

Generalized Modular Framework For Distillation Column Synthesis

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Abstract

This thesis examines the distillation column synthesis/sequencing problem, which has received a lot of attention both in academia and industry. However, most of the methods proposed for its solution either employ shortcut models based on simplifying assumptions which allow fast and easy calculations but may limit the validity and accuracy of the results, or treat the problem rigorously, typically employing a high fidelity mathematical model, but at the expense of increased computational effort.

In this work an alternative approach is proposed through the use of aggregation models based on the Generalized Modular Framework (GMF), balancing accuracy over computational efficiency. The GMF is an aggregation superstructure optimization method for process synthesis at the conceptual level. In order to obtain the Synthesis Targets set, GMF Structural Models are systematically developed in this thesis for the synthesis of Simple, Heat Integrated and Complex Column Sequences. These models are appropriately constructed, incorporating all the structural alternatives. However, in the sequencing methods proposed, the GMF goes beyond simply generating these alternatives, evaluating their energy efficiency through an appropriately arranged Physical Model. The validity of the proposed synthesis methods is tested over a number of case studies. From the solution of the *compactly* generated Mixed Integer Nonlinear Programming (MINLP) problems, the GMF obtained the optimal column sequences generating substantial energy savings, which were found in agreement with those of rigorous models.

The GMF synthesis methods are further enhanced through the incorporation of formal collocation techniques for distillation. This has led to a remarkable enhancement of the physical representation, while maintaining the advantages of the GMF. The GMF/Collocation models by being coupled to the developed sequencing Structural Models, addressed the distillation column sequencing problem for overall cost efficiency. The GMF enhancement allowed for the derivation of accurate and detailed guidelines and insights on the generated sequences' design and operation.

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Chapter 1

Introduction

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 (Mix *et al.*, 1978) that distillation consumed about 3% of the US energy and that 10% savings in distillation energy could amount to savings of about \$500 million in the national energy cost. 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-nature reasons have imposed the treatment of energy efficiency as the main design target in distillation.

Due to its importance, distillation has received particular attention in 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 a direct consequence of the dependence of 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 the 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 which could reach the order of 50%, when compared to non-heat 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 vapour 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 non-Thermally 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 are increased 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 vapour 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 which 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 its 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, though, is 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 short-cut 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 solutions, or do not cover the details of the examined problem.

Finally, 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, which has been receiving increased attention over the last years, is superstructure optimization. Superstructures are, in general, superset flowsheets 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 the expense of computational efficiency.

1.1 Thesis Objectives

Synthesis Target: Find energy efficient simple, heat integrated and complex distillation column sequences, by systematically generating and evaluating the structural alternatives in an unified and compact way.

In this work the approach proposed for addressing this problem is based on the Generalized

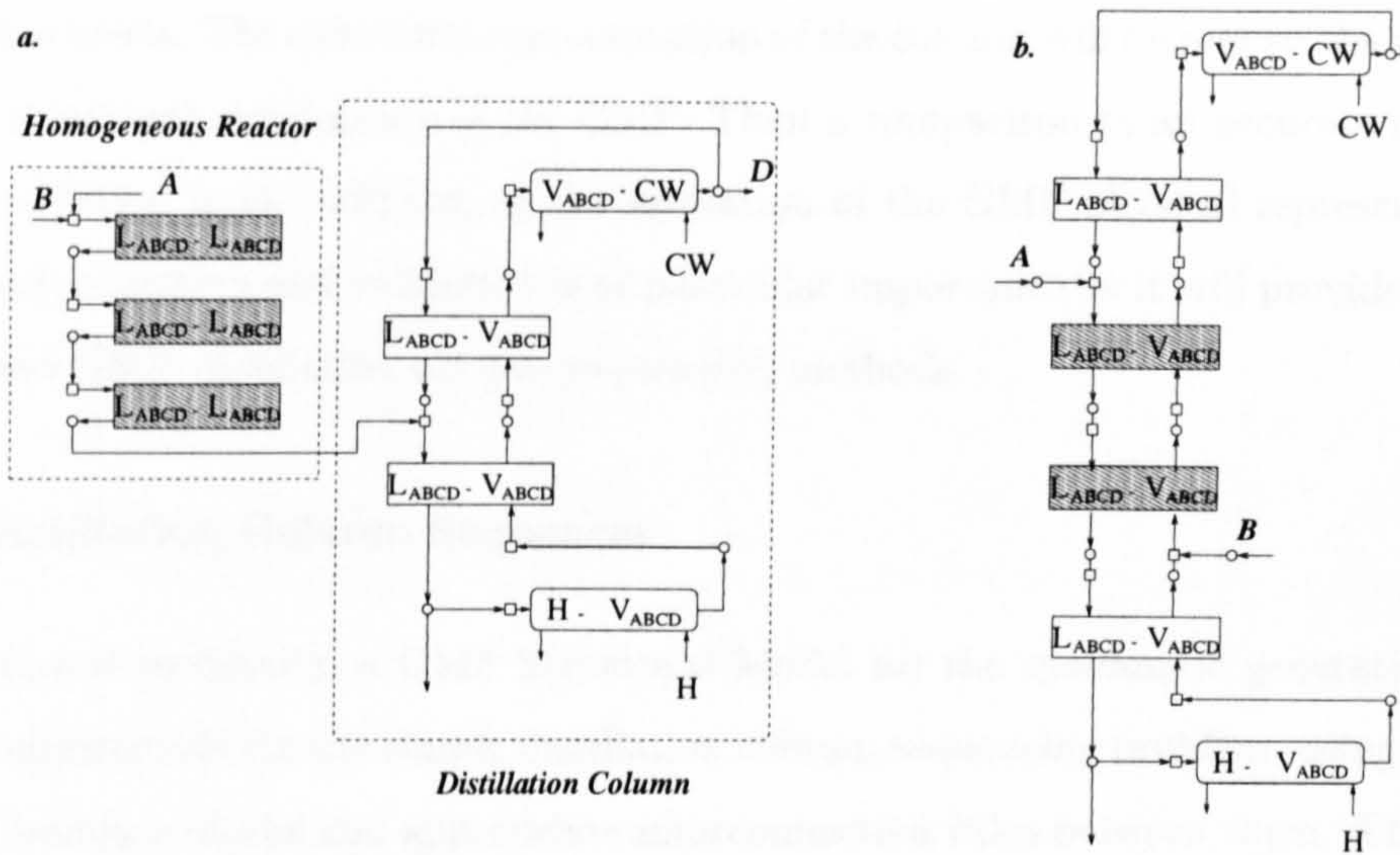


Figure 1.1: GMF Reactive and Separating System Representation (Ismail *et al*, 2001)

Modular Framework (GMF) (Papalexandri and Pistikopoulos, 1996). The GMF is an aggregation superstructure optimization method for process synthesis at the conceptual level. It provides an alternative approach to the superstructure methods mentioned above, by using multipurpose building blocks of adequate abstraction and structural possibilities in the potential structural combinations, where the represented units and their connectivities are not *rigidly* predefined. An illustration of the GMF for the representation of reactive separating and reactive distillation systems is given in Figure 1.1. However, the GMF goes beyond simply generating the structural alternatives, since it can also evaluate them physically with respect to their energy consumption. This is possible since the GMF building blocks are accompanied by aggregated physical models, which can capture the underlying physical phenomena based on fundamental mass and heat exchange principles. Moreover, due to aggregation, the generated physical problems are of a compact size, thus reducing considerably the computational effort required for their solution.

In order to efficiently and systematically obtain the synthesis target set in this work, the following objectives need to be met:

Distillation Column Physical Representation

The GMF Physical Model will be modified appropriately in order to capture efficiently the physical phenomena taking place in a simple distillation column and consequently its energy

consumption levels. The structural representation of the column will be realized by appropriately fixing the structural components of the GMF. Then a comparison to an accurate rigorous tray-by-tray distillation model will aim at the validation of the GMF physical representation. This physical representation and validation is of particular importance as it will provide the basis for the proposed GMF distillation column sequencing methods.

Simple Distillation Column Sequences

The objective is to develop a GMF Structural Model for the systematic generation of all the structural alternatives for the simple distillation column sequencing problem, using an adequate number of building blocks and appropriate interconnection rules between them. This structural model will be coupled to the GMF Physical Model and to a formal optimization solution procedure in order to address the full synthesis problem, that is, the systematic generation *and* evaluation of simple column sequences, with the aim of finding the most energy efficient column arrangement.

Heat Integrated (*HI*) Simple Distillation Column Sequences

Based on the GMF simple column sequencing method proposed, the aim is to extend the GMF for the incorporation of *HI* possibilities in order to obtain more energy efficient distillation column designs. The *HI* problem will be formally addressed through the introduction of a Heat Integration (*HI*) block. The GMF simple column sequencing Structural Model will be appropriately modified incorporating potential heat integration schemes. Furthermore, the GMF Physical Model will also incorporate physically the *HI* block, while focusing on the heat integration feasibility conditions and the pressure effects on the represented columns' operation.

Complex Distillation Column Sequences

The objective is to propose a synthesis methodology which will allow the incorporation of Thermal Coupling techniques for energy efficiency in the distillation sequences. A GMF Structural Model will be proposed incorporating, in a unified way, complex columns, such as the Petlyuk sequence (Fully Thermally Coupled column), along with simple column sequences. The GMF Physical Model will then be applied in order to capture the underlying physical phenomena and

the potential thermodynamic efficiency of thermal coupling.

GMF Physical Representation Enhancement

The GMF is an aggregation superstructure optimization method for process synthesis at the conceptual level, capturing efficiently the *general* trends in the underlying mass and heat transfer phenomena. One of the challenges in this work is the increase of the GMF physical representation detail. This is proposed through the enhancement of the GMF Physical Model, by being appropriately coupled with formal discretization techniques, used for the order reduction of distillation column models. In doing so, principles of a simulation tool will be incorporated in the GMF conceptual design tool while preserving and enhancing the latter's representational advantages.

1.1.1 Thesis Outline

This thesis is structured as follows. In Chapter 2 an overview of the GMF is given, focusing on the latter's basic structural and physical principles. The GMF is modified through the incorporation of appropriately defined Auxiliary blocks in order to enhance its physical representation. The GMF Physical Model is then presented with a special focus on distillation. The GMF distillation representation is then validated through a comparison to a rigorous distillation model over a distillation column optimization case study.

Chapter 3 extends the ideas presented in Chapter 2, for the synthesis of simple distillation sequences using the GMF. A systematic method is proposed for the mathematical representation of superstructures, based on propositional logic expressions. The proposed methodology is applied to case studies for the first two members of multicomponent distillation, namely ternary and quaternary distillation. The GMF Structural Model generates the structural alternatives and the GMF Physical Model evaluates them with respect to their energy consumption using a formal optimization solution procedure, until the most energy efficient sequence is obtained.

In Chapter 4 the GMF simple column sequencing method is modified for the formal incorporation of heat integration possibilities, through the introduction of a Heat Integration block. The *HI* column sequencing method proposed, captures the structural possibilities and the physical phenomena, with particular focus on the effects of pressure which is explicitly considered in

the GMF Physical Model. The simple column sequencing case studies are revisited and new *HI* designs are obtained leading to higher energy savings.

Chapter 5 addresses the problem of complex column sequencing through the GMF. A systematic structural model is used for the mathematical representation of a superstructure incorporating simple and complex column arrangements. The GMF Physical Model is then coupled to the structural model, in a systematic way, for the evaluation of the represented columns and the derivation of insights on the operation of simple and partially or fully thermally coupled columns.

In Chapter 6 the GMF Physical Model is enhanced through its coupling to collocation techniques for the discretization of the GMF building blocks. This enhancement allows for detailed distillation column physical representations and design results which are validated through a direct comparison to a distillation rigorous model.

The work on simple, heat integrated and complex column sequences carried out so far, is revisited in Chapter 7, while incorporating the enhanced GMF Physical Model of Chapter 6. The proposed synthesis models allow the derivation of the most energy efficient column sequences, while obtaining detailed column design explicitly and maintaining the representation advantages of the GMF.

In the last chapter the overall work on the distillation sequencing problem is evaluated and concluding remarks are made on the systematic techniques employed and on the efficiency of the proposed methodology. Finally, the work is concluded with directions for future work based on the current form of the GMF and the experience derived.

Chapter 2

GMF Fundamentals and Distillation Column Representation

2.1 Generalized Modular Framework Fundamentals

A distinct characteristic of most process operations is that they are mainly characterized by mass and heat transfer phenomena (for instance, in distillation mass and heat are simultaneously transferred between the vapour and liquid contacting phases, or in reaction mass and internal heat are transferred from the reactants to the products). Therefore, these process operations can be properly represented using building blocks which can effectively capture the mass and heat transfer phenomena. This provided the motivation for the Generalized Modular Framework (GMF), presented originally in Papalexandri and Pistikopoulos (1996), which utilized a mass and heat exchange module as a process operation building block. In this module, heat was exchanged from the hot to the cold stream and mass was exchanged, for each component, from the rich stream (decreasing concentration) to the lean stream (increasing concentration). This rich/lean stream definition was in accordance with that of the mass exchange model of El-Halwalgi and Manousiouthakis (1989). Generally, mass and heat transfer between immiscible phases is driven by a composition/temperature gradient between the system compositions and temperatures and those corresponding to phase, chemical and thermal equilibrium.

The extensions and the importance of the GMF become clear if it is taken into consideration that most process synthesis approaches are governed by an assignment of processing

tasks to processing equipment in the postulated unit operations of their various alternatives. The consequence is that the generated designs are often limited by typical flowsheet patterns (Papalexandri and Pistikopoulos, 1996). However, the GMF can potentially overcome this limitation by assigning fundamental mass and heat transfer tasks to multipurpose process operation building blocks, instead of units. The conceptual importance of this rationale was also confirmed in Smith (1996): *'if simple 'building' operators are included, then the optimal flowsheet produced may suggest the use of unit operations (alternatives) not present in this pre-postulated set'*. The GMF building blocks which are representations of higher levels of abstraction and lower dimensionality, are used for the generation of structural combinations from which conventional and even unconventional process flowsheets or units can be identified (a representation of conventional and unconventional units through the GMF can be found in Appendix A.1).

In Papalexandri and Pistikopoulos (1996) the synthesis problem was defined as follows :

Given: (i) A set of existing process streams and desired products and their specifications, (ii) a set of available heat and mass utility streams, their supply temperatures and compositions, (iii) physical property and cost data and (iv) available technology (e.g. kinetics, intermediates, by-products etc),

Objective: Identify a structural combination of building blocks that can yield products which meet the process specifications, while optimizing the designated design targets.

Generally, in order to achieve the above synthesis target, the GMF employs a mathematical model which is based on superstructure optimization techniques. Like most methods belonging to this class, the GMF model consists of:

- A Structural Model, responsible for the generation of the (structural) process alternatives.
- A Physical Model, responsible for the evaluation of the latter's performance/optimality.

2.1.1 The GMF Structural Model

The GMF Structural Model consists of the *GMF Building Blocks* and their *Interconnection Principles*.

The GMF Building Blocks

The GMF Building Blocks are representations of higher levels of abstraction and lower dimensionality where mass and heat or pure heat exchange take place. Thus, there are two main types of building blocks in the GMF (Papalexandri and Pistikopoulos, 1996):

- Mass/Heat (M/H) modules, where heat and mass transfer take place. The mass transfer is due to a concentration gradient between the contacting phases or/and to a generation part (when reaction takes place).
- Pure heat (He) modules, where the streams do not come into direct contact and only heat exchange takes place.

These building blocks are accompanied by auxiliary superstructure splitters (located after each feed stream and at the outlet of each stream leaving a M/H or a He module) and mixers (located at the inlet of each stream entering a M/H or a He module and before each product stream). In Ismail *et al.* (1999) each M/H module was explicitly associated with an optional Heater and Cooler modules (He modules with hot and cold utilities, respectively), as shown in Figure 2.1. Mathematically, the existence or not of the M/H and He modules is denoted through the use of binary ($0 - 1$) variables. The existence of the auxiliary mixers and splitters does not require the use of additional binary variables.

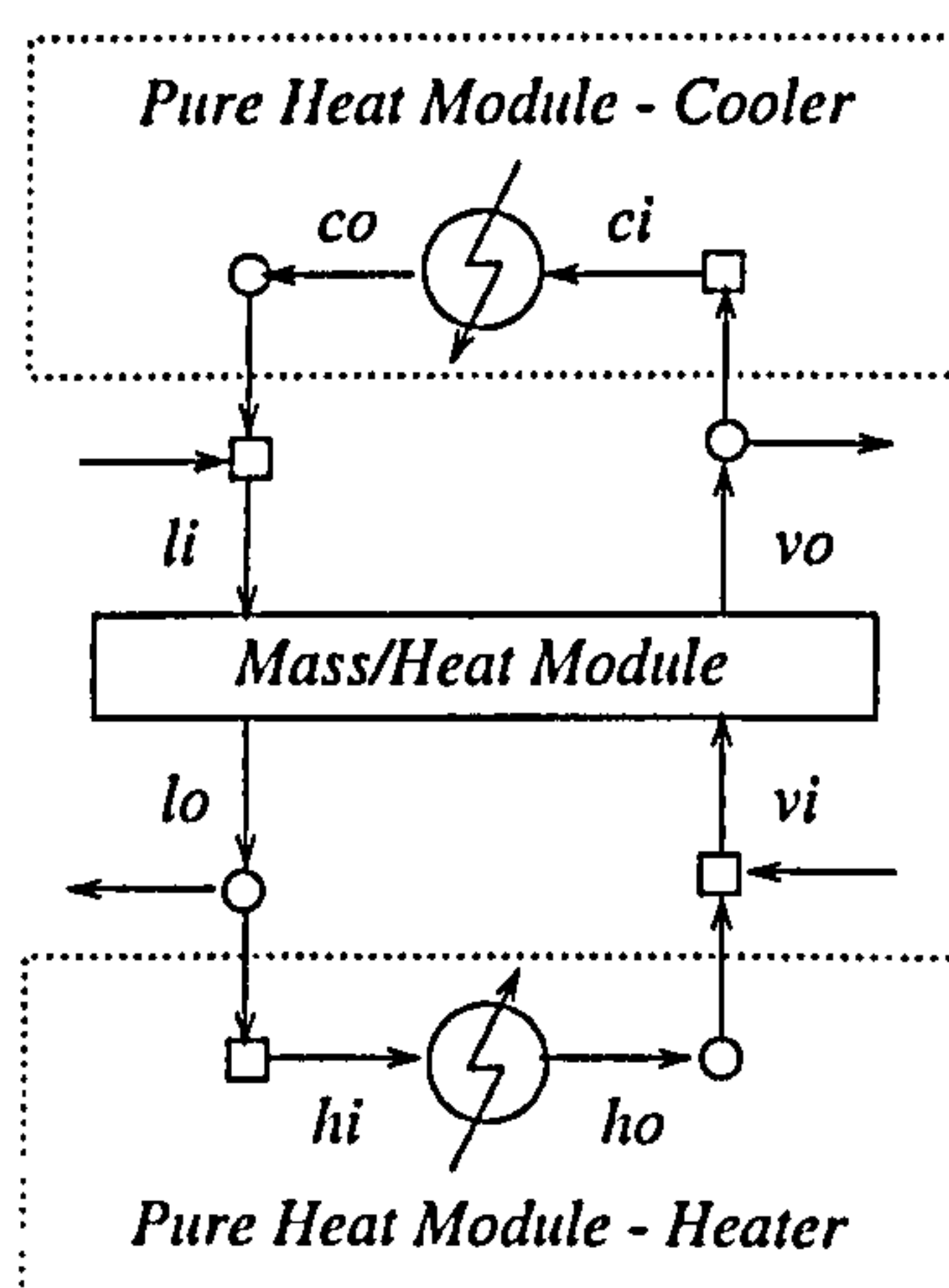


Figure 2.1: M/H Module with its associated He Modules

The GMF Interconnection Principles

The interconnection principles of the GMF define the way the various building blocks should be connected to each other in order to generate physically meaningful alternative flowsheets. These principles are mainly in the form of:

- GMF Structural Sets
- GMF Structural Constraints

The GMF Structural Sets provide information about the available building blocks and their allowed or forbidden interconnections for the specific problem solved. They can be regarded as a translation of engineering knowledge into a mathematical problem (for instance, in order to forbid the recycling of a stream already separated in a M/H module, a forbidden interconnection is incorporated from the splitter to the mixer of the same module). The GMF Structural Sets also provide information on the topology of the GMF Building Blocks in a generated superstructure. The GMF Structural Constraints are pure integer constraints (constraints involving only binary variables) used in structural optimization. Qualitatively, some of these constraints are generic (found in the same form in every GMF Structural Model) and some are problem-specific (depending on the synthesis problem examined). For illustration purposes, below are given some of the generic GMF interconnection principles, which impose that:

- Each M/H module has an associated Heater and Cooler (He modules). If a M/H module does not exist, then both its He modules are discarded (Ismail *et al.*, 1999).
- Only streams of the same phase are merged at the mixers prior to each side of potential building blocks and prior to final products.
- Each existing module must have at least one inlet stream and one outlet stream.
- Each feed stream must have at least one destination module and each product stream must have at least one source module.
- Interconnections to and from nonexistent building blocks must be eliminated.

