Modular Representation Synthesis Framework for Homogeneous Azeotropic Distillation. *AIChE J.* 45, 1701–1720.

42 *Ismail, S. R., P. Proios, E. N. Pistikopoulos* (2001) Modular Synthesis Framework for Combined Separation/Reactive Systems. *AIChE J.* 47, 629–650.

43 *Jaksland, C., Gani R., Lien K.* (1995) Separation Process Design and Synthesis Based on Thermodynamic Insights. *Chem. Eng. Sci.* 50, 511–530.

44 *Jobson, M., D. Hildebrandt, D. Glasser* (1995) Attainable Regions for the Vapour-Liquid Separation of Homogeneous Ternary Mixtures. *Chem. Eng. J.* 59(1), 51–70.

45 *Julka, V., M. F. Doherty* (1990) Geometric Behaviour and Minimum Flows for Nonideal Multicomponent Distillation. *Chem. Eng. Sci.* 45, 1801–1822.

46 *Kakhu, A. I., J. R. Flower* (1988) Synthesising Heat-Integrated Distillation Sequences Using Mixed Integer Programming. *Chem. Eng. Res. Des.* 66, 241–254.

47 *Knight, J. R., M. F. Doherty* (1986) Design and Synthesis of Homogeneous Azeotropic Distillations. 5. Columns with Nonnegligible Heat Effects. *Ind. Eng. Chem. Fundam.* 25, 279–289.

48 *Knapp, J. P., M. F. Doherty* (1994) Minimum Entrainer Flows for Extractive Distillation: a Bifurcation Theoretic Approach. *AIChE J.* 40(2), 243–268.

49 *Kocis, G. R., I. E. Grossmann* (1989) Computational Experience with DICOPT Solving MINLP Problems in Process Systems Engineering. *Comput. Chem. Eng.* 13, 307–315.

50 *Kravanja, Z., I. E. Grossmann* (1993) PROSYN-An Automated Topology and Parameter Process Synthesizer. *Comput. Chem. Eng.* 17, S87–S94.

51 *Kravanja, Z., I. E. Grossmann* (1994) New Developments and Capabilities in PROSYN-An Automated Topology and Parameter Process Synthesizer. *Comput. Chem. Eng.* 18, 1097–1114.

52 *Levy, S. G., D. B. Van Dongen, M. F. Doherty* (1985) Design and Synthesis of Homogeneous Azeotropic Distillations. 2. Minimum Reflux Calculations for Nonideal and Azeotropic Columns. *Ind. Eng. Chem. Fundam.* 24, 463–474.

53 *Linnhoff, B., H. Dunford, R. Smith* (1983) Heat integration of distillation columns into overall processes. *Chem. Eng. Sci.* 35, 1175–1188.

54 *Mei, D.* (1995) An SQP Based MINLP Algorithm and its Application to Synthesis of Distillation Systems. Dissertation, Imperial College of Science, Technology and Medicine, London.

55 *Mix, T. W., J. S. Dweck, M. Weiberg, R. C. Armstrong* (1978) Energy Conservation in Distillation. *Chem. Eng. Prog.* 74(4), 49–55.

56 *Morari, M., C. Faith* (1980) The Synthesis of Distillation Trains with Heat Integration. *AIChE J.* 26, 916–928.

57 *Nishida, N., G. Stephanopoulos, A. W. Westerberg* (1981) A Review of Process Synthesis. *AIChE J.* 27, 321–351.

58 *Novak, Z., Z. Kravanja, I. E. Grossmann* (1996) Simultaneous Synthesis of Distillation Sequences in Overall Process Schemes Using an Improved MINLP Approach. *Comput. Chem. Eng.* 20, 1425–1440.

59 *Papalexandri, K. P., E. N. Pistikopoulos* (1994) A Multiperiod MINLP Model for the Synthesis of Flexible Heat and Mass Exchange Networks. *Comput. Chem. Eng.* 18, 1125–1139.

60 *Papalexandri, K. P., E. N. Pistikopoulos* (1996) Generalized Modular Representation Framework for Process Synthesis. *AIChE J.* 42(4), 1010–1032.

61 *Papoulias, S., I. E. Grossmann* (1983) A Structural Optimization Approach in Process Synthesis. I: Utility Systems, II: Heat Recovery Networks, III: Total Processing Systems. *Comput. Chem. Eng.* 7(6), 695–734.

62 *Paules, G. E., C. A. Floudas* (1988) A Mixed Integer Nonlinear Programming Formulation for the Synthesis of Heat Integrated Distillation Sequences. *Comput. Chem. Eng.* 12(6), 531–546.

63 *Proios, P.* (2004) Generalized Modular Framework for Distillation Column Synthesis. Dissertation, Imperial College London, University of London.

64 *Raman, R., I. E. Grossmann* (1991) Relation Between MILP Modeling and Logical Inference for Chemical Process Synthesis. *Comput. Chem. Eng.* 15(2), 73–84.

65 *Raman, R., I. E. Grossmann* (1993) Symbolic Integration of Logic in Mixed Integer Linear Programming Techniques for Process Synthesis. *Comput. Chem. Eng.* 17, 909–927.

66 *Raman, R., I. E. Grossmann* (1994) Modelling and Computational Techniques for Logic Based Integer Programming. *Comput. Chem. Eng.* 18(7), 563–578.

67 *Rathore, R., K. van Wormer, G. Powers* (1974) Synthesis Strategies for Multicomponent Separation Systems with Energy Integration. *AIChE J.* 20, 491–502.

68 *Rooks, R. E., V. Julka, M. F. Doherty, M. F. Malone* (1998) Structure of Distillation Regions for Multicomponent Azeotropic Mixtures. *AIChE J.* 44(6), 1382–1391.