The GMF Structural Model is the mathematical translation of the GMF Interconnection Principles. It consists of the pure integer (structural) constraints defined over the appropriately

defined GMF Structural Sets. The utilized GMF binary variables are categorized into primary and secondary. The former denote the existence of the GMF Building Blocks (M/H and He modules). The latter denote the existence of interconnection streams between the GMF Building Blocks. They are characterized as secondary because their values depend on those of the primary binary variables and because their use is optional. However, in the GMF they are used throughout since it has been observed that their use facilitates considerably the construction of the GMF Structural Model and the performance of the structural optimization. Another possible formulation of the structural problem can avoid the use of these variables by including only their corresponding continuous variables (flowrates), to be optimized in the continuous part of the problem (as in the State Operator Network (SON) method, proposed by Smith (1996)). However, due to the complexities caused by non-convexities of the physical model, the utilized local optimization solvers tend to trap the solution to locally optimal designs (as reported by Dunnebir and Pantelides (1999)). Unless, global optimization or extremely robust solution techniques are employed, this could have a direct effect on the generated structures, which in the SON method are defined by the existing units and their (continuous) interconnections. In the GMF the interconnections (secondary binary variables) are chosen in the discrete part of the problem. Although, from a first glance this could lead to a large increase of the problem combinatorics, however, using a tight structural model the discrete space can be largely reduced, generating efficiently the structural alternatives for the examined problem (structural optimization performance). The secondary binary variables also facilitate the automatic construction of each generated structure's GMF Physical Model, through their incorporation in the form of big- M structural-physical constraints and as logical parameters in the construction of the various physical model constraints.

2.1.2 The GMF Physical Model

The GMF Physical Model is employed for the representation of the underlying physical phenomena of the structures generated by the GMF Structural Model. Then, these structural alternatives can be evaluated with respect, initially, to their feasibility (*i.e.* their ability to meet the synthesis targets) and then to their optimality (with respect to an appropriate economic or physical objective function). Each GMF Building Block is accompanied by its physical model which depends on the block's function in the framework. In the M/H modules, mass and heat

transfer can take place simultaneously or sequentially, whereas in the *He* modules only heat transfer is allowed. The mixers are modelled so that no phase change is taking place (no flash operations). Phase changes occur only in the *He* exchange modules.

In general, the physical model of each building block is based on fundamental (and thus general) mass and heat exchange principles at the blocks' boundaries, consisting of: total and component mass balances, energy balances, molar fraction summation corrections and appropriate Phase Defining and Driving Force Constraints. The latter are particularly important since, along with the conservation laws, they are responsible for the arrangement of the mass and heat transfer and the distribution of the components in the various GMF building blocks (a more detailed description of these constraints can be found in Appendices A.2 and A.3). From a mathematical point of view, the GMF Physical Model corresponds to a nonconvex problem, due to the inherent mixing terms involved in the conservation laws.

2.1.3 The GMF Mathematical Model Formulation

The GMF mathematical model is a combination of the GMF Physical and Structural Models. This model is presented in a compact form in problem P, below:

$$\begin{aligned}
 \text{(P)} \quad & \min \quad f(x, y^{pr}) && \text{- Objective Function} \\
 & \text{s.t.} \quad h(x) = 0 && \text{- Continuous Equality Constraints} \\
 & \quad \quad g(x) \leq 0 && \text{- Continuous Inequality Constraints} \\
 & \quad \quad g^{MI}(x, y^{pr}, y^{sec}) \leq 0 && \text{- Mixed Integer Constraints} \\
 & \quad \quad g^{PI}(y^{pr}, y^{sec}) \leq 0 && \text{- Pure Integer Constraints} \\
 & \quad \quad x^{LO} \leq x \leq x^{UP} && \text{- General Bounds}
 \end{aligned}$$

where,

x : continuous GMF variables

y^{pr} : primary GMF binary variables (presence of GMF building blocks)

y^{sec} : secondary GMF binary variables (presence of block interconnections)

The Objective Function may represent design targets such as minimization of operating or total annualized cost or even minimization of environmental impact, *etc.* The bounds may represent process specifications in purity, safety, *etc.* The GMF Physical Model consists of the Continuous Equality and Inequality and Mixed Integer Constraints. The Continuous Equality

Constraints correspond to the conservation law constraints and to the thermodynamic functions at the boundaries of M/H and He modules. The inequality constraints correspond to the Driving Force and Phase Defining constraints. The Mixed Integer Constraints are big- M constraints generally arranging *existing* and *non-existing* interconnections between modules, thus transferring information between GMF Structural and Physical models. The GMF Structural Model consists of the Pure Integer Constraints, which are specific to the problem examined (as will be shown in the following Chapters).

The resulting mathematical problem is a Mixed Integer Nonlinear Programming (MINLP) problem. This is due to the existence of binary and continuous variables and to the nonlinear constraints. For the solution of the MINLP problem several methods can be used, like the Branch and Bound (Beale, 1977), the Generalized Benders Decomposition (Geoffrion, 1972) and the Outer Approximation (Duran and Grossmann, 1986a) methods (for a discussion on MINLP solution techniques, see Floudas (1995)). In the GMF, the GBD method has been employed since it provides more control during the solution procedure (as all decomposition MINLP methods), which is essential for the type of nonconvex MINLP problems encountered, and due to the simplicity of its formulation. In the GBD method the problem is decomposed into a Primal NLP subproblem (by fixing the binary complicating variables) and into a Master MILP subproblem (created by the projection of the continuous-discrete problem into the discrete space). For a minimization problem, the Primal subproblem can be solved using any NLP solver (CONOPT2, MINOS, etc) generating an upper bound to the solution and the Master subproblem can be solved using any MILP solver (CPLEX, ZOOM, etc) generating a lower bound to the solution. The main termination criterion is the crossing of the upper and lower bounds.

2.2 Synthesis Procedure in the GMF

In the GMF the procedure for generating and evaluating alternative process flowsheets consists of the following phases:

Phase I Generation of *All Numerically Possible* Alternatives (Initial Set - I)

Phase II Generation of *All Feasible* Alternatives (Feasible Subset - F)

Phase III Generation of *Optimality Candidate* Alternatives (Optimal Sub-subset - O)

Phase I

The Initial Set of alternatives is the largest possible set and it is generated by all the combinations of the binary variables (primary and secondary). For a total of N binary variables, the Initial Set of alternatives (I) will have 2^N elements. Appropriate structural modelling (building blocks and Structural Sets) should aim at keeping N as small as possible, while still incorporating efficiently the process alternatives. This phase is equivalent to a MINLP problem without any Pure Integer Constraints, or the GMF Model without any Structural Constraints.

Phase II

The Feasible Subset (F) includes all physically allowed alternatives. The GMF is based on aggregated models, which due to their abstraction can generate new units and flowsheets. However, their abstraction *requires careful logical modelling* so that, to the extent possible, only feasible (physically meaningful) alternatives are included in Subset F (if some infeasible alternatives are also included, then they should be identified in Phase III). The elements of subset F are determined by the use of appropriate structural constraints defined over structural sets (complete GMF Structural Model). In the decomposition-based MINLP solution approach employed in the GMF, the Feasible Subset corresponds to the feasible space of the first MILP Master subproblem (pure integer constraints).

Therefore, in Phase II from the Initial Set I , a subset F is generated, including a greatly reduced number of allowable alternatives, based on engineering knowledge and structural optimization.

Phase III

The Sub-subset of Optimality Candidate Alternatives (O), in the MINLP decomposition algorithm employed, includes the structures generated by the solution of each MILP Master subproblem. For every iteration, optimality in the Master subproblem depends on:

- (i) the Master subproblem objective function
- (ii) the GMF Structural Model pure integer constraints
- (iii) the past Master subproblems' objective functions

(iv) the Integer Cuts

Criteria (iv) and (iii), respectively, discard past candidate alternatives from being re-evaluated and constrain the initial integer feasible space (as defined by the first Master subproblem), leading to improved lower bounds.

In the GBD algorithm the optimal solution is found iteratively by evaluating physically in the Primal NLP subproblem each structure generated by the Master subproblem. Contrary to enumeration synthesis approaches, these alternative structures belong to the Optimal Sub-subset - O and not to set F of all the feasible alternatives. The importance of this solution approach lies in avoiding the solution of a large number of computationally expensive Primal nonconvex subproblems, each corresponding to an element of subset F .

Finally, a last remark should be made about each physical problem (Primal NLP) which is a vital part of Phase III. Due to its usual nonconvexity, the (local) solvers might get trapped into local solutions, not corresponding to the true potential of the examined alternative. Since this solution generates the Upper Bound to the solution and the supporting function for the construction of each Master subproblem (and thus determining the convergence of the algorithm), efforts should be taken that an accurate solution is found. This is mainly achieved by:

- Accurate physical (process) modelling
- Efficient NLP solution strategies (bounding and initialization)

Having presented the principal components of the GMF, it will be shown how the GMF can be applied and improved for the representation (structural and physical) of distillation columns. This will essentially provide the basis for the distillation column sequencing studies presented in the following chapters.

2.3 GMF Simple Distillation Column Representation

As shown in Appendix A.1, the GMF has been employed for the representation of simple distillation columns. The simple column GMF structural representation requires the use of two Liquid-Vapour M/H modules and two He modules, interconnected as illustrated in Figure 2.2.

Mathematically, this is achieved by fixing the primary binary variables corresponding to the two M/H modules to 1, while using only one He module from each M/H module, *i.e.* the Heater of the lower and the Cooler of the upper M/H module, respectively. The same applies to the interconnections between the building blocks (secondary binary variables), which are fixed to 1 for the existing interconnections and to 0 for the nonexistent.

Physically, each M/H module is an aggregation of trays and represents a column section (*'portion of a column not interrupted by entering or exiting streams or heat flows'*, Hohmann *et al.* (1982)). For the simple column representation, the lower M/H module and its Heater represent the column stripper and reboiler, respectively, while the upper M/H module and its Cooler represent the column rectifier and condenser, respectively. The accompanying physical model is based on the fact that, since trays in the column sections are not considered, a tray-by-tray model is not employed and thus the stagewise equilibrium constraints are being replaced by Driving Force Constraints at the two M/H modules' boundaries, according to the type of

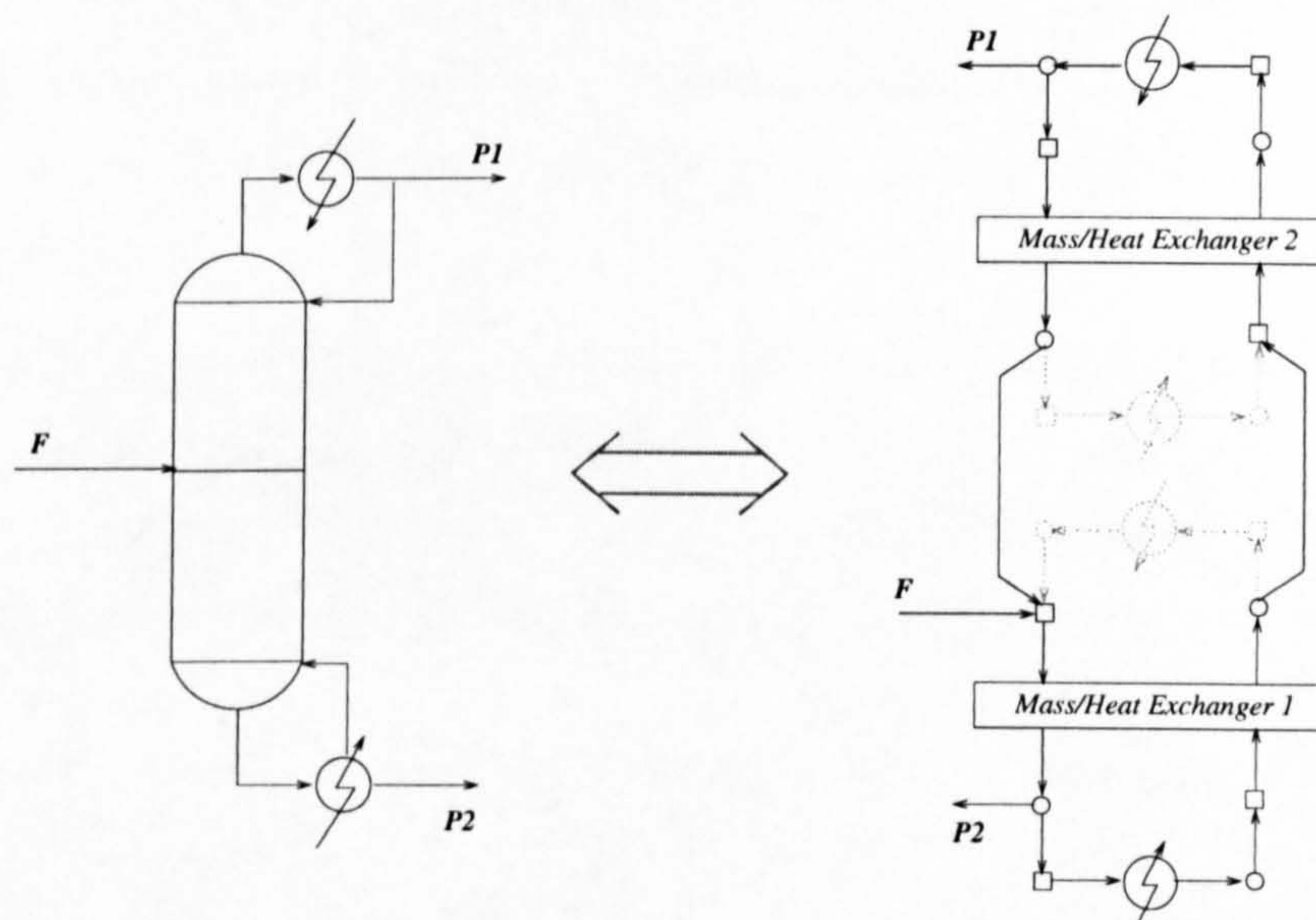


Figure 2.2: Conventional and GMF Representations of a Simple Column

contact (countercurrent in distillation). These constraints along with the Phase Defining and the conservation law constraints ensure mass and heat transfer feasibility and define the distribution of the components in the existing building blocks.

The main motivation and advantages derived from the representation of distillation columns through the GMF are summarized below:

- (i) The method is not limited by simplifying assumptions of sharp splits but it allows the free distribution of components. Therefore, the framework provides a more accurate and general representation of the physical phenomena taking place in a distillation column.
- (ii) No simplifying assumptions of equimolar flowrates and constant volatilities or shortcut calculations are employed, increasing the reliability and applicability of the method.
- (iii) The suggested framework represents columns in an aggregated way, not requiring the solution of detailed tray-by-tray synthesis problems (determination of number of trays, feed tray and, for complex columns, side stream tray location(s)), leading to smaller and easier to solve problems.
- (iv) The Driving Force and the Phase Defining Constraints which are responsible for the mass transfer and distribution of the components can represent columns operating at conditions of phase equilibrium or nonequilibrium. If equilibrium prevails, the streams leaving the module (corresponding to the liquid and vapour exiting streams of the first and last trays of the section) should be saturated. This would be derived from the Phase Defining Constraints.
- (v) The framework is not limited to the representation of simple columns but can be readily extended to the synthesis of both simple and complex distillation columns and their sequences. In this case the physical model of the GMF Building Blocks remains the same and only the GMF Structural Model needs to be adjusted.

However, before developing GMF Structural Models for the sequencing problems defined in the Synthesis Target of this work, the current physical model of the M/H modules need to be appropriately modified, in order for the GMF to capture the underlying physical phenomena more accurately and consistently, thus further improving its representational validity.

2.3.1 GMF Physical Modelling Issues Revisited

The GMF has been utilized and proven successful in capturing the mass and heat exchange phenomena of various types of separation, reaction and heat exchange processes. This has been achieved in a generalized manner using only fundamental principles and without including unit specific design equations. However, it has been observed that for phenomena with simultaneous mass and heat exchange (such as distillation), although the framework managed to capture successfully the general trends of the process, such as component distributions and energy consumption, it exhibited some temperature-related discrepancies (Proios, 1999). For instance, temperature profiles have been encountered for ideal separations which showed an upper section of a represented column operating at a higher temperature than a lower section. Since this behaviour can be encountered only in nonideal distillation, it necessitated the close examination of some of the modelling principles behind the GMF.

It has been noted that such discrepancies were occurring in sections where feed streams were entering in the columns. In the GMF, the feed streams, the product streams and the interconnecting streams do not enter or exit a module directly. Instead they enter in the liquid or vapour side mixer and they exit from the liquid or vapour side splitter, according to their phase (Figure 2.3.a). The phase of each stream is defined through the Phase Defining Constraints which state that, if a stream is considered liquid, then it has to be subcooled or, at the limit, saturated and a vapour stream superheated or, at the limit, saturated.

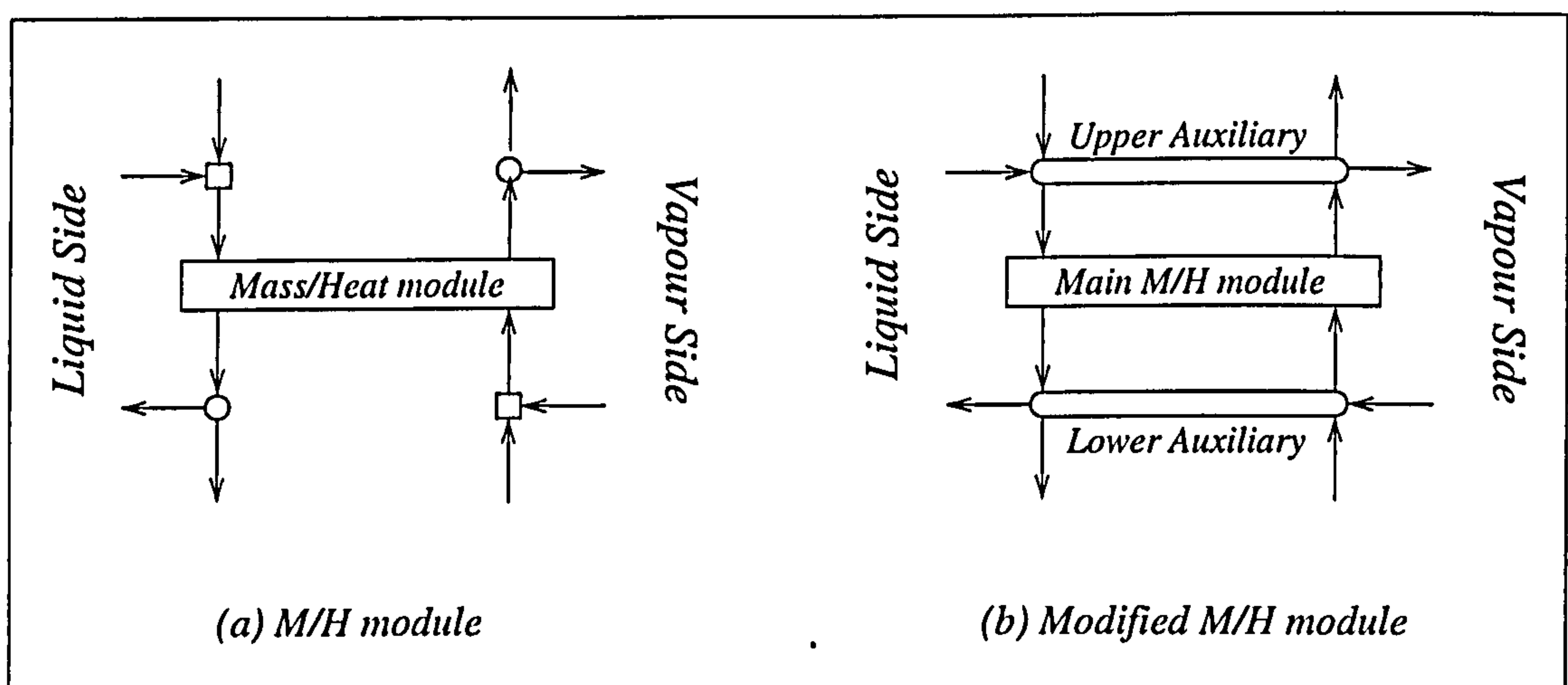


Figure 2.3: Proposed mixer and splitter reformulation

Since the temperature discrepancies were occurring at the mixers, the principles of the GMF around the mixers were analyzed. In the vapour side mixers, only streams that were considered vapour (and imposed as such by the Phase Defining Constraints) were allowed to be mixed. The effluent stream was also imposed to be of the vapour phase (by the same type of Phase Defining Constraints). The same was imposed for the liquid mixers. This type of mixing in the superstructure mixers originated from simplified network studies, such as Mass Exchange Networks (Papalexandri *et al.*, 1995) and Distillation Column Networks (Aggarwal and Floudas, 1990), where temperature differences between streams were considered minimal and no energy balances were included. However, using these principles in the GMF mixers had the implication of imposing the generation of single phase streams from the mixing of streams of the same phase, but of different temperatures and compositions. This assumption does not always hold since the mixing of same phase streams but of different compositions and temperatures does not always guarantee a single phase. The consequence was that the temperatures of the streams involved had to be adjusted accordingly, in order to *impose* single phase conditions in the outflowing streams of the superstructure mixers, thus leading to the temperature profile discrepancies.

In order to rectify this situation, the following actions are proposed. From a structural point of view, the liquid mixer and the vapour splitter from the upper end of a M/H module are incorporated into an Upper Auxiliary block (Figure 2.3.b). That means that if the mixed liquid streams develop a vapour fraction then this will be removed through the effluent vapour stream(s) of this Auxiliary block. The same is done for the vapour mixer and liquid splitter at the lower side of the M/H module forming a Lower Auxiliary block.

The Auxiliary block physical model will have the following constraints:

- Total Mass Balance
- Component Mass Balances, for all components
- Molar Fraction Summation Corrections
- Energy Balance
- Phase Defining Constraints for the exiting liquid and vapour streams

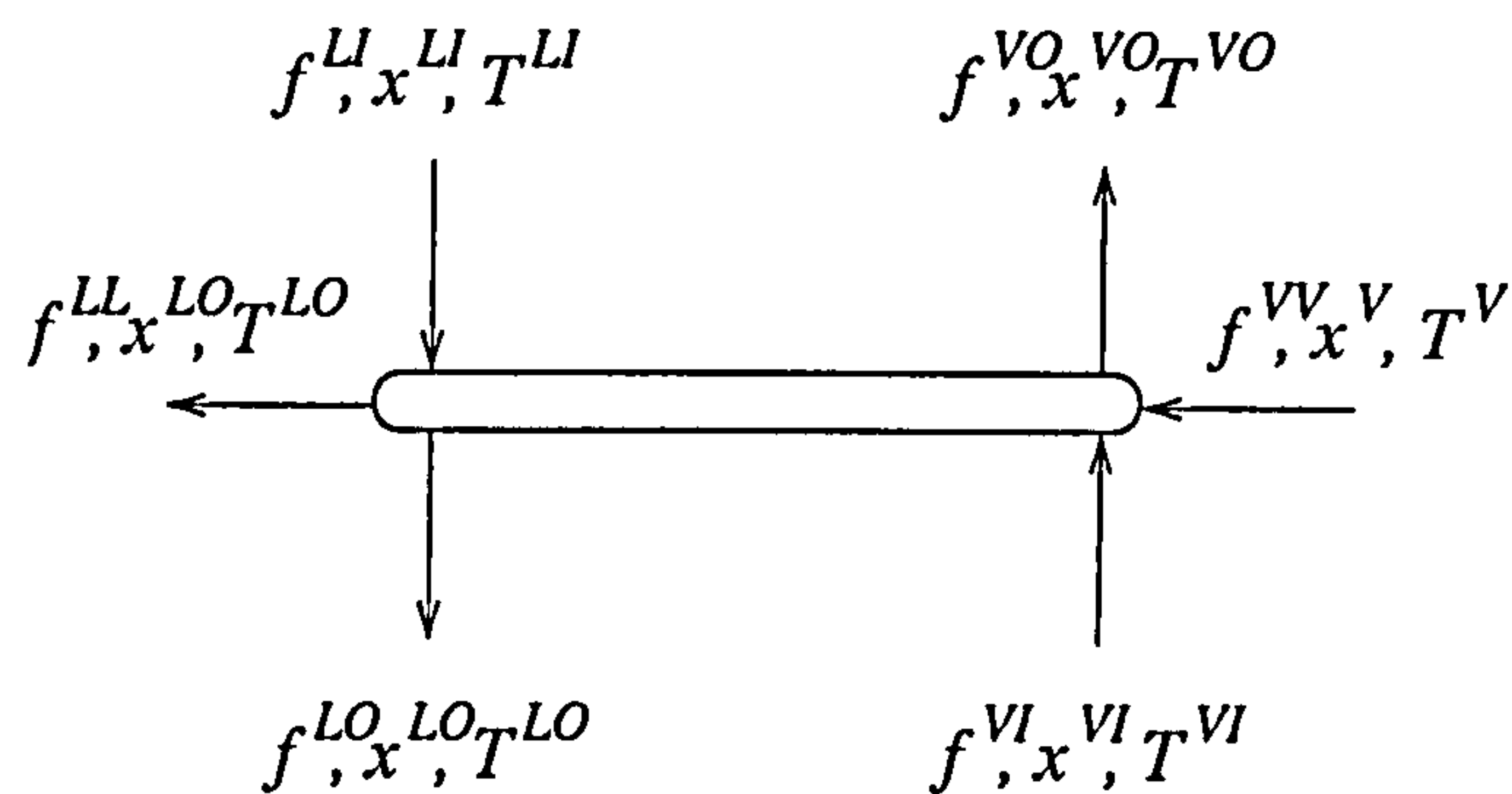


Figure 2.4: Details of a (Lower) Auxiliary block

Remark

The above constraints do not include any phase equilibrium relations between the exiting vapour and liquid streams. If equilibrium relations are to be imposed, then each Auxiliary block will be essentially a multifeed flash and the exiting streams will be saturated (rendering the Phase Defining Constraints redundant). Then, the temperature within each Auxiliary block will be constant and the exiting streams will be at the same temperature (thermal equilibrium). However, it is an open question if equilibrium relations have to be applied. A closer look at the constraints and the degrees of freedom of an Auxiliary block has proved of assistance at this stage. For this analysis, a lower Auxiliary block is employed, as shown in Figure 2.4.

Constraints

- Total Mass Balance

$$f^{LI} + f^{VI} + f^{VV} - f^{LO} - f^{VO} - f^{LL} = 0 \quad (2.1)$$

- Component Mass Balances

$$f^{LI}x_c^{LI} + f^{VI}x_c^{VI} + f^{VV}x_c^V - f^{LO}x_c^{LO} - f^{VO}x_c^{VO} - f^{LL}x_c^{LO} = 0, \quad \forall c \quad (2.2)$$

- Energy Balance

$$f^{LI}h(\underline{x}^{LI}, T^{LI}, P) + f^{VI}h(\underline{x}^{VI}, T^{VI}, P) + f^{VV}h(\underline{x}^V, T^V, P) - f^{LO}h(\underline{x}^{LO}, T^{LO}, P) - f^{VO}h(\underline{x}^{VO}, T^{VO}, P) - f^{LL}h(\underline{x}^{LO}, T^{LO}, P) = 0 \quad (2.3)$$

- Molar Fraction Summation Corrections

$$\sum_c (x_c^{LO} - x_c^{VO}) = 0 \quad (2.4)$$

Total: $3+C$

Variables

$f^{LI}, f^{LO}, f^{LL}, f^{VI}, f^{VO}, f^{VV}, x_c^{LI}, x_c^{LO}, x_c^{VI}, x_c^{VO}, x_c^V, T^{LI}, T^{LO}, T^{VI}, T^{VO}, T^V, P$

Total: $12+5*C$

Known (from other blocks):

$f^{VV}, T^V, x_c^V, f^{LI}, x_c^{LI}, T^{LI}, f^{VI}, x_c^{VI}, T^{VI}$

Total: $6+3*C$

Degrees of Freedom

$$12+5*C-(3+C)-(6+3*C) = 3+C$$

If phase equilibrium constraints are applied (C equations), then thermal equilibrium has to be imposed as well (1 equation), meaning that the Auxiliary block has 2 degrees of freedom remaining (that is, the pressure, P , and the outgoing flowrate, f^{LL} - if more such streams exist they will increase the degrees of freedom by an equal number). In the case where these constraints are not applied, $1+C$ additional degrees of freedom per Auxiliary block will be generated.

From a physical modelling point of view, if the Auxiliary blocks are modelled so that no mass exchange takes place between liquid and vapour streams, then no phase equilibrium constraints should be imposed. However, since the Auxiliary blocks are points of entering or exiting streams in distillation columns (feed and sidestream trays) then they should incorporate mass transfer, thus requiring the use of phase equilibrium constraints.

As a final point of consideration, it must be stated that as indicated in page 18 of this thesis, one of the advantages of the GMF is that it does not require assumptions of phase equilibrium. Therefore, an argument against using equilibrium constraints for the Auxiliary blocks is that the above advantage will be lost. At the same time there is the argument in favour of the above equilibrium constraints which states that, since phase equilibrium will be applied *solely* to the Auxiliary blocks, which represent only a small and supplementary part of the complete set of the GMF building blocks, the advantage in question will be preserved. This and the enhancement of the GMF physical representation in the examined case studies has led to the formal incorporation of the Upper and Lower Auxiliary blocks in each GMF M/H module.

2.3.2 GMF Simple Distillation Column Structural Model

The revised GMF Building Blocks employed for the representation of a simple distillation column with their associated binary and continuous variables and other structural components are given in Figure 2.5. The GMF Structural Model for the examined problem, as indicated before, is generated by the utilized building blocks and their interconnection principles. For the distillation column representation/synthesis the following general interconnection principles are considered, which should be added to the generic ones of Section 2.1.1:

- M/H modules are numbered from bottom to top.
- If a feed is given as liquid (saturated), it must be directed to the Upper Auxiliary block of an odd-numbered M/H module. Any different feed phase can be accordingly accommodated.
- Heaters of even-numbered M/H modules are discarded, same as Coolers of odd-numbered M/H modules.
- M/H and Cooler module vapour interconnections (VC) occur only between a M/H module and its accompanying (same module number) Cooler.

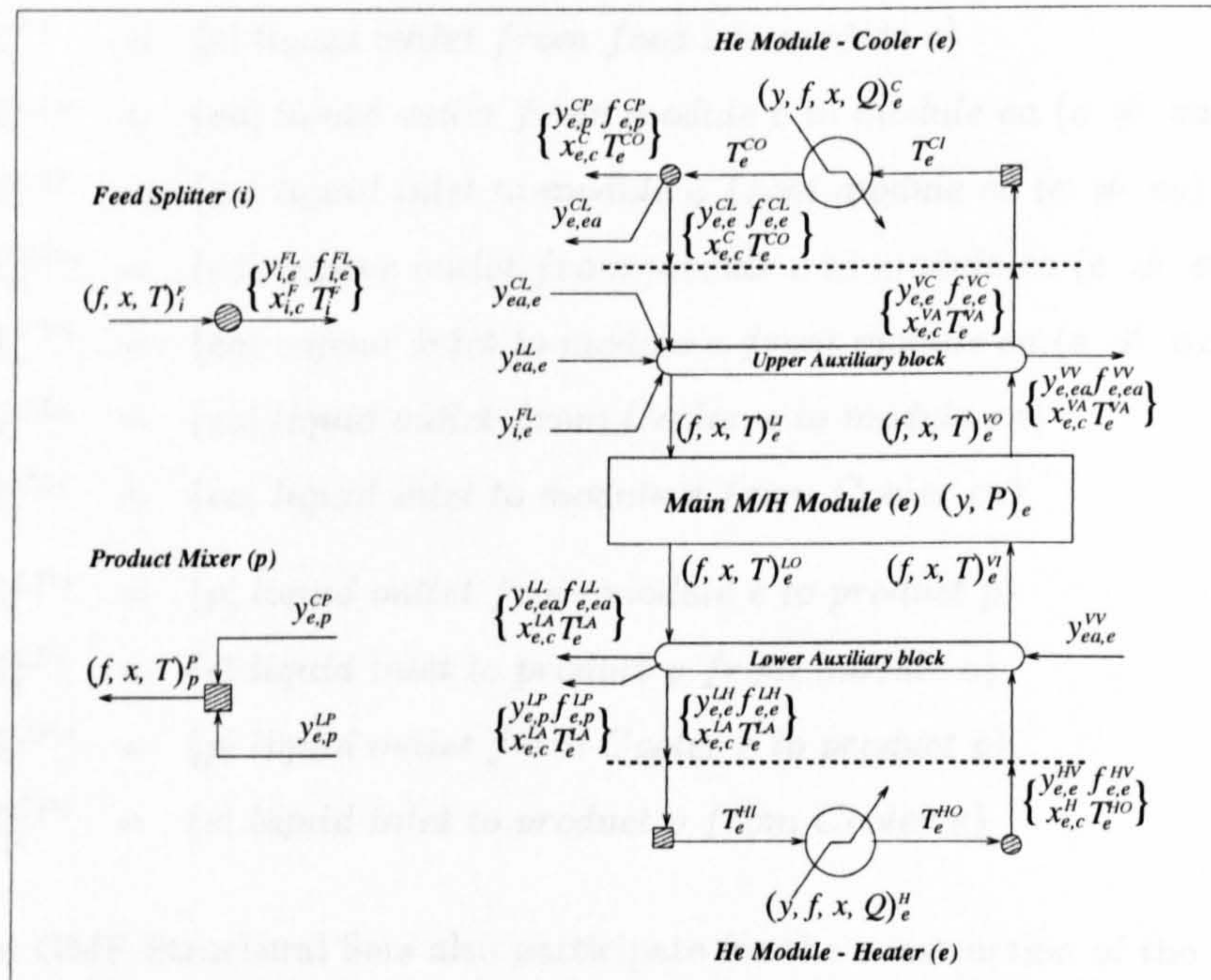


Figure 2.5: Details of the GMF Structural Components for Distillation Representation

- M/H and Heater module liquid interconnections (LH) occur only between a M/H module and its accompanying Heater.
- Heater and M/H module vapour interconnections (HV) occur only between a M/H module and its accompanying Heater.
- Liquid (saturated) product streams, are drawn by liquid streams from Coolers and Lower Auxiliary blocks. Similarly to the feeds' treatment, any different product phase can be accommodated accordingly.

For the mathematical translation of the above Interconnection Principles for the distillation problem, the following GMF Structural Sets are defined:

$$\begin{aligned}
 I &= \{i \mid \text{available feeds}\} \\
 C &= \{c \mid \text{components}\} \\
 P &= \{p \mid \text{product streams}\} \\
 E &= \{e \mid \text{available } M/H \text{ modules}\} \\
 E^H &= \{e \mid \text{available Heater modules (odd module numbers)}\} \\
 E^C &= \{e \mid \text{available Cooler modules (even module numbers)}\} \\
 E_i^{FL} &= \{e \mid \text{liquid outlet from feed } i \text{ to module } e\} \\
 E_e^{LLo} &= \{ea \mid \text{liquid outlet from module } e \text{ to module } ea \ (e \neq ea)\} \\
 E_e^{LLi} &= \{ea \mid \text{liquid inlet to module } e \text{ from module } ea \ (e \neq ea)\} \\
 E_e^{VVo} &= \{ea \mid \text{vapour outlet from module } e \text{ to module } ea \ (e \neq ea)\} \\
 E_e^{VVi} &= \{ea \mid \text{vapour inlet to module } e \text{ from module } ea \ (e \neq ea)\} \\
 E_e^{CLo} &= \{ea \mid \text{liquid outlet from Cooler } e \text{ to module } ea\} \\
 E_e^{CLi} &= \{ea \mid \text{liquid inlet to module } e \text{ from Cooler } ea\} \\
 E_e^{LPo} &= \{p \mid \text{liquid outlet from module } e \text{ to product } p\} \\
 E_p^{LPi} &= \{e \mid \text{liquid inlet to product } p \text{ from module } e\} \\
 E_e^{CPo} &= \{p \mid \text{liquid outlet from Cooler } e \text{ to product } p\} \\
 E_p^{CPi} &= \{e \mid \text{liquid inlet to product } p \text{ from Cooler } e\}
 \end{aligned}$$

The above GMF Structural Sets also participate for the construction of the GMF Physical Model. For the automatic solution of the complete GMF model, the GMF Physical and Structural Models need to interact and to exchange information. Using the Structural Sets in the

Physical Model, reduces the problem size, since physically infeasible conditions (for instance, redundant mixing and splitting) are not considered.

2.3.3 GMF Physical Model For Distillation Columns

The GMF Physical Model is generated for each chosen structural alternative through the corresponding physical model of each one of the *existing* building blocks and their interconnections. For this reason and due to the fact that the GMF Structural and Physical Models are decomposed during the MINLP solution, new Structural Sets are developed for the generation of the GMF Physical Model, representing the *existing* building blocks in each iteration (building blocks whose primary binary variables are 1). These sets are not static since their members are updated after the generation of each structure (from the solution of each Master subproblem). A discussion on this formulation follows at the end of this section. For simplicity reasons an index denoting the iteration counter on these sets is omitted.

$$\begin{aligned} E^E &= \{e \mid \text{existing } M/H \text{ modules } (y_e = 1)\}, & \text{where } E^E \subseteq E \\ E^{HE} &= \{e \mid \text{existing Heater modules } (y_e^H = 1)\}, & \text{where } E^{HE} \subseteq E^H \\ E^{CE} &= \{e \mid \text{existing Cooler modules } (y_e^C = 1)\}, & \text{where } E^{CE} \subseteq E^C \end{aligned}$$

Feed Splitter

The feed splitter (Figure 2.5) is a fixed structural component of the GMF and does not form an additional building block, nor does it require the assignment of a binary variable to it. In each problem the number of feed splitters will be equal to the number of feeds in the Set I .

- Mass Balances

$$\sum_{e \in E_i^{FL}} f_{i,e}^{FL} - f_i^F = 0, \quad i \in I \quad (2.5)$$

- Phase Defining Constraints (for saturated liquid feeds)

$$\sum_{c \in C} (x_{i,c}^F K_{i,c}^F) - 1 = 0, \quad i \in I \quad (2.6)$$

- Mixed Integer physical-structural Constraints

$$f_{i,e}^{FL} - y_{i,e}^{FL} \mathcal{F}^{max} \leq 0, \quad i \in I, e \in E_i^{FL} \quad (2.7)$$

M/H Module

As it can be seen in Figure 2.5, each *M/H* module *always* consists of an Upper Auxiliary, of a Main *M/H* and of a Lower Auxiliary block. However, each one of these blocks has a different physical model, as given below:

Upper Auxiliary Block

- Mass, Component and Energy Balances

$$f_e^{LI} + f_{e,e}^{VC} + \sum_{ea \in E_e^{VV_o}} f_{e,ea}^{VV} - f_e^{VO} - \sum_{i \in E_e^{FL}} f_{i,e}^{FL} - \sum_{ea \in E_e^{LL_i}} f_{ea,e}^{LL} - \sum_{ea \in E_e^{CL_i}} f_{ea,e}^{CL} = 0, \quad e \in E^E \quad (2.8)$$

$$f_e^{LI} x_{e,c}^{LI} + \left(f_{e,e}^{VC} + \sum_{ea \in E_e^{VV_o}} f_{e,ea}^{VV} \right) x_{e,c}^{VA} - f_e^{VO} x_{e,c}^{VO} - \sum_{i \in E_e^{FL}} f_{i,e}^{FL} x_{i,c}^F - \sum_{ea \in E_e^{LL_i}} f_{ea,e}^{LL} x_{ea,c}^{LA} - \sum_{ea \in E_e^{CL_i}} f_{ea,e}^{CL} x_{ea,c}^C = 0, \quad e \in E^E, c \in C \quad (2.9)$$

$$f_e^{LI} h_e^{LI} + \left(f_{e,e}^{VC} + \sum_{ea \in E_e^{VV_o}} f_{e,ea}^{VV} \right) h_e^{VA} - f_e^{VO} h_e^{VO} - \sum_{i \in E_e^{FL}} f_{i,e}^{FL} h_i^F - \sum_{ea \in E_e^{LL_i}} f_{ea,e}^{LL} h_{ea}^{LA} - \sum_{ea \in E_e^{CL_i}} f_{ea,e}^{CL} h_{ea}^{CO} = 0, \quad e \in E^E \quad (2.10)$$

- Phase and Thermal Equilibrium and Molar Fraction Summations

$$x_{e,c}^{VA} - K^{LI}(x_{e,c}^{LI}, x_{e,c}^{VA}, T_e^{LI}, T_e^{VA}, P_e) x_{e,c}^{LI} = 0, \quad e \in E^E, c \in C \quad (2.11)$$

$$T_e^{VA} - T_e^{LI} = 0, \quad e \in E^E \quad (2.12)$$

$$\sum_{c \in C} (x_{e,c}^{VA} - x_{e,c}^{LI}) = 0, \quad e \in E^E \quad (2.13)$$