69 *Safrit, B. T., A. W. Westerberg* (1997) Algorithm for Generating the Distillation Regions for Azeotropic Multicomponent Mixtures. *Ind. Eng. Chem. Res.* 36(5), 1827–1840.

70 *Sargent, R. W. H.* (1998) A Functional Approach to Process Synthesis and its Application to Distillation Systems. *Comput. Chem. Eng.* 22(1-2), 31–45.

71 *Sargent, R. W. H., K. Gaminibandara* (1976) *Optimal Design of Plate Distillation Columns.* Optimization in Action. Academic Press, London.

71 *Seader, J. D., A. W. Westerberg* (1977) A Combined Heuristic and Evolutionary Strategy for Synthesis of Simple Separation Sequences. *AIChE J.* 23, 951–954.

73 *Shah, P. B., A. C. Kokossis* (2002) Synthesis Framework for the Optimization of Complex Distillation Systems. *AIChE J.* 48, 527–550.

74 *Smith, E. M.* (1996) On the Optimal Design of Continuous Processes. Dissertation, Imperial College of Science, Technology and Medicine, London.

75 *Smith, E. M. B., C. C. Pantelides* (1995) Design of Reaction/Separation Networks Using Detailed Models. *Comput. Chem. Eng.* 19, S83–S88.

76 *Sophos, A., G. Stephanopoulos, M. Morari* (1978) Synthesis of Optimum Distillation Sequences with Heat Integration Schemes. Paper 42d. 71st Annual AIChE Meeting. Miami, FL.

77 *Sorel, E.* (1889) Sur la Rectification de 1' Alcohol. *Comptes Rendus* CVIII, 1128.

78 *Stephanopoulos, G., A. W. Westerberg* (1976) Studies in Process Synthesis, ILEvolutionary Synthesis of Optimal Process Flowsheets. *Chem. Eng. Sci.* 31, 195–204.

79 *Stichlmair, J., J. Herguijuela* (1992) Separation Regions and Processes of Zeotropic and Azeotropic Ternary Distillation. *AIChE J.* 38(10), 1523–1535.

80 *Stichlmair, J., H. Offers, R. W. Potthoff* (1993) Minimum Reflux and Minimum Reboil in Ternary Distillation. *Ind. Eng. Chem. Res.* 32(10), 2438–2445.

81 *Tedder, D. W., D. F. Rudd* (1978) Parametric Studies in Industrial Distillation: Part 1. Design Comparisons. *AIChE J.* 24(2), 303–315.

82 *Thompson, R. W., C. J. King* (1972) Systematic Synthesis of Separation Schemes. *AIChE J.* 18, 941–948.

83 *Thong, D. Y. -C, G. Liu, M. Jobson, R. Smith* (2004) Synthesis of Distillation Sequences for Separating Multicomponent Azeotropic Mixtures. *Chem. Eng. Process.* 43, 239–250.

84 *Triantafyllou, C., R. Smith* (1992) The Design and Optimisation of Fully Thermally Coupled Distillation Columns. *Trans. Inst. Chem.* 70, 118–132.

85 *Viswanathan, J., I. E. Grossmann* (1993) Optimal Feed Locations and Number of Trays for Distillation Columns with Multiple Feeds. *Ind. Eng. Chem. Res.* 32, 2942–2949.

86 *Wahnschafft, O. M., J. W. Koehler, E. Blass, A. W. Westerberg* (1992) The Product Composition Regions of Single-Feed Azeotropic Distillation Columns. *Ind. Eng. Chem. Res.* 31, 2345–2362

87 *Wehe, R. R., A. W. Westerberg* (1987) An Algorithmic Procedure for the Synthesis of Distillation Sequences with Bypass. *Comput. Chem. Eng.* 11(6), 619–627.

88 *Westerberg, A. W.* (1980) Review of Process Synthesis. In: R. G. Squires, G. V. Reklaitis (eds.) *Computers Applications to Chemical Engineering*, pp. 53–87, ACS Symposium Series, No. 124.

89 *Westerberg, A. W.* (2004) A Retrospective on Design and Process Synthesis. *Comput. Chem. Eng.*, 28 (2004) p. 2192–2208.

90 *Yee, T. F., I. E. Grossmann* (1990) Simultaneous Optimization Models for Heat Integration – III. Heat Exchanger Network Synthesis. *Comput. Chem. Eng.* 14, 1165–1184.

91 *Yee, T. F, I. E. Grossmann, Z. Kravanja* (1990) Simultaneous Optimization Models for Heat Integration. 1. Area and Energy Targeting and Modelling of Multistream Exchangers. *Comput. Chem. Eng.* 14, 1151–1164.

92 *Yeomans, H., I. E. Grossmann* (1999a) A Systematic Modelling Framework of Superstructure Optimization in Process Synthesis. *Comput. Chem. Eng.* 23, 709–731.

93 *Yeomans, H., I. E. Grossmann* (1999b) Nonlinear Dis3unctive Programming Models for the Synthesis of Heat Integrated Distillation Sequences. *Comput. Chem. Eng.* 23, 1135–1151.

94 *Yeomans, H., I. E. Grossmann* (2000a) Disjunctive Programming Models for the Optimal Design of Distillation Columns and Separation Sequences. *Ind. Eng. Chem. Res.* 39, 1637–1648.

95 *Yeomans, H., I. E. Grossmann* (2000b) Optimal Design of Complex Distillation Columns Using Rigorous Tray-by-Tray Disjunctive Programming Models. *Ind. Eng. Chem. Res.* 39, 4326–4335.