- Mixed Integer Physical-Structural Constraints

$$f_{e,e}^{VC} - y_{e,e}^{VC} \mathcal{F}^{max} \leq 0, \quad e \in E^C \quad (2.14)$$

$$f_{e,ea}^{VV} - y_{e,ea}^{VV} \mathcal{F}^{max} \leq 0, \quad e \in E, ea \in E_e^{VV_o} \quad (2.15)$$

Main M/H Block

- Mass, Component and Energy Balances

$$f_e^{LO} + f_e^{VO} - f_e^{LI} - f_e^{VI} = 0, \quad e \in E^E \quad (2.16)$$

$$f_e^{LO} x_{e,c}^{LO} + f_e^{VO} x_{e,c}^{VO} - f_e^{LI} x_{e,c}^{LI} - f_e^{VI} x_{e,c}^{VI} = 0, \quad e \in E^E, c \in C \quad (2.17)$$

$$f_e^{LO} h_e^{LO} + f_e^{VO} h_e^{VO} - f_e^{LI} h_e^{LI} - f_e^{VI} h_e^{VI} = 0, \quad e \in E^E \quad (2.18)$$

- Driving Force Constraints and Molar Fraction Summation Corrections

$$(f_e^{VI} x_{e,c}^{VI} - f_e^{VO} x_{e,c}^{VO}) (x_{e,c}^{VI} - x_{e,c}^{LO} K_{e,c}^{LO}) \geq 0, \quad e \in E^E, c \in C \quad (2.19)$$

$$(f_e^{VI} x_{e,c}^{VI} - f_e^{VO} x_{e,c}^{VO}) (x_{e,c}^{VO} - x_{e,c}^{LI} K_{e,c}^{LI}) \geq 0, \quad e \in E^E, c \in C \quad (2.20)$$

$$\sum_{c \in C} (x_{e,c}^{VO} - x_{e,c}^{LO}) = 0, \quad e \in E^E \quad (2.21)$$

- Phase Defining Constraints

$$\sum_{c \in C} (x_{e,c}^{VO} / K_{e,c}^{VO}) - 1 \leq 0, \quad e \in E^E \quad (2.22)$$

$$\sum_{c \in C} (x_{e,c}^{LO} K_{e,c}^{LO}) - 1 \leq 0, \quad e \in E^E \quad (2.23)$$

- Mixed Integer Physical-Structural Constraints

$$f_e^{LO} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (2.24)$$

$$f_e^{LI} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (2.25)$$

$$f_e^{VO} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (2.26)$$

$$f_e^{VI} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (2.27)$$

Lower Auxiliary Block

- Mass, Component and Energy Balances

$$f_e^{VI} + f_{e,e}^{LH} + \sum_{ea \in E_e^{LLo}} f_{e,ea}^{LL} + \sum_{p \in E_e^{LPo}} f_{e,p}^{LP} - f_e^{LO} - f_{e,e}^{HV} - \sum_{ea \in E_e^{VV i}} f_{ea,e}^{VV} = 0 \quad e \in E^E \quad (2.28)$$

$$\begin{aligned} f_e^{VI} x_{e,c}^{VI} + \left(f_{e,e}^{LH} + \sum_{ea \in E_e^{LLo}} f_{e,ea}^{LL} + \sum_{p \in E_e^{LPo}} f_{e,p}^{LP} \right) x_{e,c}^{LA} - f_e^{LO} x_{e,c}^{LO} - f_{e,e}^{HV} x_{e,c}^H \\ - \sum_{ea \in E_e^{VV i}} f_{ea,e}^{VV} x_{ea,c}^{VA} = 0, \quad e \in E^E, c \in C \end{aligned} \quad (2.29)$$

$$\begin{aligned} f_e^{VI} h_e^{VI} + \left(f_{e,e}^{LH} + \sum_{ea \in E_e^{LLo}} f_{e,ea}^{LL} + \sum_{p \in E_e^{LPo}} f_{e,p}^{LP} \right) h_e^{LA} - f_e^{LO} h_e^{LO} - f_{e,e}^{HV} h_e^{HO} \\ - \sum_{ea \in E_e^{VV i}} f_{ea,e}^{VV} h_{ea}^{VA} = 0, \quad e \in E^E \end{aligned} \quad (2.30)$$

- Phase and Thermal Equilibrium and Molar Fraction Summation Corrections

$$x_{e,c}^{VI} - K^{LA}(x_{e,c}^{VI}, x_{e,c}^{LA}, T_e^{VI}, T_e^{LA}, P_e) x_{e,c}^{LA} = 0, \quad e \in E^E, c \in C \quad (2.31)$$

$$T_e^{VI} - T_e^{LA} = 0, \quad e \in E^E \quad (2.32)$$

$$\sum_{c \in C} (x_{e,c}^{VI} - x_{e,c}^{LA}) = 0, \quad e \in E^E \quad (2.33)$$

- Mixed Integer Physical-Structural Constraints

$$f_{e,e}^{LH} - y_{e,e}^{LH} \mathcal{F}^{max} \leq 0, \quad e \in E^H \quad (2.34)$$

$$f_{e,p}^{LP} - y_{e,p}^{LP} \mathcal{F}^{max} \leq 0, \quad e \in E, p \in E_e^{LPo} \quad (2.35)$$

$$f_{e,ea}^{LL} - y_{e,ea}^{LL} \mathcal{F}^{max} \leq 0, \quad e \in E, ea \in E_e^{LLo} \quad (2.36)$$

Cooler Module

The Cooler module (Figure 2.5) is a *He* module where only heat exchange takes place between a process and a cold utility stream. It is a formal GMF Building Block and has a primary binary variable associated with it.

- Mass, Component and Energy Balances

$$f_e^C - f_{e,e}^{VC} = 0, \quad e \in E^{CE} \quad (2.37)$$

$$\sum_{ea \in E_e^{CLo}} f_{e,ea}^{CL} + \sum_{p \in E_e^{CPo}} f_{e,p}^{CP} - f_e^C = 0, \quad e \in E^{CE} \quad (2.38)$$

$$f_e^C x_{e,c}^C - f_{e,e}^{VC} x_{e,c}^{VA} = 0, \quad e \in E^{CE}, c \in C \quad (2.39)$$

$$f_e^C h_e^{CI} - f_{e,e}^{VC} h_e^{VA} = 0, \quad e \in E^{CE} \quad (2.40)$$

$$Q_e^C - f_e^C (h_e^{CI} - h_e^{CO}) = 0, \quad e \in E^{CE} \quad (2.41)$$

- Phase Defining Constraints

$$\sum_{c \in C} (x_{e,c}^C / K_{e,c}^{CI}) - 1 \leq 0, \quad e \in E^{CE} \quad (2.42)$$

$$\sum_{c \in C} (x_{e,c}^C K_{e,c}^{CO}) - 1 \leq 0, \quad e \in E^{CE} \quad (2.43)$$

- Mixed Integer Physical-Structural Constraints

$$f_e^C - y_e^C \mathcal{F}^{max} \leq 0, \quad e \in E^C \quad (2.44)$$

$$f_{e,ea}^{CL} - y_{e,ea}^{CL} \mathcal{F}^{max} \leq 0, \quad e \in E^C, ea \in E_e^{CLo} \quad (2.45)$$

$$f_{e,p}^{CP} - y_{e,p}^{CP} \mathcal{F}^{max} \leq 0, \quad e \in E^C, p \in E_e^{CPo} \quad (2.46)$$

$$Q_e^C - y_e^C Q^{max} \leq 0, \quad e \in E^C \quad (2.47)$$

$$T^{cw} - T_e^{CI} + EMTA - \mathcal{M}^C (1 - y_e^C) \leq 0, \quad e \in E^C \quad (2.48)$$

$$T^{cw} - T_e^{CO} + EMTA - \mathcal{M}^C (1 - y_e^C) \leq 0, \quad e \in E^C \quad (2.49)$$

In the above constraints *EMTA* stands for the Exchange Minimum Temperature Approach.

Heater Module

The Heater module (Figure 2.5) is also a *He* module with a primary binary variable associated to it, where heat exchange takes place between a process and a hot utility stream.

- Mass, Component and Energy Balances

$$f_e^H - f_{e,e}^{LH} = 0, \quad e \in E^{HE} \quad (2.50)$$

$$f_{e,e}^{HV} - f_e^H = 0, \quad e \in E^{HE} \quad (2.51)$$

$$f_e^H x_{e,c}^H - f_{e,e}^{LH} x_{e,c}^{LA} = 0, \quad e \in E^{HE}, c \in C \quad (2.52)$$

$$f_e^H h_e^{HI} - f_{e,e}^{LH} h_e^{LA} = 0, \quad e \in E^{HE} \quad (2.53)$$

$$Q_e^H - f_e^H (h_e^{HO} - h_e^{HI}) = 0, \quad e \in E^{HE} \quad (2.54)$$

- Phase Defining Constraints

$$\sum_{c \in C} (x_{e,c}^H K_{e,c}^{HI}) - 1 \leq 0, \quad e \in E^{HE} \quad (2.55)$$

$$\sum_{c \in C} (x_{e,c}^H / K_{e,c}^{HO}) - 1 \leq 0, \quad e \in E^{HE} \quad (2.56)$$

- Mixed Integer Physical-Structural Constraints

$$f_e^H - y_e^H \mathcal{F}^{max} \leq 0, \quad e \in E^H \quad (2.57)$$

$$f_{e,e}^{HV} - y_{e,e}^{HV} \mathcal{F}^{max} \leq 0, \quad e \in E^H \quad (2.58)$$

$$Q_e^C - y_e^C Q^{max} \leq 0, \quad e \in E^H \quad (2.59)$$

$$T_e^{HI} - T^{st} + EMTA - \mathcal{M}^H (1 - y_e^H) \leq 0, \quad e \in E^H \quad (2.60)$$

$$T_e^{HO} - T^{st} + EMTA - \mathcal{M}^H (1 - y_e^H) \leq 0, \quad e \in E^H \quad (2.61)$$

Product Mixer

The product mixer (Figure 2.5), like the feed splitter, is an integral structural component of the GMF framework. The product mixers are not treated as separate GMF Building Blocks and, thus, no binary variables are attached to them. Their existence depends inherently on the number of product streams, as defined by Set P in the synthesis problem statement.

- Mass, Component and Energy Balances

$$f_p^P - \sum_{e \in E_p^{LP}} f_{e,p}^{LP} - \sum_{e \in E_p^{CP}} f_{e,p}^{CP} = 0, \quad p \in P \quad (2.62)$$

$$f_p^P x_{p,c}^P - \sum_{e \in E_p^{LP}} f_{e,p}^{LP} x_{e,c}^{LA} - \sum_{e \in E_p^{CP}} f_{e,p}^{CP} x_{e,c}^C = 0, \quad p \in P, c \in C \quad (2.63)$$

$$f_p^P h_p^P - \sum_{e \in E_p^{LP}} f_{e,p}^{LP} h_e^{LA} - \sum_{e \in E_p^{CP}} f_{e,p}^{CP} h_e^{CO} = 0, \quad p \in P \quad (2.64)$$

- Phase Defining Constraints (saturated liquid products)

$$\sum_{c \in C} (x_{p,c}^P K_{e,c}^P) - 1 = 0, \quad p \in P \quad (2.65)$$

Thermodynamic Functions

These equations relate enthalpies and phase equilibrium constants to temperatures and to vapour and liquid molar fractions. Any thermodynamic model can be readily used for their calculation.

$$h^V - h_c^V(x_c^V, T^V) = 0, \quad \forall \text{ stream} \in V \quad (2.66)$$

$$h^L - h_c^L(x_c^L, T^L) = 0, \quad \forall \text{ stream} \in L \quad (2.67)$$

$$K_c^{LV} - K_c(x_c^{LV}, T^{LV}, P) = 0, \quad \forall \text{ stream} \in LV, c \in C \quad (2.68)$$

In the above, L denotes liquid streams ($L: F, LI, LO, LA, CO, HI, P$), V vapour streams ($V: VI, VO, VA, CI, HO$), while LV an appropriate liquid and vapour combination.

Physical Model Formulation Remark

In the GMF formulation, at each iteration the GMF Physical Model is generated *only* for the existing M/H and He modules. This can be achieved due to the decomposition approach employed for the solution of the generated MINLP problems and to the versatility of the GAMS programming environment (Brooke *et al.*, 2003), making use of its special \$ (dollar) operators in the definition of each equation. Each Primal subproblem solved takes account of only the necessary information (of *existing* modules and interconnections), thus generating a problem of even

smaller size and avoiding numerical problems related to the disappearance of streams and building blocks. An alternative formulation, would have included, in addition to the existing building blocks' constraints also the '*shadow constraints*' (Ciric and Gu, 1994), that is, constraints referring to *non-existing* building blocks, by multiplying each constraint in the MINLP formulation with the corresponding building block's primary binary variable (*i.e.*, $h_e(x) y_e = 0, e \in E$). This formulation however leads to the generation of highly large and sparse Jacobian matrices (with many zero element lines and rows) and to the potential generation of discontinuities due to the disappearance of flows and building blocks, thus reducing the robustness and overall efficiency of the proposed method. An alternative approach, which shares the same rationale as the employed GMF formulation, utilizes the principles of Generalized Disjunctive Programming (GDP, Yeomans and Grossmann (2000b)). This approach also considers in each Primal subproblem only the *exact* physical model of the chosen structure, by discarding the constraints and variables of the non-existing building blocks of the superstructure.

From a mathematical point of view (according to the GBD methodology), theoretical consistency is maintained since the formulation employed in the GMF and the one with includes the shadow constraints generate the same Master MILP Subproblems. The GBD Master Subproblem for both formulations consists of the same objective functions and constraints. The objective functions consist of the projection of the MINLP problem objective function into the discrete space and of the mixed integer constraints. It must be noted that the latter should include all the constraints of existing or non-existing building blocks where the binary variables participate *within* the functions (*i.e.* $g_e(x, y) \leq 0$). Due to the KKT complementarity conditions, the mixed integer constraints where the binary variables are multiplied externally to the functions (*i.e.* $h_e(x) \cdot y = 0$ or $g_e(x) \cdot y \leq 0$) do not participate in the Master subproblem since their product with their corresponding lagrange multipliers is zero at the solution of the Primal Subproblem. Consequently, in the GMF Master objective function the participating mixed integer constraints are the MINLP problem objective function and the big- M mixed integer Physical-Structural constraints (for flowrates, heat loads and heat exchange feasibility), defined for *all* the building blocks, irrespectively if they exist or not. An analysis of the GBD algorithm for the GMF and the shadow constraint formulations is given in Appendix A.4.

Another remark must be also made on the formulation of the Driving Force Constraints. Due to the high nonlinearity and to the relaxed form of the phase equilibrium relations involved in the Driving Force Constraints, the latter may require particular treatment in order to avoid

problems related to the determination of feasible mass transfer directions. A discussion on this issue and an appropriate reformulation of the Driving Force Constraints were reported in a previous publication (Ismail *et al.*, 1999) where binary variables were introduced for the mass transfer direction of each component, along with a Nested Decomposition MINLP algorithm. This reduced the nonlinearities in the Driving Force Constraints and ensured the derivation of feasible mass transfer patterns. However, since in our work no such problems were encountered, the Driving Force Constraints were employed in the form shown in Equations (2.19) and (2.20).

2.4 Case Study: Binary Distillation Column

2.4.1 Problem Statement

The GMF Physical Model presented in detail in the previous sections, will be validated with a special focus on distillation systems through a motivating case study for the separation of the ideal binary mixture of Benzene and Toluene. The problem data was based on the EX5FEED test problem from Viswanathan and Grossmann (1990) and is given in Table 2.1.

Table 2.1: Binary Distillation Case Study Physical System Data

System	<i>Benzene-Toluene</i>
Thermodynamic Model	<i>Liquid Phase - Ideal</i> <i>Vapour Phase - Ideal</i>
Source of Thermodynamic Data	<i>Reid (1987)</i>
Feed Flowrate	$F = 100 \text{ mol/s}$
Feed Compositions	$x_{F,Benzene} = 0.7$ $x_{F,Toluene} = 0.3$
Column Pressure	$P = 1 \text{ atm}$
Feed Temperature	$T_F = 359.98 \text{ K}$

In the examined problem the column pressure was considered fixed to 1 atm and the feed temperature corresponded to that of the feed bubble point (also at 1 atm). Cubic polynomials in temperature were used for the specific heat capacities, constant values were used for the enthalpy of vaporization and the vapour pressures were calculated using a three coefficient Antoine equation (Reid, 1987). As indicated in Table 2.1, ideal liquid and vapour behaviour were assumed. Although, as already noted, the GMF Physical Model can incorporate any

pre-specified for this GMF structural representation. This is translated mathematically through appropriately assigned Structural Sets and through fixing the primary and secondary binary variables to 0 or to 1 values. The *non-zero* GMF Structural Sets and primary and secondary binary variables are also given in Table 2.3.

Two M/H modules are required (structural set: $E = E^E = \{1, 2\}$) representing the column stripper and rectifier, respectively. Also two He modules (structural sets: $E^{HE} = \{1\}$ and $E^{CE} = \{2\}$) are enforced representing the column reboiler and condenser, respectively. In the figure of Table 2.3, the enforced (existing) building blocks and interconnections are shown with solid lines whereas the heat units in dotted lines depict those removed. For figure clarity reasons the removed interconnections are not shown.

Once the GMF Structural Model is arranged and the structural alternative generated, the column is represented physically by the GMF Physical Model. The latter is mathematically generated by the model of Section 2.3.3 for the Structural Sets and binary variable values of Table 2.3 (3 additional equality constraints are also added, for the definition of the column reflux as $r = f_{2,2}^{CL}/f_{2,P1}^{CP}$ and for fixing each module's pressure to 1 atm). Thus for the GMF representation of a single simple distillation column the GMF generated mathematical problem, is reduced to a Nonlinear Programming Problem (NLP), since the structural alternative is unique and its associated binary variables fully assigned.

From a computational point of view, the problem was implemented in GAMS. From all the GMF Structural Sets only the I , C , P and E sets, were programmed as GAMS SETS. The remaining GMF Structural Sets were programmed as GAMS PARAMETERS, over the aforementioned sets, so that they could be readily used in logical statements (using GAMS dollar operators, \$).

2.4.3 Problem Solution and Results

The generated NLP problem was solved using CONOPT2 (Drud, 1995) as the nonlinear solver and the solution provided the column's energy consumption and an insight of its optimal operating conditions. However, since the focus of this case study is laid upon the accuracy of the GMF distillation physical representation, the latter had to be validated over a well-established rigorous model, which essentially provides the most accurate physical column representation. For this purpose, the GMF-derived results were compared *quantitatively* and *qualitatively*, to those derived using the rigorous tray-by-tray (*MESH*) model of Viswanathan and Grossmann

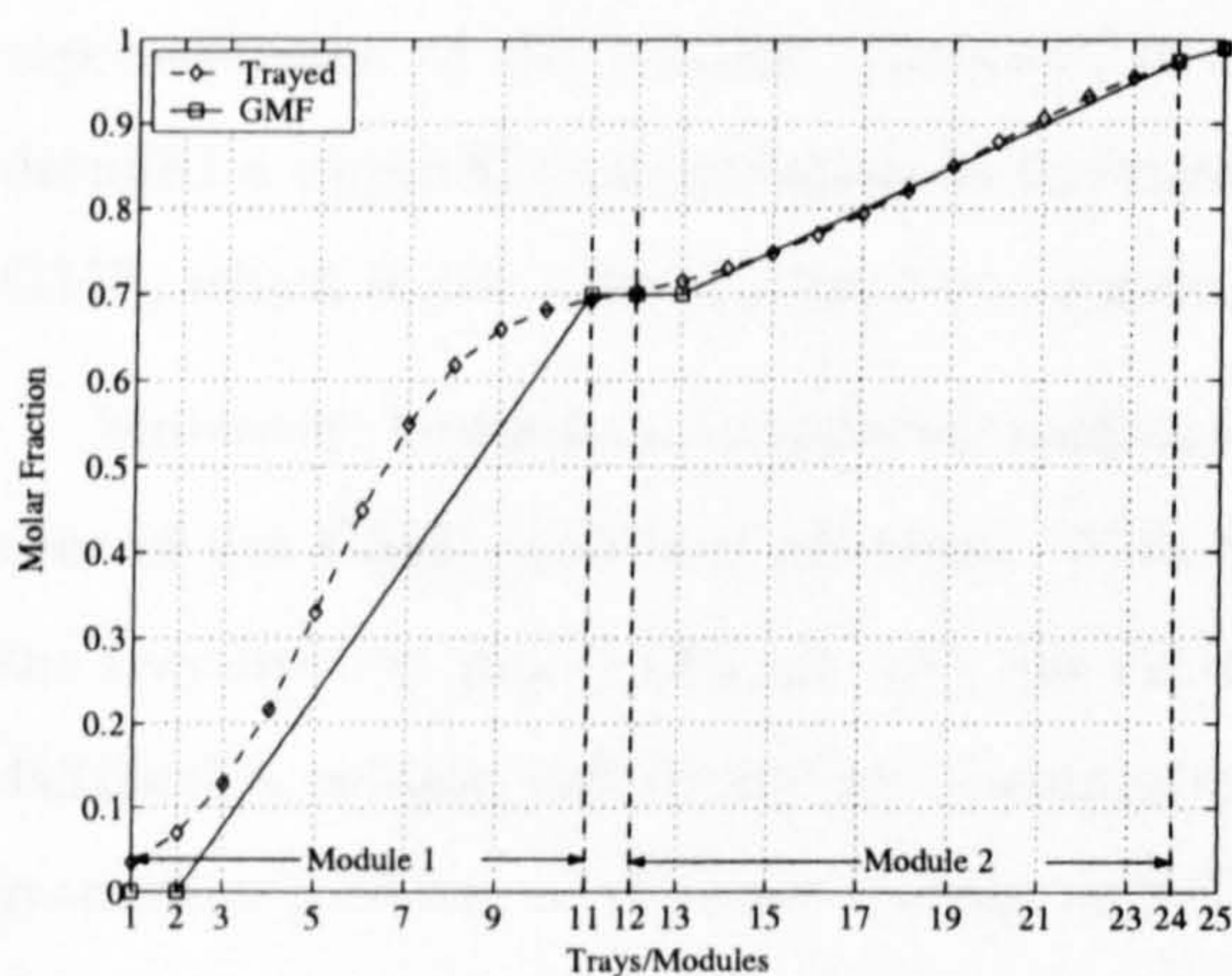
Table 2.4: GMF Quantitative Validation for Binary Distillation

	$Q_{reboiler} \text{ kW}$	$Q_{condenser} \text{ kW}$	$P1 \text{ mol/s}$	r
<i>GMF</i>	4194	4149.5	70.7	0.91
<i>Trayed Model</i>	4401	4398.6	69.7	0.97

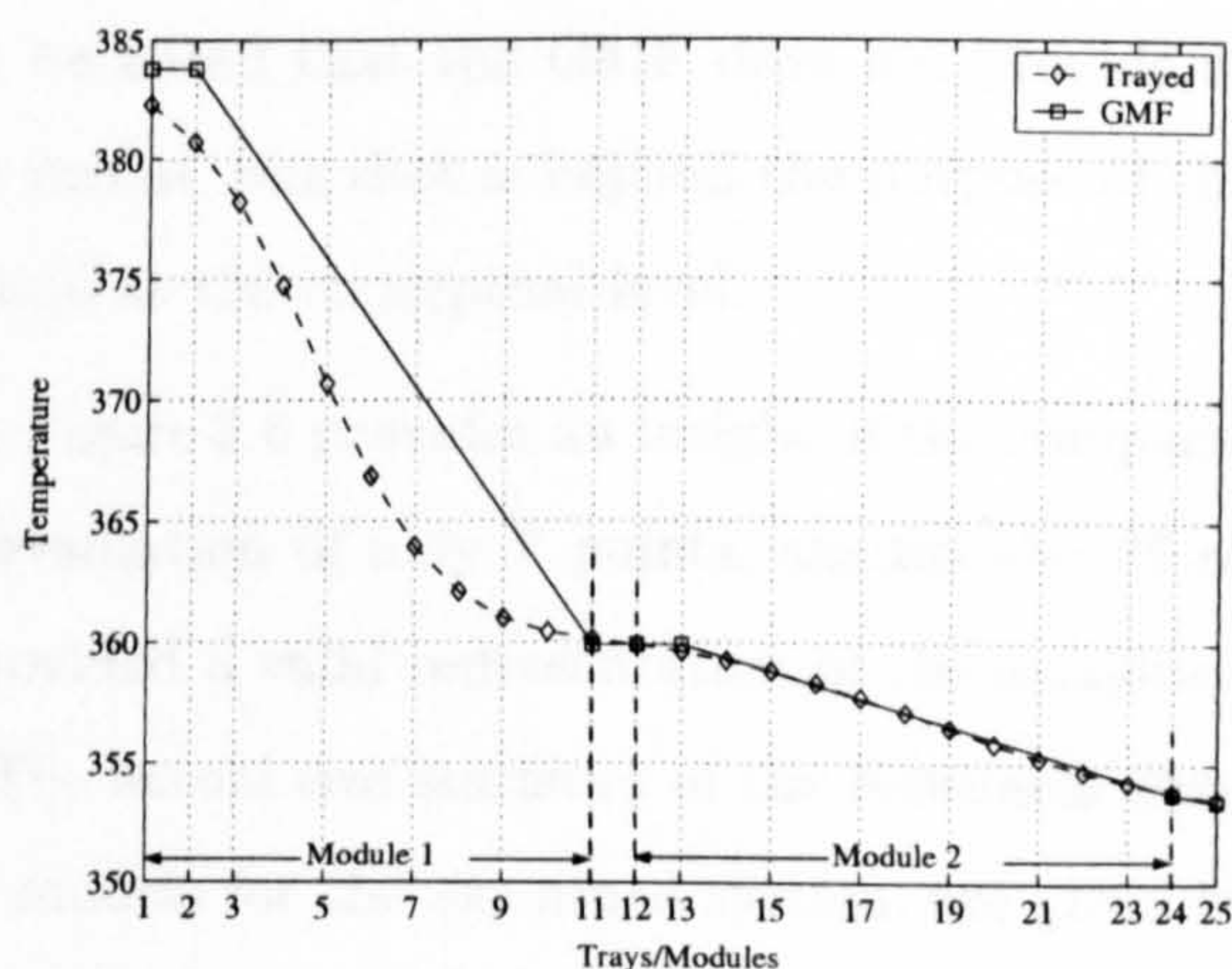
(1993). The problem definition, specifications and objective function were the same as in Section 2.4.1. The design of the column was assumed fixed and was based on the EX5FEED case study data, employing 25 equilibrium stages and with the feed located at the 11th stage from the bottom. The column operating conditions were optimized, thus providing a comparison basis for the GMF representation.

The *quantitative* results of the GMF and tray-by-tray models are shown in Table 2.4. Attention should be given to the energy consumption levels in the reboiler and condenser of the tray-by-tray model and in the Heater and Cooler of the GMF, which are in a *quantitative* agreement. The GMF despite its aggregation provides a valid lower bound to the energy consumption and the energy efficiency of the examined system.

However, for the above quantitative agreement to hold, it should be the direct result of a qualitative agreement, that is, an agreement of the mass and heat transfer phenomena over the column sections/building blocks. This comparison is presented in Figure 2.6, where the GMF



(a) Benzene Composition



(b) Temperature Profile

Figure 2.6: GMF Qualitative Validation for Binary Distillation

Table 2.5: Binary Distillation Optimization Statistics

	Trayed	GMF	% Difference
Continuous Variables	283	134	53%
Continuous Equalities	282 †	127 ‡	55%

where:

$$C=2, N=25, E^E=2, E^{CE}=E^{HE}=1, P=2, I=1$$

$$† N(3C+5)+2I+5 = 282$$

$$‡ E^E(11C+18)+(E^{CE}+E^{HE})(3C+6)+P(2C+4)+I(C+3)+2 = 127$$

and rigorous model results are plotted on the same graphs. Since the GMF does not provide information at the tray level, in order to realize this comparison, the feed location in the GMF representation (boundary of M/H modules 1 and 2) was placed on the corresponding feed tray of the rigorous model, so that along with the column top and bottom, a common x -axis could be constructed.

The results for both sections of the binary column demonstrate the *qualitative* agreement of the two models. As can be seen, the GMF captures the general trends of the components' distribution and the temperature profile in the examined parts of the column. It must be noted that this qualitative agreement between the two models has been particularly aided by the incorporation of the Auxiliary blocks in each GMF M/H module. This led to the elimination of any inconsistencies in the GMF temperature profiles and helped provide a more accurate physical representation of the column. However, it must be noted that the GMF does not provide as detailed a physical representation as the rigorous model, but that is beyond the purpose of the GMF, which is not a simulation but a synthesis tool at the conceptual level.

Moreover, beyond the qualitative comparison, Figure 2.6 provides an insight of the compactness of the GMF generated problem. With the evaluation of only 7 points, against the 25 of the tray-by-tray model (Figure 2.6), the GMF provided a valid representation of the examined distillation column and its energy consumption. The actual size statistics of the Nonlinear Programming problem of the tray-by-tray and GMF models for the examined system, are given in Appendix A.6 and summarized in Table 2.5.

From this table, it is apparent that the aggregation in the GMF representation leads to a significantly smaller problem to solve compared to that of the trayed model. Moreover, while

the size of the trayed model increases with any additional tray, the size of the GMF problem remains the same, as long as the number of sections remains the same. For instance, if the number of trays in the examined problem increases from 25 to 35 (which is a moderate number of trays for a distillation column) the number of equality constraints becomes 385 and the size difference by employing the GMF representation becomes 67% (the size of the GMF-generated problem becomes $1/3$ of that of the trayed model). This GMF Physical Model advantage can have substantial effects on the computational effort, especially when columns of large numbers of trays are employed. Another remark related to the problem statistics is that the GMF in its present form can only be used for optimization and not simulation purposes. This is due to the aggregated nature of the GMF which requires the replacement of the equilibrium relations (equality constraints) in each M/H block by appropriate Driving Force Constraints (inequality constraints). However, as will be shown in Chapter 6, while the GMF will be enhanced employing Order Reduction techniques, the model will be appropriately arranged so that simulations can also be carried out.

2.5 Conclusions

As shown, the GMF provides a sound and useful tool for the physical representation of distillation columns. This is based theoretically on the fact that the GMF Physical Model does not utilize simplifying assumptions or shortcut calculations which can be potentially limiting. Moreover, it is validated through a comparison with a well established rigorous model and the two models are found to be in *quantitative and qualitative* agreement, demonstrating the ability of the GMF to capture efficiently the mass and heat transfer phenomena of the examined system. At the same time, due to the aggregation of the GMF physical model, a significantly smaller optimization problem was generated. The above results provide the basis for the extension of the GMF, beyond the representation of single distillation columns, into formal distillation sequencing problems, where the GMF Physical Model (as presented in Section 2.3.3) will be coupled to appropriate GMF Structural Models. More specifically, the complete GMF synthesis model with its representational and size-related advantages will be used for the automatic generation and evaluation of the structural alternatives, under the Synthesis Target of finding the most energy efficient distillation column sequence for a given separation problem.

Chapter 3

Synthesis of Simple Distillation Column Sequences

3.1 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 need 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 level which can in fact be quite apart 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 being 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 (Figure 3.1). However, an illustration of the difficulty of the problem is realized when the next problem is considered, namely the quaternary separation.

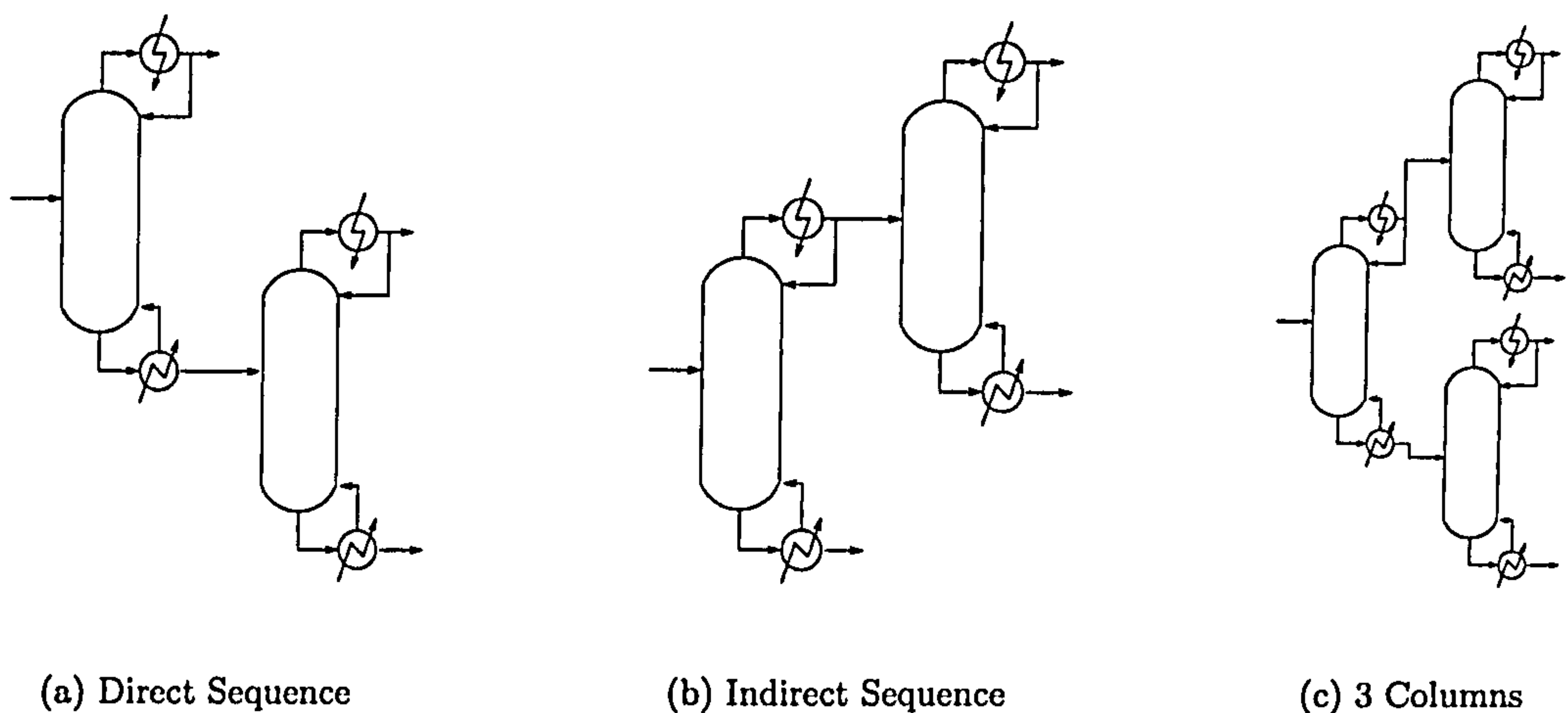


Figure 3.1: Ternary Simple Column Sequencing Alternatives

For this problem, if sharp split assumptions are used only 5 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 may be desirable since when general design targets are optimized, such as the Total Annualized Cost (TAC), these structures may potentially exhibit an optimal trade-off 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 behaviour of distillation columns with models based on a number of simplifying assumptions, thus trading off accuracy and applicability over ease of calculations.

Finally, due to the aforementioned complexities, an efficient sequencing method must also be accompanied by an appropriate solution procedure. For the cases involving a few (*e.g.* up to 5) structural alternatives, an implicit enumeration solution procedure is acceptable. However, for

even the quaternary case including non-sharp 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 decomposition (Douglas, 1988), implicit enumeration (Fraga and McKinnon, 1995) and thermodynamic insights (Bek-Pedersen, 2003), to name but a few. However, one approach that has received a lot of attention, is the superstructure optimization approach. In this approach a superstructure of the problem is generated, that according to Westerberg (Andreovich and Westerberg, 1985a): *'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 and because the GMF belongs to this class of methods, particular attention will be given to the various superstructure optimization methods proposed for the synthesis of simple distillation column sequences.

3.1.1 Superstructure Methods for Simple Column Sequencing

An early systematic superstructure method for the simple column sequencing problem was proposed by Andreovich and Westerberg (1985a). 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 lin-

ear, 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 to be 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, 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 modelled using simple models of total and component mass balances, resulting to 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 employed 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 modelled as a function of the column feed flowrate. 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 flowrates. 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 modelled based on the assumption of non-distributed non-key components. The construction of the superstructures, and therefore the generation of the alternatives, was based on the assumption that in each column there 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 the other non-key components were allowed to appear only 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 flowrates, compositions and key component recoveries and the problem was modelled as an MINLP. Finally, the method was extended to incorporate cases of non-adjacent 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 Andreovich and Westerberg (1985a) for sharp separations. It was also a modification of the superstructure provided by Floudas and Anastasiadis (1988) using fewer 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):

$$S = \frac{(2(n-1))!}{n!(n-1)!}$$

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

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

The distillation columns were modelled 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 modelled 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 flowrates. 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 flowrate 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 non-zero 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.

Yeomans and Grossmann (1999a) proposed a systematic modelling 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 ((Smith, 1996) and (Smith and Pantelides, 1995)) representations. These two representations can be regarded as complementary 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 modelled with the Generalized Disjunctive Programming (GDP) (Raman and Grossmann, 1994). In order to use GDP, conditional constraints had to be distinguished from permanent 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 the 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 modelled using simple mass balances and recoveries, generating linear physical models. The above modelling 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 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 GMF (Papalexandri and Pistikopoulos, 1996). However, the two models have many structural and physical modelling 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 M/H module and each He module constitute different building blocks. Moreover, as shown in Chapter 2, the GMF building blocks by definition have more extensive interconnection possibilities. From a physical modelling point of view, in Caballero and Grossmann (1999) simplifying assumptions of equimolar flowrates, 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. In the GMF mass transfer is arranged through the Driving Force Constraints, which are formulated in such a way that the mass transfer direction does not need to be pre-postulated 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 modelled as permanent and all the other stages as conditional, assigned to a Boolean variable. The disjunctions were modelled so that for existing stages (whose boolean variables had a value of true), phase equilibrium constraints were enforced along with the 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 non-existing 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 3.1: Summary of Superstructure Methods for Simple Column Sequencing

Authors	Features
Simplified Methods (<i>Sharp Splits</i>)	
Andrecovich & Westerberg (1985)	Network Superstructure, Simple Mass Balances
Wehe & Westerberg (1987)	General Separation, non-distr/non-key, Mass Balances
Floudas (1987)	General Separation, Mass Balances
Floudas & Anastasiadis (1988)	General Separation, Mass Balances
Aggarwal & Floudas (1990)	General Separation, non-distr/non-key, Mass Balances
Novak <i>et al</i> (1996)	Network & Compact Superstructures, Mass Balances
Yeomans & Grossmann (1999a)	STN & SON Superstructures, GDP, Mass Balances
Yeomans & Grossmann (1999b)	STN & SON Superst., GDP, Nonlinear Shortcut Models
Caballero & Grossmann (1999)	STN, SON & Intermediate Superst., Aggregated Models
Rigorous Methods (<i>MESH Model, Viswanathan & Grossmann (1993)</i>)	
Smith (1996)	SON Superstructure, <i>MESH</i> Modified Model
Yeomans & Grossmann (2000)	SON Superstructure, GDP

Having presented the superstructure methods for the simple distillation column sequencing problem (which are summarized in Table 3.1), in the following sections this problem will be addressed through the GMF synthesis model. The proposed method will focus on the first two members of the multicomponent distillation problem, namely the ternary and quaternary separations, which can be viewed as the most appropriate candidates upon which a general distillation column sequencing method can be developed and validated. Higher separations could be viewed as an extension of these two separations. From a structural point of view, a GMF Structural Model will be developed that can generate the feasible structural alternatives for the examined problems, aiming to address 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 presented in Section 2.3.3. This model, which is based on aggregation, can be viewed as an intermediate between the simplified and the rigorous models. On the one hand it avoids potentially limiting simplifying assumptions, such as equimolar flowrates, 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 size which are easier to solve. Both of these features of the GMF Physical Model for distillation columns were demonstrated in the Binary Distillation case study in Chapter 2. Finally, the GMF will be accompanied by a solution procedure, using formal MINLP solution techniques, that finds the optimal sequence without having to evaluate all the structural alternatives. This will be demonstrated in the presented case studies.

3.2 GMF Structural Model For Simple Distillation Column Sequences

The GMF Structural Model for the simple column sequencing problem is an extension of the structural model utilized for the representation of a single simple distillation column through the GMF, comprising of the GMF Building Blocks and of appropriately defined Interconnection Principles.

However, for the column sequencing case the following generic GMF interconnection principles are added to the ones already defined in Chapter 2:

- Liquid interconnection streams are allowed from the Lower Auxiliary block of each M/H module into, either the mixer of the *same* module's Heater (LH), or into the Upper Auxiliary block of *another* M/H module (LL).
- Liquid interconnection streams are allowed from the splitter of a Cooler into the Upper Auxiliary block of *any* M/H module (CL).
- Liquid product streams are allowed from the splitter of a Cooler (CP) or from the Lower Auxiliary block of a M/H module (LP).

The above interconnections can also be observed in Figure 2.5 as part of the allowed interconnections of each GMF Building Block. Their corresponding Structural Sets of Section 2.3.2 will take values according to these additions.

Moreover, in order to build the GMF Structural Model for the examined sequencing problem it proved necessary to also add new GMF Structural Sets to the ones of Section 2.3.2, which classify the M/H modules according to their topology in the problem superstructure. These

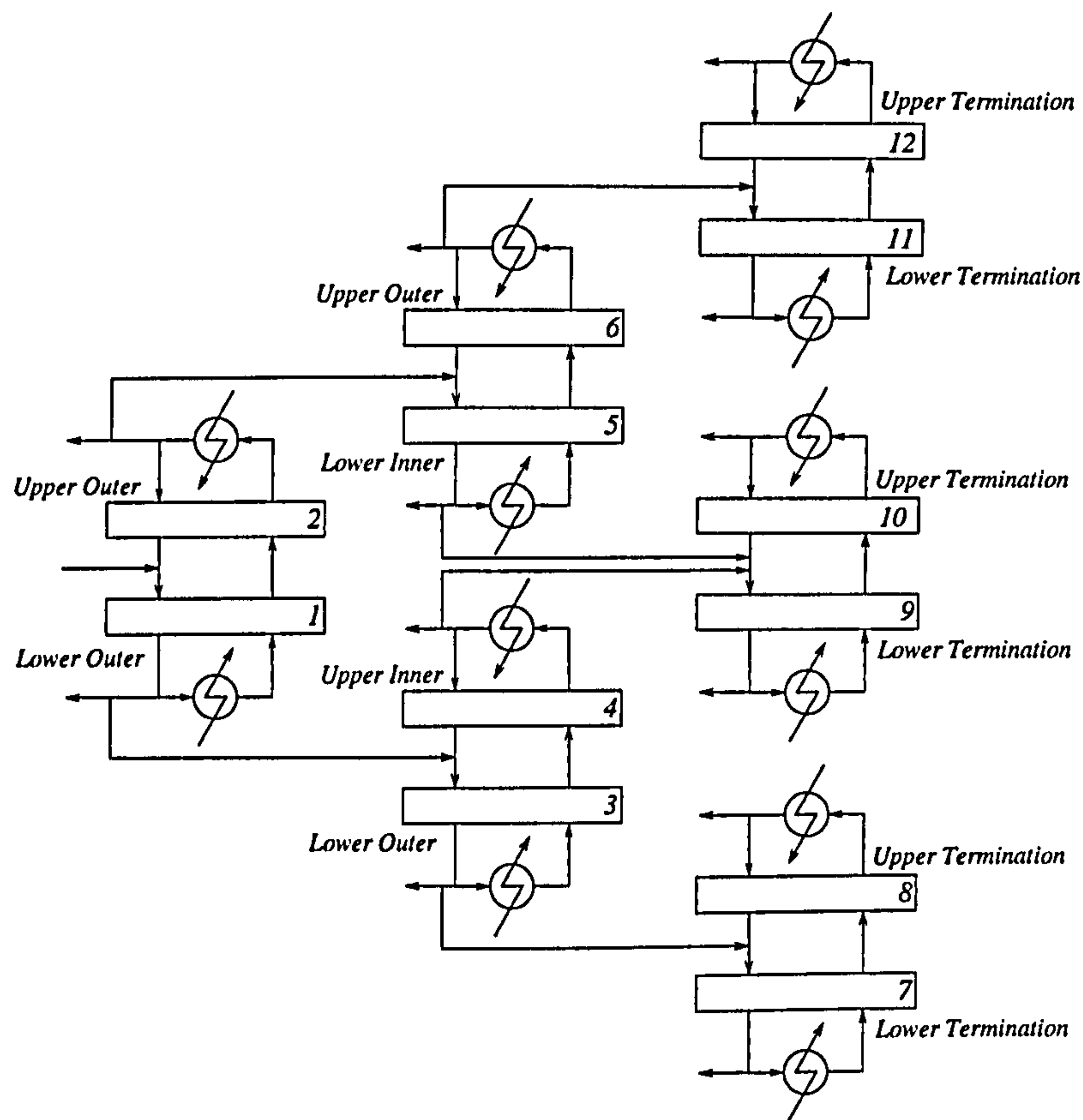


Figure 3.2: M/H Module Characterization in a Superstructure

new sets participate only in the GMF Structural Model (and not in the Physical Model). The new GMF Structural Sets are defined next and are illustrated in Figure 3.2.

$$E^U = \{e | \text{Upper modules (even module numbers)}\}$$

$$E^L = \{e | \text{Lower modules (odd module numbers)}\}$$

$$E^{UO} = \{e | \text{Upper Outer modules}\}$$

$$E^{LO} = \{e | \text{Lower Outer modules}\}$$

$$E^{UI} = \{e | \text{Upper Inner modules}\}$$

$$E^{LI} = \{e | \text{Lower Inner modules}\}$$

$$E^{UT} = \{e | \text{Upper Termination modules}\}$$

$$E^{LT} = \{e \mid \text{Lower Termination modules}\}$$

The construction of the GMF Structural Model is carried out in three stages. In the 1^{st} Stage, the GMF Structural Constraints are posed as Propositional Logic Expressions. In the 2^{nd} Stage, the generated expressions are translated into their corresponding pure integer constraints, using

the systematic procedure of Raman and Grossmann (1991) (an illustration is given in Table 3.2). In the 3rd Stage, the GMF Structural Sets, utilized for the generation of the above constraints, are assigned their specific members in order to construct the specific GMF Structural Models for the examined problem, from the generic model of Stage 2. This 3-stage procedure, which is presented in detail in the following sections, is followed throughout the GMF as it has been found to be the most *systematic* for the accurate generation of the structural constraints.

Table 3.2: Logical and Integer Expressions (Raman and Grossmann, 1991)

Logic relation	Comments	Logical Expression	Linear Inequality
Logical OR		$P_1 \vee P_2 \vee \dots \vee P_r$	$y_1 + y_2 + \dots + y_r \geq 1$
Logical AND		$P_1 \wedge P_2 \wedge \dots \wedge P_r$	$y_1 \geq 1; y_2 \geq 1; \dots; y_r \geq 1$
Implication	$P_1 \Rightarrow P_2$	$\neg P_1 \vee P_2$	$1 - y_1 + y_2 \geq 1$
Equivalence	$P_1 \Leftrightarrow P_2$	$(\neg P_1 \vee P_2) \wedge (\neg P_2 \vee P_1)$	$y_1 = y_2$
	P_1 if and only if P_2		
Exclusive OR	(Exactly one variable is true)	$P_1 \oplus P_2 \oplus \dots \oplus P_r$	$y_1 + y_2 + \dots + y_r = 1$
Classification	$Q = \{P_1, P_2, \dots, P_r\}$ (Q true if any of the variables in the brackets are true)		$y_q = y_1 + y_2 + \dots + y_r$

3.2.1 GMF Propositional Logic Expressions - Stage 1

In order to *systematically* generate the GMF Structural Model for the examined sequencing problem, the GMF Structural Constraints are initially posed as Propositional Logic Expressions, which use Boolean variables taking values of true or false. In this 1st Stage, the GMF binary variables are replaced, for consistency, by their corresponding Boolean variables, which participate along with the GMF Structural Sets in the Propositional Logic Expressions. The following expressions are categorized into Superstructure Basis, Intra-Column and Inter-Column logical expressions according to their function in the model.

Superstructure Basis Logical Expressions

These are general constraints providing a maximum or a minimum number of M/H modules used in the superstructure of the examined problem and fix the existence of building blocks that participate in all the structural alternatives.



- There must be an initial module.

$$y_1 : \text{true} \quad (3.1)$$

- The minimum number of sharp split columns according to Freshwater and Henry (1975) is $|C| - 1$, where $|C|$ is the number of components to be separated¹. As sloppy split flowsheets require more columns than those of sharp splits, the sharp split lower bound is also applicable. Since in the GMF each column consists of 2 M/H modules, the constraint becomes:

$$\sum_{e \in E} y_e \geq 2(|C| - 1) \quad (3.2)$$

Note: In this case (along with the next constraint) the pure integer constraint is easier to produce than its corresponding logical expression, so the former is posed here for simplification.

- There must be at least one intermediate column between the initial and termination columns:

$$\sum_{e \in E^{LI}} (y_e + y_{e-1}) \geq 1 \quad (3.3)$$

Intra-Column Logical Expressions

Due to the fact that the GMF consists of separate building blocks, the Intra-Column Logical Expressions are introduced, which provide the rules that arrange the connectivities of the building blocks in order to systematically represent *each* simple column of the superstructure.

$$y_e \Leftrightarrow y_{e+1}, \quad e \in E^L \quad (3.4)$$

$$y_e \Leftrightarrow y_e^H, \quad e \in E^L \quad (3.5)$$

$$y_e \Leftrightarrow y_e^C, \quad e \in E^U \quad (3.6)$$

$$y_{e,e}^{LH} \Leftrightarrow y_e \wedge y_e^H, \quad e \in E^L \quad (3.7)$$

$$y_{e,e}^{HV} \Leftrightarrow y_e^H \wedge y_e, \quad e \in E^L \quad (3.8)$$

$$y_{e,e}^{VC} \Leftrightarrow y_e \wedge y_e^C, \quad e \in E^U \quad (3.9)$$

$$y_{e,e}^{CL} \Leftrightarrow y_e^C \wedge y_e, \quad e \in E^U \quad (3.10)$$

$$y_{e,e-1}^{LL} \Leftrightarrow y_e \wedge y_{e-1}, \quad e \in E^U \quad (3.11)$$

$$y_{e,e+1}^{VV} \Leftrightarrow y_e \wedge y_{e+1}, \quad e \in E^L \quad (3.12)$$

¹ $|C|$ is the cardinality of the components' set

The first three expressions state that if a Lower module exists (*even module number*) it should be accompanied by an Upper module (*next immediate odd module number*) and their corresponding Cooler and Heater modules. The remaining expressions impose the liquid (LL , LH , CL) and vapour (VV , HV , VC) interconnections between Lower, Upper, Cooler and Heater modules that belong to the *same* simple column.

Inter-Column Logical Expressions

Once each single column is structurally defined, the Inter-Column Logical Expressions provide the rules that arrange the connectivities between building blocks belonging to *different* columns, in order to generate all the feasible column sequences for the examined problem.

- If a Lower module exists (excluding the 1st), then it should receive *at least* one liquid interconnection from other existing M/H modules and/or Coolers².

$$y_{ea} \Rightarrow \bigvee_{e \in E_{ea}^{LLi}} y_{e,ea}^{LL} \bigvee_{e \in E_{ea}^{CLi}} y_{e,ea}^{CL}, \quad ea \in E^L, ea \neq 1, e \neq ea + 1 \quad (3.13)$$

- If a Cooler module exists, then *one and only one* interconnecting stream is allowed from it, *either* to a product mixer *or* to a M/H module of *another* column ($ea \neq e$). Coolers of Upper Termination modules have only product mixer interconnections.

$$y_e^C = \{ \{y_{e,p1}^{CP}, \dots, y_{e,pn}^{CP}\}_{p \in E_e^{CPo}}, \{y_{e,ea1}^{CL}, \dots, y_{e,ean}^{CL}\}_{ea \in E_e^{CLo}} \}, \quad e \in E^C, ea \neq e \quad (3.14)$$

Note: These constraints are written as Logical Classifications.

- If a Lower module exists, then *one and only one* interconnecting stream is allowed from it, *either* to a product mixer *or* to another M/H module. Lower Termination modules have only product mixer interconnection.

$$y_e = \{ \{y_{e,p1}^{LP}, \dots, y_{e,pn}^{LP}\}_{p \in E_e^{LPo}}, \{y_{e,ea1}^{LL}, \dots, y_{e,ean}^{LL}\}_{ea \in E_e^{LLo}} \}, \quad e \in E^L \quad (3.15)$$

- A product stream leaves the Cooler of an Upper Outer module *if and only if* no other module belonging to *another* column exists that receives an interconnection from this Cooler.

$$y_{e,p}^{CP} \Leftrightarrow y_e^C \wedge \neg y_{ea}, \quad e \in E^{UO}, p \in E_e^{CPo}, ea \in E_e^{CLo}, ea \neq e \quad (3.16)$$

² $\bigvee_{e \in E_{ea}^{LLi}} y_{e,ea}^{LL} = y_{e_1,ea}^{LL} \vee \dots \vee y_{e_n,ea}^{LL}$, where $e \in E_{ea}^{LLi}$

- A liquid interconnection leaves the Cooler of an Upper Outer module towards *another* column *if and only if* the destination M/H module exists.

$$y_{e,ea}^{CL} \Leftrightarrow y_e^C \wedge y_{ea}, \quad e \in E^{UO}, \quad ea \in E_e^{CLo}, \quad ea \neq e \quad (3.17)$$

- A product stream leaves a Lower Outer module *if and only if* no other M/H module exists that receives an interconnection from this module.

$$y_{e,p}^{LP} \Leftrightarrow y_e \wedge \neg y_{ea}, \quad e \in E^{LO}, \quad p \in E_e^{LPo}, \quad ea \in E_e^{LLo} \quad (3.18)$$

- A liquid interconnection leaves a Lower Outer module *if and only if* the destination M/H module also exists.

$$y_{e,ea}^{LL} \Leftrightarrow y_e \wedge y_{ea}, \quad e \in E^{LO}, \quad ea \in E_e^{LLo} \quad (3.19)$$

- If a liquid interconnection leaves the Cooler of an Upper Inner module, then the destination module also exists.

$$y_{e,ea}^{CL} \Rightarrow y_e^C \wedge y_{ea}, \quad e \in E^{UI}, \quad ea \in E_e^{CLo}, \quad ea \neq e \quad (3.20)$$

- A product stream $(P-1)$ leaves the Cooler of an Upper Inner module (e) , *if and only if* a product stream containing the immediately heavier fraction (P) leaves the Lower Outer module of the same column $(e-1)$ *and* no interconnection exists from the Cooler in question to another module (ea) .

$$y_{e,p-1}^{CP} \Leftrightarrow y_{e-1,p}^{LP} \wedge \neg y_{e,ea}^{CL}, \quad e \in E^{UI}, \quad p \in E_{e-1}^{LPo}, \quad ea \in E_e^{CLo}, \quad ea \neq e \quad (3.21)$$

Note: Product streams are characterized according to the volatility of their enriched components, starting from the lightest $(P1)$ and ending to the heaviest $(P4)$.

- If a liquid interconnection leaves a Lower Inner module, then the destination module also exists.

$$y_{e,ea}^{LL} \Rightarrow y_e \wedge y_{ea}, \quad e \in E^{LI}, \quad ea \in E_e^{LLo} \quad (3.22)$$

- A product stream $(P+1)$ leaves a Lower Inner module (e) , *if and only if* a product stream containing the immediately lighter fraction (P) leaves the same column's Cooler $(e+1)$ and no interconnection is chosen from the Lower Inner module in question to another module (ea) .

$$y_{e,p+1}^{LP} \Leftrightarrow y_{e+1,p}^{CP} \wedge \neg y_{e,ea}^{LL}, \quad e \in E^{LI}, \quad p \in E_{e+1}^{CPo}, \quad ea \in E_e^{LLo} \quad (3.23)$$

- Every product mixer should receive *at least* one interconnection from a cooler or M/H module:

$$\bigvee_{e \in E_p^{CPi}} y_{e,p}^{CP} \quad \bigvee_{e \in E_p^{LPi}} y_{e,p}^{LP}, \quad p \in P \quad (3.24)$$

3.2.2 GMF Structural Integer Constraints - Stage 2

Once the Logical Expressions have been generated, they should be transformed into their *conjunctive normal form*, i.e. a set of clauses which include OR operators linked by AND operators. A systematic procedure to achieve this has been proposed by Clocksin and Mellish (1981) and can also be found in Raman and Grossmann (1991) and Biegler *et al.* (1997). Then in the 2nd Stage of the GMF Structural Model generation, the logical expressions in their conjunctive form are translated into their respective pure integer Structural Constraints, by replacing the Boolean with their corresponding binary variables and by following the rules presented in Table 3.2.

Superstructure Basis Structural Constraints

$$y_1 = 1 \quad (3.25)$$

$$\sum_{e \in E} y_e \geq 2(|C| - 1) \quad (3.26)$$

$$\sum_{e \in E^{LI}} (y_e + y_{e-1}) \geq 1 \quad (3.27)$$

Intra-Column Structural Constraints

$$y_e - y_{e+1} = 0, \quad e \in E^L \quad (3.28)$$

$$y_e - y_e^H = 0, \quad e \in E^L \quad (3.29)$$

$$y_e - y_e^C = 0, \quad e \in E^U \quad (3.30)$$

$$1 - y_{e,e}^{LH} + y_e \geq 1, \quad e \in E^L \quad (3.31)$$

$$1 - y_{e,e}^{LH} + y_e^H \geq 1, \quad e \in E^L \quad (3.32)$$

$$y_{e,e}^{LH} + 1 - y_e + 1 - y_e^H \geq 1, \quad e \in E^L \quad (3.33)$$

$$1 - y_{e,e}^{HV} + y_e^H \geq 1, \quad e \in E^L \quad (3.34)$$

$$1 - y_{e,e}^{HV} + y_e \geq 1, \quad e \in E^L \quad (3.35)$$

$$y_{e,e}^{HV} + 1 - y_e^H + 1 - y_e \geq 1, \quad e \in E^L \quad (3.36)$$

$$1 - y_{e,e}^{VC} + y_e \geq 1, \quad e \in E^U \quad (3.37)$$

$$1 - y_{e,e}^{VC} + y_e^C \geq 1, \quad e \in E^U \quad (3.38)$$

$$y_{e,e}^{VC} + 1 - y_e + 1 - y_e^C \geq 1, \quad e \in E^U \quad (3.39)$$

$$1 - y_{e,e}^{CL} + y_e^C \geq 1, \quad e \in E^U \quad (3.40)$$

$$1 - y_{e,e}^{CL} + y_e \geq 1, \quad e \in E^U \quad (3.41)$$

$$y_{e,e}^{CL} + 1 - y_e^C + 1 - y_e \geq 1, \quad e \in E^U \quad (3.42)$$

$$1 - y_{e,e-1}^{LL} + y_e \geq 1, \quad e \in E^U \quad (3.43)$$

$$1 - y_{e,e-1}^{LL} + y_{e-1} \geq 1, \quad e \in E^U \quad (3.44)$$

$$y_{e,e-1}^{LL} + 1 - y_e + 1 - y_{e-1} \geq 1, \quad e \in E^U \quad (3.45)$$

$$1 - y_{e,e+1}^{VV} + y_e \geq 1, \quad e \in E^L \quad (3.46)$$

$$1 - y_{e,e+1}^{VV} + y_{e+1} \geq 1, \quad e \in E^L \quad (3.47)$$

$$y_{e,e+1}^{VV} + 1 - y_e + 1 - y_{e+1} \geq 1, \quad e \in E^L \quad (3.48)$$

Inter-Column Structural Constraints

$$\sum_{e \in E_{ea}^{LLi}} y_{e,ea}^{LL} + \sum_{e \in E_{ea}^{CLi}} y_{e,ea}^{CL} \geq y_{ea}, \quad ea \in E^L, ea \neq 1, e \neq ea + 1 \quad (3.49)$$

$$\sum_{p \in E_e^{CPo}} y_{e,p}^{CP} + \sum_{ea \in E_e^{CLo}} y_{e,ea}^{CL} = y_e^C, \quad e \in E^C, ea \neq e \quad (3.50)$$

$$\sum_{p \in E_e^{LPo}} y_{e,p}^{LP} + \sum_{ea \in E_e^{LLo}} y_{e,ea}^{LL} = y_e, \quad e \in E^L \quad (3.51)$$

$$1 - y_{e,p}^{CP} + y_e^C \geq 1, \quad e \in E^{UO}, p \in E_e^{CPo} \quad (3.52)$$

$$1 - y_{e,p}^{CP} + 1 - y_{ea} \geq 1, \quad e \in E^{UO}, p \in E_e^{CPo}, ea \in E_e^{CLo}, ea \neq e \quad (3.53)$$

$$y_{e,p}^{CP} + 1 - y_e^C + y_{ea} \geq 1, \quad e \in E^{UO}, p \in E_e^{CPo}, ea \in E_e^{CLo}, ea \neq e \quad (3.54)$$

$$1 - y_{e,ea}^{CL} + y_e^C \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (3.55)$$

$$1 - y_{e,ea}^{CL} + y_{ea} \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (3.56)$$

$$y_{e,ea}^{CL} + 1 - y_e^C + 1 - y_{ea} \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (3.57)$$

$$1 - y_{e,p}^{LP} + y_e \geq 1, \quad e \in E^{LO}, p \in E_e^{LPo} \quad (3.58)$$

$$1 - y_{e,p}^{LP} + 1 - y_{ea} \geq 1, \quad e \in E^{LO}, p \in E_e^{LPo}, ea \in E_e^{LL} \quad (3.59)$$

$$y_{e,p}^{LP} + 1 - y_e + y_{ea} \geq 1, \quad e \in E^{LO}, p \in E_e^{LPo}, ea \in E_e^{LL} \quad (3.60)$$

$$1 - y_{e,ea}^{LL} + y_e \geq 1, \quad e \in E^{LO}, \quad ea \in E_e^{LLo} \quad (3.61)$$

$$1 - y_{e,ea}^{LL} + y_{ea} \geq 1, \quad e \in E^{LO}, \quad ea \in E_e^{LLo} \quad (3.62)$$

$$y_{e,ea}^{LL} + 1 - y_e + 1 - y_{ea} \geq 1, \quad e \in E^{LO}, \quad ea \in E_e^{LLo} \quad (3.63)$$

$$1 - y_{e,ea}^{CL} + y_e^C \geq 1, \quad e \in E^{UI}, \quad ea \in E_e^{CLo}, \quad ea \neq e \quad (3.64)$$

$$1 - y_{e,ea}^{CL} + y_{ea} \geq 1, \quad e \in E^{UI}, \quad ea \in E_e^{CLo}, \quad ea \neq e \quad (3.65)$$

$$1 - y_{e,p-1}^{CP} + y_{e-1,p}^{LP} \geq 1, \quad e \in E^{UI}, \quad p \in E_{e-1}^{LPo} \quad (3.66)$$

$$1 - y_{e,p-1}^{CP} + 1 - y_{e,ea}^{CL} \geq 1, \quad e \in E^{UI}, \quad p \in E_{e-1}^{LPo}, \quad ea \in E_e^{CLo}, \quad ea \neq e \quad (3.67)$$

$$y_{e,p-1}^{CP} + 1 - y_{e-1,p}^{LP} + y_{e,ea}^{CL} \geq 1, \quad e \in E^{UI}, \quad p \in E_{e-1}^{LPo}, \quad ea \in E_e^{CLo}, \quad ea \neq e \quad (3.68)$$

$$1 - y_{e,ea}^{LL} + y_e \geq 1, \quad e \in E^{LI}, \quad ea \in E_e^{LLo} \quad (3.69)$$

$$1 - y_{e,ea}^{LL} + y_{ea} \geq 1, \quad e \in E^{LI}, \quad ea \in E_e^{LLo} \quad (3.70)$$

$$1 - y_{e,p+1}^{LP} + y_{e+1,p}^{CP} \geq 1, \quad e \in E^{LI}, \quad p \in E_{e+1}^{CPo} \quad (3.71)$$

$$1 - y_{e,p+1}^{LP} + 1 - y_{e,ea}^{LL} \geq 1, \quad e \in E^{LI}, \quad p \in E_{e+1}^{CPo}, \quad ea \in E_e^{LL} \quad (3.72)$$

$$y_{e,p+1}^{LP} + 1 - y_{e+1,p}^{CP} + y_{e,ea}^{LL} \geq 1, \quad e \in E^{LI}, \quad p \in E_{e+1}^{CPo}, \quad ea \in E_e^{LL} \quad (3.73)$$

$$\sum_{e \in E_p^{CPi}} y_{e,p}^{CP} + \sum_{e \in E_p^{LPi}} y_{e,p}^{LP} \geq 1, \quad p \in P \quad (3.74)$$

The above constraints defined over the appropriate Structural Sets (Stage 3), along with the GBD Integer Cuts, constitute the GMF Structural Model for the generation of Ternary and Quaternary Simple Distillation Column Sequences. The above model in conjunction with the GMF Physical Model (Section 2.3.3) define the complete GMF synthesis model for the simple distillation column sequencing problem for energy efficiency, as it will be employed for the case studies of the following sections.

3.3 Case Study: Ternary Simple Distillation Sequencing

3.3.1 Problem Statement

The proposed GMF column sequencing synthesis model was employed for the ternary separation of Benzene, Toluene and o-Xylene into 3 near-pure product streams (based on a case study appeared in Chavez *et al.* (1986)). The problem statement is shown in Table 3.3.

Table 3.3: Ternary Case Study Physical System Data

System	<i>Benzene - Toluene - o-Xylene</i>
Thermodynamic Model	<i>Liquid Phase - Ideal</i> <i>Vapour Phase - Ideal</i>
Source of Thermodynamic Data	<i>Reid (1987)</i>
Feed Flowrate	$F = 1000 \text{ kmol/hr}$
Feed Compositions	$x_{F,Benzene} = 0.2$ $x_{F,Toluene} = 0.4$ $x_{F,o-Xylene} = 0.4$
Column Pressure	$P = 1 \text{ atm}$
Feed Temperature	$T_F = 383.2 \text{ K}$

As in the case study of Section 2.4, the column pressure was considered fixed to 1 atm and the feed temperature corresponded to that of the feed bubble point (also at 1 atm). The thermodynamic model used was based on ideal liquid and vapour phases. The objective function, the separation specifications and the utility stream costs are given in Table 3.4.

Table 3.4: Ternary Problem Specifications

Objective Function	$\min \sum_{e \in E^H} C^{st} Q_e^H y_e^H + \sum_{e \in E^C} C^{cw} Q_e^C y_e^C$
Benzene at product ($P1$)	$x_{P1,Benzene}^P \geq 0.95$
Toluene at product (S)	$x_{S,Toluene}^P \geq 0.95$
o-Xylene at product ($P2$)	$x_{P2,o-Xylene}^P \geq 0.95$
C^{st} (\$/kWyr)	137.27
C^{cw} (\$/kWyr)	26.19

3.3.2 GMF Problem Formulation - Stage 3

Contrary to the binary distillation separation of Section 2.4, where a unique simple distillation column structural alternative was available, for the ternary distillation separation problem, there exist three simple column structural alternatives, as shown in Figure 3.1. That means that for the ternary simple distillation column sequencing problem, the complete GMF Synthesis Model must be coupled to a formal decomposition MINLP algorithm in order to find the most energy efficient structure. It must be noted that the examined case study provides an ideal candidate

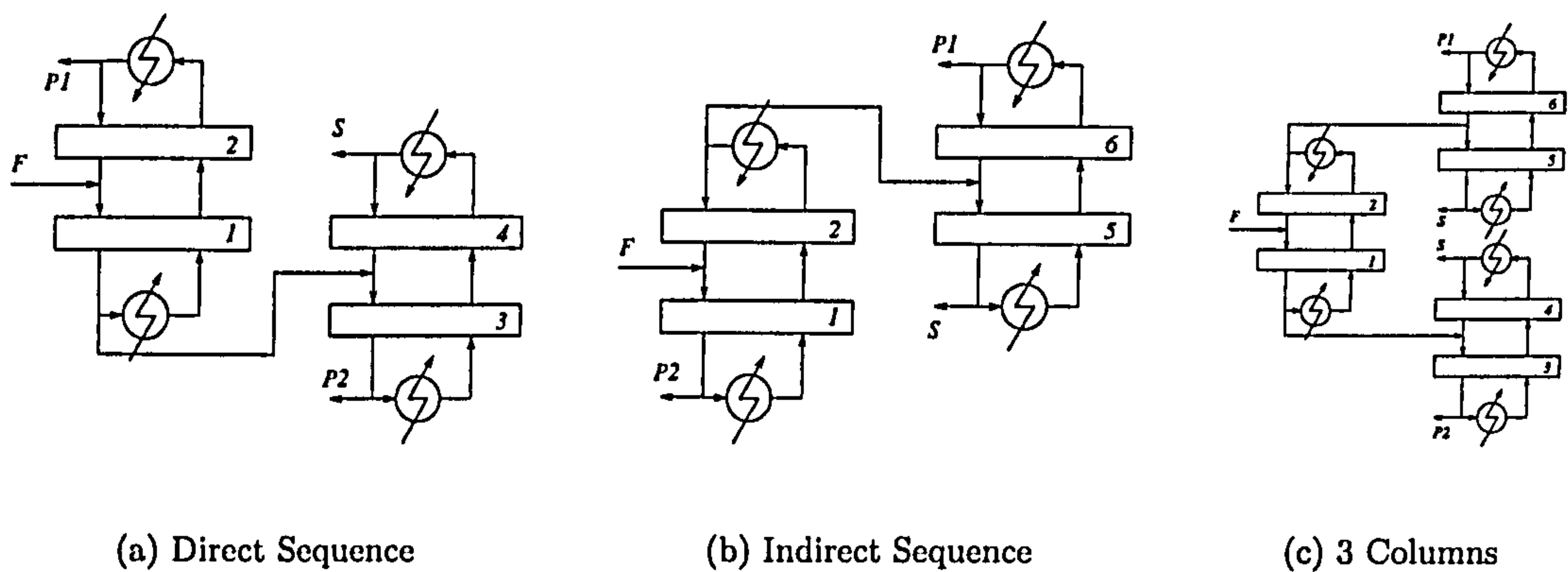


Figure 3.3: GMF Representation of Ternary Simple Column Alternatives

for the validation of the coupling between the GMF Structural and Physical Models with the MINLP algorithm, due to the small number of structural alternatives and the relatively small continuous size of the generated problem.

The GMF representation of the structural alternatives, namely the Direct, Indirect and 3-Column sequences, are shown in Figure 3.3 (for representational simplicity only the M/H and He building blocks are depicted for each alternative). As it can be seen, a maximum of 6 M/H modules is utilized for the generation of all the alternatives, defining the number of building blocks that must be employed in the problem superstructure (shown in Figure 3.4). The number

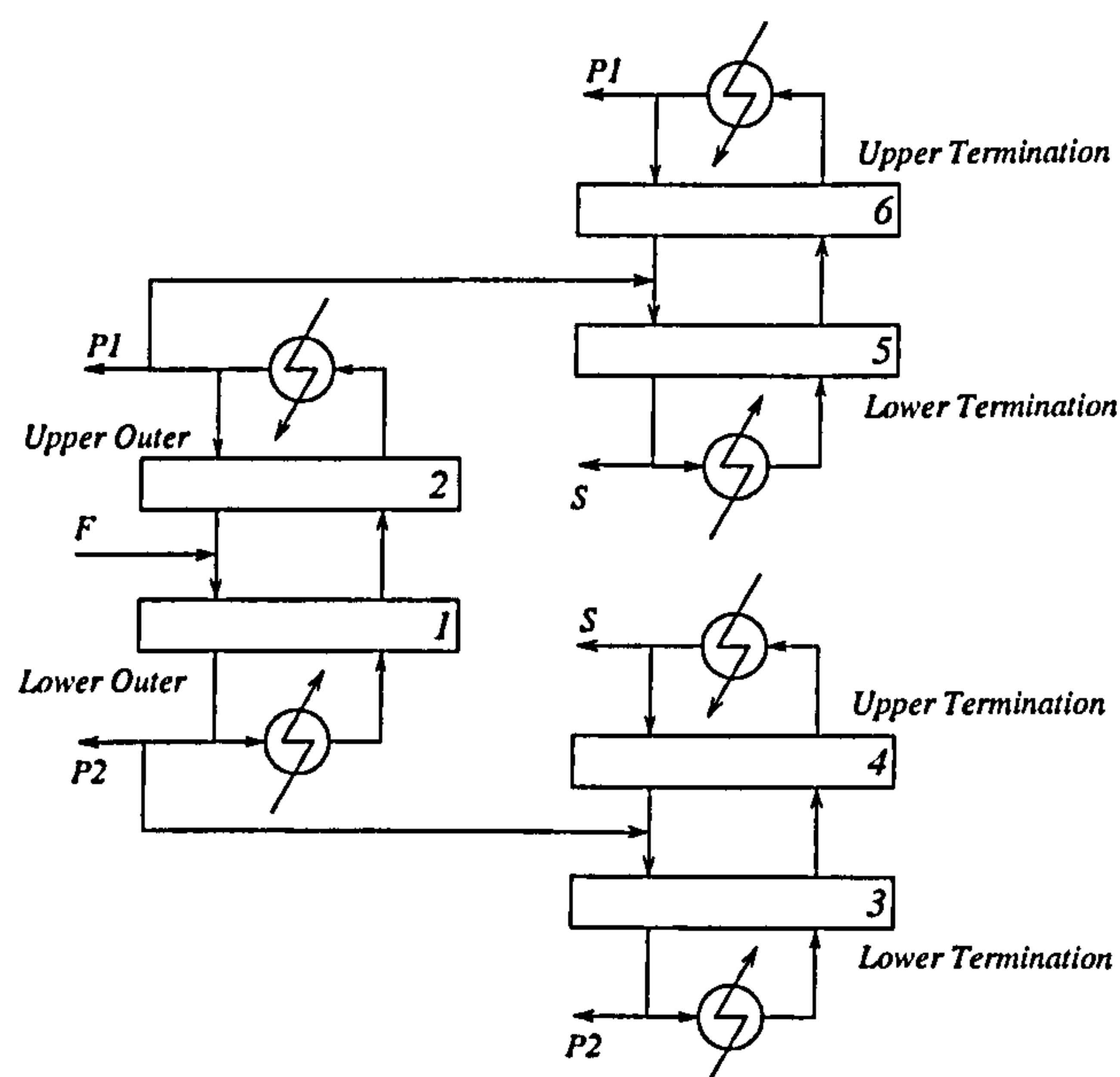


Figure 3.4: GMF Ternary Simple Distillation Column Superstructure

of He modules will be determined by the GMF Structural Model, as mentioned already.

The Ternary Simple Column Sequencing superstructure is translated mathematically into the GMF Structural Model once the Structural Sets have been assigned. From Figure 3.4 it can be seen that for the ternary sequencing case there are no Upper and Lower Inner M/H modules ($E^{UI} = E^{LI} = \{\emptyset\}$). The *non-empty* GMF Structural Sets for the ternary simple distillation column sequencing problem are given in Table 3.5 (Stage 3 of the GMF Structural Model for ternary sequencing).

Table 3.5: Ternary GMF Structural Sets (Stage - 3)

$I = \{F\}$	$E^L = \{1, 3, 5\}$
$C = \{Benz., Tol., o-Xyl.\}$	$E^U = \{2, 4, 6\}$
$P = \{P1, S, P2\}$	$E^{UO} = \{2\}$
$E = \{1, 2, 3, 4, 5, 6\}$	$E^{LO} = \{1\}$
$E^H = \{1, 3, 5\}$	$E^{UT} = \{4, 6\}$
$E^C = \{2, 4, 6\}$	$E^{LT} = \{3, 5\}$
$E_F^{FL} = \{1\}$	
$E_e^{VVo} = \{ea \mid ea = e + 1\}, e \in E^L$	$E_e^{VVl} = \{ea \mid ea = e - 1\}, e \in E^U$
$E_e^{LLo} = \{ea \mid ea = e - 1\}, e \in E^U \text{ and } E_1^{LLo} = \{3\}$	$E_e^{LLl} = \{ea \mid ea = e + 1\}, e \in E^L \text{ and } E_3^{LLl} = \{1\}$
$E_e^{CLo} = \{ea \mid ea = e\}, e \in E^U \text{ and } E_2^{CLo} = \{5\}$	$E_e^{CLl} = \{ea \mid ea = e\}, e \in E^U \text{ and } E_5^{CLl} = \{2\}$
$E_1^{LPo} = \{P2\}, E_3^{LPo} = \{P2\}, E_5^{LPo} = \{S\}$	$E_{P2}^{LPi} = \{1, 3\}, E_S^{LPi} = \{5\}$
$E_2^{CPo} = \{P1\}, E_4^{CPo} = \{S\}, E_6^{CPo} = \{P1\}$	$E_{P1}^{CPi} = \{2, 6\}, E_S^{CPi} = \{4\}$

For illustration of the above sets, for instance, in the case of E_e^{LLo} the corresponding sets are: $E_2^{LLo} = \{1\}$, $E_4^{LLo} = \{3\}$, $E_6^{LLo} = \{5\}$ (since $E^U = \{2, 4, 6\}$) and $E_1^{LLo} = \{3\}$. Based on the above structural sets, the generated GMF Structural Model will include all the constraints of Section 3.2.2, apart from those defined over the Upper and Lower Inner M/H modules (that is, constraints (3.27) and (3.64)-(3.73)). For the GAMS implementation all the above GMF Structural Sets are included as GAMS PARAMETERS, apart from I , C , P and E , which are included as GAMS SETS.

3.3.3 Problem Solution and Results

The complete GMF ternary sequencing synthesis model corresponded to a MINLP problem which was solved using the Generalized Benders Decomposition (GBD) algorithm (Geoffrion

Table 3.6: Optimal Ternary Sequence and Operating Conditions

		$F(\text{kmol/hr})$	x_{Benz}	x_{Tol}	$x_o - x_{yl}$
	$P1$	210.5	0.95	0.05	0
	S	393.3	0	0.95	0.05
	$P2$	396.2	0	0.05	0.95
	Heat Duties (kW)				
	Q_1^H	6633.4			
	Q_2^C	6335.3			
	Q_3^H	7936.5			
	Q_4^C	7783.3			

(1972) and Floudas (1995)). The automation and interaction between Primal NLP and Master MILP subproblems followed the guidelines of the APROS approach for the GBD algorithm in GAMS (Paules and Floudas, 1989).

From the solution of the generated MINLP problem the Direct Sequence was found to be the most energy efficient structure with an Operating Cost of 2,369,000\$/yr. This sequence was found to be achieving savings of 21%/yr when compared to the sub-optimal Indirect Sequence. At the same time, the GMF through the solution of the synthesis problem for energy efficiency also provided useful guidelines on the chosen sequence’s optimal operating policy. The optimal sequence along with its operating conditions are given in Table 3.6.

From a computational point of view, the solution was obtained in 2 GBD iterations. Starting from the Direct Sequence, the 1st Master MILP subproblem generated the Indirect Sequence as the second structure to be evaluated and a lower bound to the solution. In the 2nd Master subproblem the 3-Column sequence was generated as the solution, along with an improved lower bound (due to the non-decreasing property of the Master subproblem). At that point, the lower bound crossed the current best upper bound, achieving convergence and determining the optimal solution to the problem, as the sequence that corresponded to the best upper bound (the Direct Sequence). The direct advantage from this formal solution procedure was that the 3-Column sequence did not need to be physically evaluated (as would have occurred in enumeration methods). This was particularly important for the computational efficiency of the proposed method since that sequence would have generated the largest GMF Physical Model problem, thus increasing unnecessarily the overall required computational effort.

3.4 Case Study: Quaternary Simple Distillation Sequencing

3.4.1 Problem Statement

The second case study examines the separation of a quaternary mixture of Benzene, Toluene, o-Xylene and Diphenyl into four product streams of high purity specifications ($P1$, $P2$, $P3$, $P4$) and is taken from Novak *et al.* (1996). The problem statement is given in Table 3.7.

Table 3.7: Quaternary Case Study Physical System Data

System	<i>Benzene - Toluene - o-Xylene - Diphenyl</i>
Thermodynamic Model	<i>Liquid Phase - Ideal</i> <i>Vapour Phase - Ideal</i>
Source of Thermodynamic Data	<i>Reid (1987)</i>
Feed Flowrate	$F = 1900 \text{ kmol/hr}$
Feed Compositions	$x_{F,Benzene} = 0.4$ $x_{F,Toluene} = 0.3$ $x_{F,o-Xylene} = 0.2$ $x_{F,Diphenyl} = 0.1$
Column Pressure	$P = 1 \text{ atm}$
Feed Temperature	$T_F = 374 \text{ K}$

The feed temperature corresponded to that of the feed bubble point (at 1 atm). Raoult's law was used for the equilibrium constant and Antoine's law for the vapour pressures. The objective function, separation specifications and utility prices are shown in Table 3.8. Only High Pressure Steam was used as a hot utility. Moreover, no product recovery specifications were imposed.

Table 3.8: Quaternary Problem Specifications

Objective Function	$\min \sum_{e \in E^H} C^{st} Q_e^H y_e^H + \sum_{e \in E^C} C^{cw} Q_e^C y_e^C$
Benzene at product ($P1$)	$x_{P1,Benzene}^P \geq 0.99$
Toluene at product ($P2$)	$x_{P2,Toluene}^P \geq 0.99$
o-Xylene at product ($P3$)	$x_{P3,o-Xylene}^P \geq 0.99$
Diphenyl at product ($P4$)	$x_{P4,Diphenyl}^P \geq 0.99$
C^{st} (\$/10 ⁶ kJ)	5.333
C^{cw} (\$/10 ⁶ kJ)	0.159

3.4.2 GMF Problem Formulation - Stage 3

The complexity of the examined problem has increased considerably with the addition of a fourth component. By examining the Subset of Feasible Alternatives (F), it has been found that there exist 22 different single column sequences, employing from 3 to 6 simple columns. The generation of the structural alternatives was achieved through the GMF Structural Model. Based on the maximum number of columns for the required separation, the GMF superstructure employed 12 M/H modules, as illustrated in Figure 3.5.

In order to translate the quaternary superstructure mathematically into its corresponding GMF Structural Model, the members of the GMF Structural Sets had to be assigned (Stage 3 of Structural Model for quaternary sequencing). The *non-zero* Sets are given in Table 3.9.

Contrary to the GMF Structural Model for the sequencing of ternary simple distillation columns, the model for the quaternary sequencing problem consists of *all* the pure integer

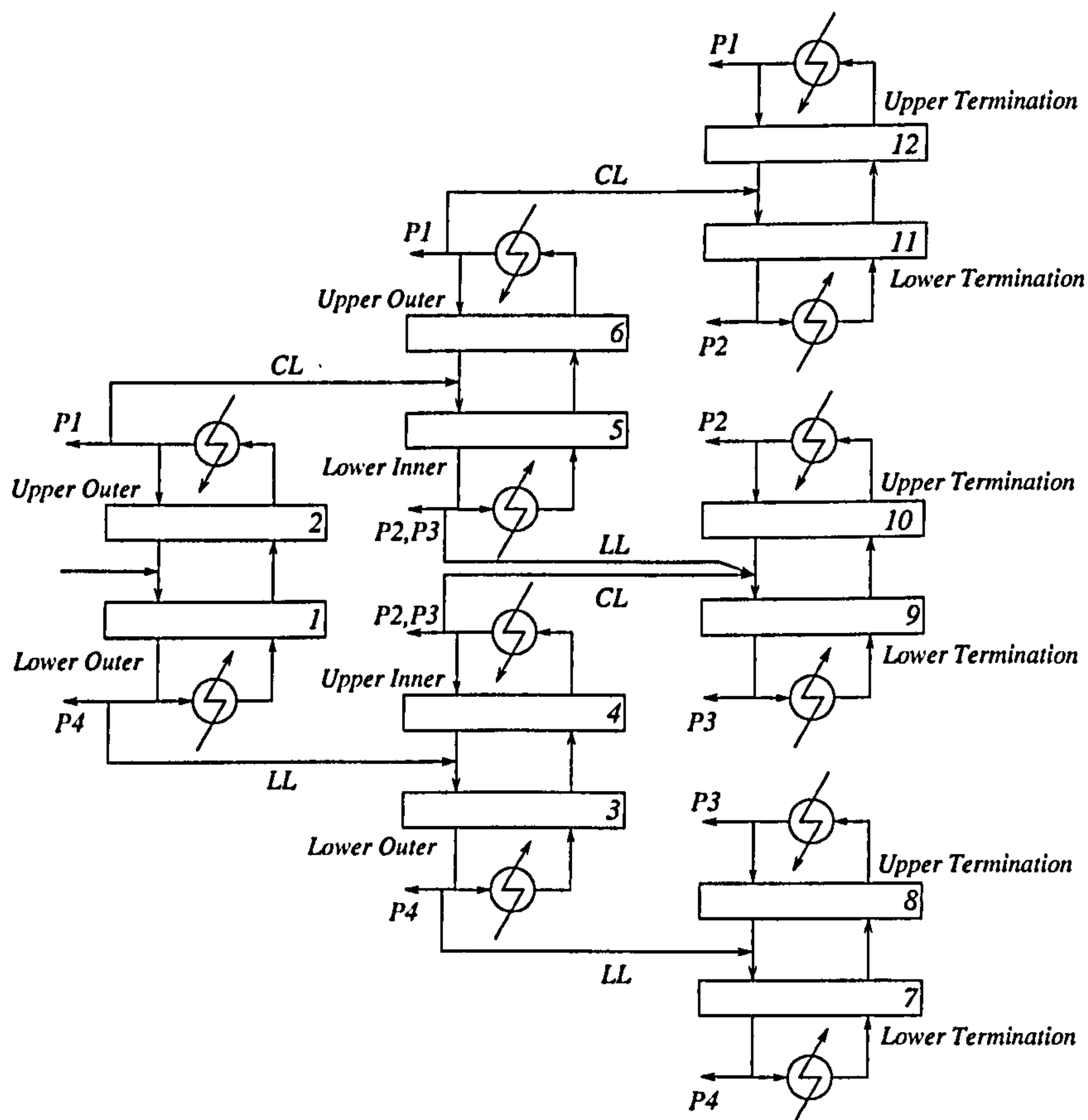


Figure 3.5: GMF Quaternary Simple Distillation Column Superstructure

Table 3.9: Quaternary GMF Structural Sets (Stage-3)

$I = \{F\}$	$E^L = \{1, 3, 5, 7, 9, 11\}$
$C = \{\text{Benz.}, \text{Tol.}, \text{o-Xyl.}, \text{Diphenyl}\}$	$E^U = \{2, 4, 6, 8, 10, 12\}$
$P = \{P1, P2, P3, P4\}$	$E^{UO} = \{2, 6\}$
$E = \{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12\}$	$E^{LO} = \{1, 3\}$
$E^H = \{1, 3, 5, 7, 9, 11\}$	$E^{UI} = \{4\}$
$E^C = \{2, 4, 6, 8, 10, 12\}$	$E^{LI} = \{5\}$
	$E^{UT} = \{8, 10, 12\}$
	$E^{LT} = \{7, 9, 11\}$
$E_F^{FL} = \{1\}$	
$E_e^{VV^o} = \{ea \mid ea = e + 1\}, e \in E^L$	$E_e^{VV^i} = \{ea \mid ea = e - 1\}, e \in E^U$
$E_e^{LL^o} = \{ea \mid ea = e - 1\}, e \in E^U$ and $E_1^{LL^o} = \{3\}, E_3^{LL^o} = \{7\}, E_5^{LL^o} = \{9\}$	$E_e^{LL^i} = \{ea \mid ea = e + 1\}, e \in E^L$ and $E_3^{LL^i} = \{1\}, E_7^{LL^i} = \{3\}, E_9^{LL^i} = \{5\}$
$E_e^{CL^o} = \{ea \mid ea = e\}, e \in E^U$ and $E_2^{CL^o} = \{5\}, E_4^{CL^o} = \{9\}, E_6^{CL^o} = \{11\}$	$E_e^{CL^i} = \{ea \mid ea = e\}, e \in E^U$ and $E_5^{CL^i} = \{2\}, E_9^{CL^i} = \{4\}, E_{11}^{CL^i} = \{6\}$
$E_1^{LP^o} = \{P4\}, E_3^{LP^o} = \{P4\}, E_5^{LP^o} = \{P2, P3\},$ $E_7^{LP^o} = \{P4\}, E_9^{LP^o} = \{P3\}, E_{11}^{LP^o} = \{P2\}$	$E_{P2}^{LP^i} = \{5, 11\}, E_{P3}^{LP^i} = \{5, 9\}, E_{P4}^{LP^i} = \{1, 3, 7\}$
$E_2^{CP^o} = \{P1\}, E_4^{CP^o} = \{P2, P3\}, E_6^{CP^o} = \{P1\},$ $E_8^{CP^o} = \{P3\}, E_{10}^{CP^o} = \{P2\}, E_{12}^{CP^o} = \{P1\}$	$E_{P1}^{CP^i} = \{2, 6, 12\}, E_{P2}^{CP^i} = \{4, 10\}, E_{P3}^{CP^i} = \{4, 8\}$

constraints of Section 3.2.2, since the Upper and Lower Inner M/H module Sets are no longer empty.

3.4.3 Problem Solution and Results

The examined MINLP quaternary sequencing problem was solved in the same way as the one for the ternary case, employing the GBD algorithm and implemented in GAMS using the APROS methodology. The solution of the MINLP problem (most energy efficient sequence) is depicted in Figure 3.6 and corresponds to a Direct Sequence involving 3 simple columns.

In the optimal sequence of Figure 3.6, the feed stream (F) was split in the first column into a distillate ($P1$) (containing the main fraction of the light component, Benzene) and into a bottoms liquid interconnection (LL) between Lower M/H modules 1 and 3, providing the feed to the second column. The latter was split into distillate $P2$ (rich in Toluene) and into a

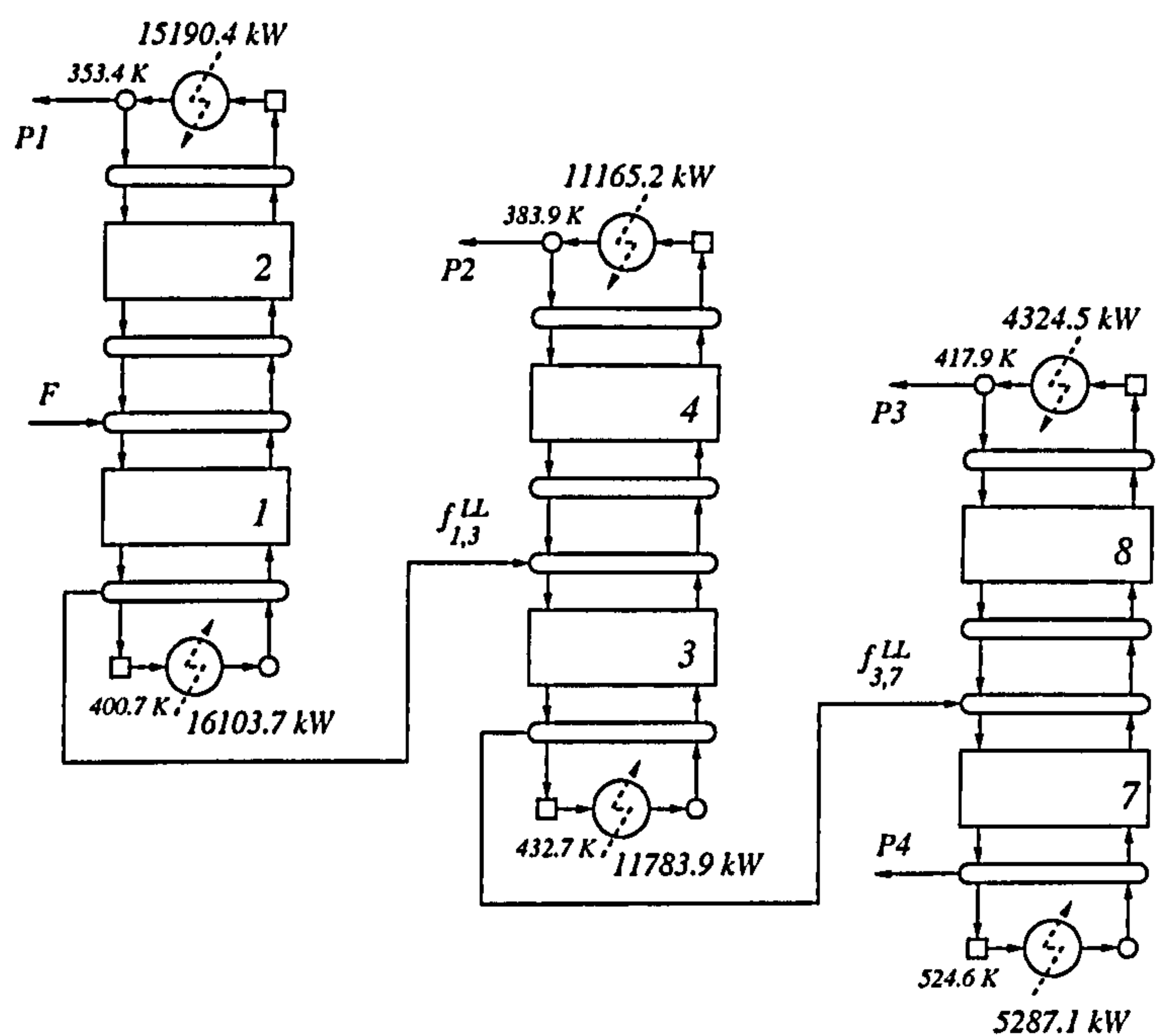


Figure 3.6: Optimal Solution of the Quaternary Simple Column Sequencing Problem

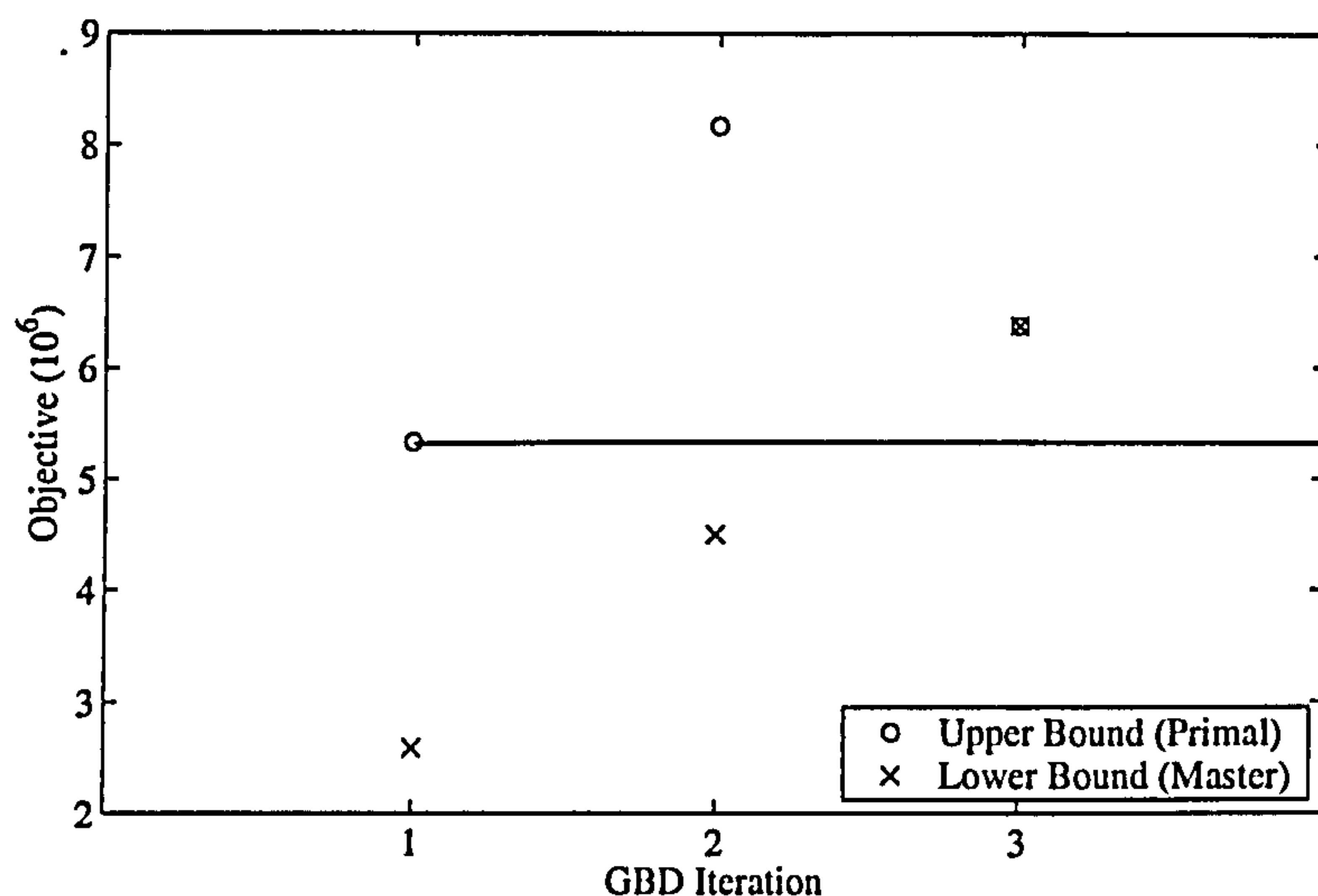
bottoms liquid interconnection (*LL*) between Lower *M/H* modules 3 and 7 (feed into the third column). In the last column the two remaining product streams were obtained, *i.e.* the distillate *P3* (rich in *o*-Xylene) and the bottoms product *P4* (rich in the heaviest component Diphenyl). The optimal operating conditions of this structure, as determined by the GMF Physical Model, are given in Table 3.10.

From a computational point of view, convergence was achieved in 3 GBD iterations. The starting point was the Direct Sequence (generating also the best upper bound, which proved to be the optimal solution). The 1st Master subproblem generated the Indirect Sequence and the 2nd Master generated a column sequence that combined the columns represented by the following

Table 3.10: Quaternary Optimal Sequence Operating Conditions

	$F(kmol/hr)$	$T(K)$	x_{Benz}	x_{Tol}	x_{o-Xyl}	x_{Diph}
$P1$	767.67	353.45	0.99	0.01	0	0
$f_{1,3}^{LL}$	1132.32	400.77	0	0.497	0.336	0.168
$P2$	568	383.99	0	0.99	0.01	0
$f_{3,7}^{LL}$	564.32	432.77	0	0	0.663	0.337
$P3$	376.2	417.92	0	0	0.99	0.01
$P4$	188.12	524.62	0	0	0.01	0.99

Table 3.11: GMF Quaternary Column Sequencing GBD Convergence



Iter.	<i>Primal</i>	<i>Master</i>
1	5.334 10 ⁶	2.591 10 ⁶
2	8.164 10 ⁶	4.487 10 ⁶
3	6.369 10 ⁶	6.369 10 ⁶

M/H module pairs (1-2, 3-4 and 9-10). The convergence history and the related economic savings (determined by comparing the Primal subproblem solutions) are given in Table 3.11.

Remark

A note must be made here regarding the results obtained through the GMF and those of Novak *et al.* (1996). The latter also solved the problem for single utility (High Pressure Steam) and had the same specifications for the product purities. The only differences lied in an additional specification of 99.5% recovery for all product streams and in the physical model employed (shortcut). The high recoveries were a necessary specification since the shortcut model utilized was based on the assumption of sharp splits in every column. From the results presented in the aforementioned publication, the temperature levels in the pertinent figure are in agreement with those of the GMF. However, the column heat duties and therefore the objective function values are almost double the ones obtained by the GMF. In the latter, although no recovery specifications were imposed, these were found (from Table 3.10) as 99.9%, 98.6%, 98% and 98% for products *P1*, *P2*, *P3* and *P4*, respectively. This large divergence in the results imposed the need for a validation of the GMF Physical Model results. The latter were checked against results obtained by ASPEN PLUS, initially using the DSTWU shortcut model, which employs the Winn-Underwood-Gilliland method for column design, specifying, according to the Douglas heuristic, an actual reflux equal to 1.2 times the minimum reflux. These results (which specified

heat duties for all columns similar to those of the GMF) provided the design data (tray numbers, feed tray location and reflux ratios) for the simulation of these columns using the RadFrac model which employs rigorous *MESH* models. The heat loads of the columns were again found similar to those of the GMF.

3.5 Conclusions

The results of the examined synthesis problems confirm the validity of the proposed GMF simple column sequencing method for energy efficiency. The latter satisfies the formal algorithmic process synthesis validity conditions, *i.e.* (i) it generates a superstructure which encompasses all the structural alternatives (subset F of all feasible alternatives), (ii) it incorporates a physical model that can evaluate accurately each structure belonging to the Sub-subset of Optimality Candidate Alternatives (O), and (iii) it is based on a formal mathematical algorithm that can lead to the optimal solution with respect to the synthesis objectives.

In the physical representation, the GMF can capture efficiently the mass and heat transfer phenomena, thus providing accurate energy consumption estimates and guidelines for the optimal operation of the derived designs. At the same time, taking into consideration the generated size reductions achieved in the GMF Physical Model (Primal NLP subproblems) due to the aggregation of the GMF Building Blocks, the GMF can prove a particularly useful tool for the conceptual design of distillation column sequences.

Moreover, the GMF can demonstrate its computational efficiency by finding the optimal solution without evaluating all the feasible structural alternatives, contrary to the enumeration approaches. In particular, in the Ternary case study the optimal solution was found without having to evaluate physically the 3-Column Sequence, which generates the largest and most difficult to solve Primal NLP subproblem. In the Quaternary case study, this advantage is even more pronounced since the optimal solution was found after examining only 3 of the 22 candidate alternative sequences. A simple exhaustive enumeration technique would have required the *manual* generation of all these alternatives and their evaluation through the solution of 22 NLP problems. Therefore, the examined sequencing problems beyond proving the efficiency of the GMF synthesis method, also demonstrate the necessity for the use of algorithmic methods in process synthesis, where all the alternatives are included in the generated problem, but only some of them are evaluated in order to formally obtain the optimal solution.

Chapter 4

Synthesis of Heat Integrated Distillation Column Sequences

4.1 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 recovered 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 Figure 4.1). The heat in the column's condenser is produced by the condensation of the vapour effluent of the column's top end, through heat exchange with a cold utility (cooling water), due to a temperature gradient. On the contrary, in a column's reboiler, heat is required for the vapourization of the liquid effluent of a column's bottom end, through heat exchange with a hot utility (steam). Structurally, two types of process stream exist, one vapour (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. Providing there is a sufficient temperature gradient between those two streams, the latter can be made to exchange heat with each other. In order to achieve the necessary temperature gradients the column pressures are shifted appropriately, since the column pressure has a direct effect on the column temperature levels

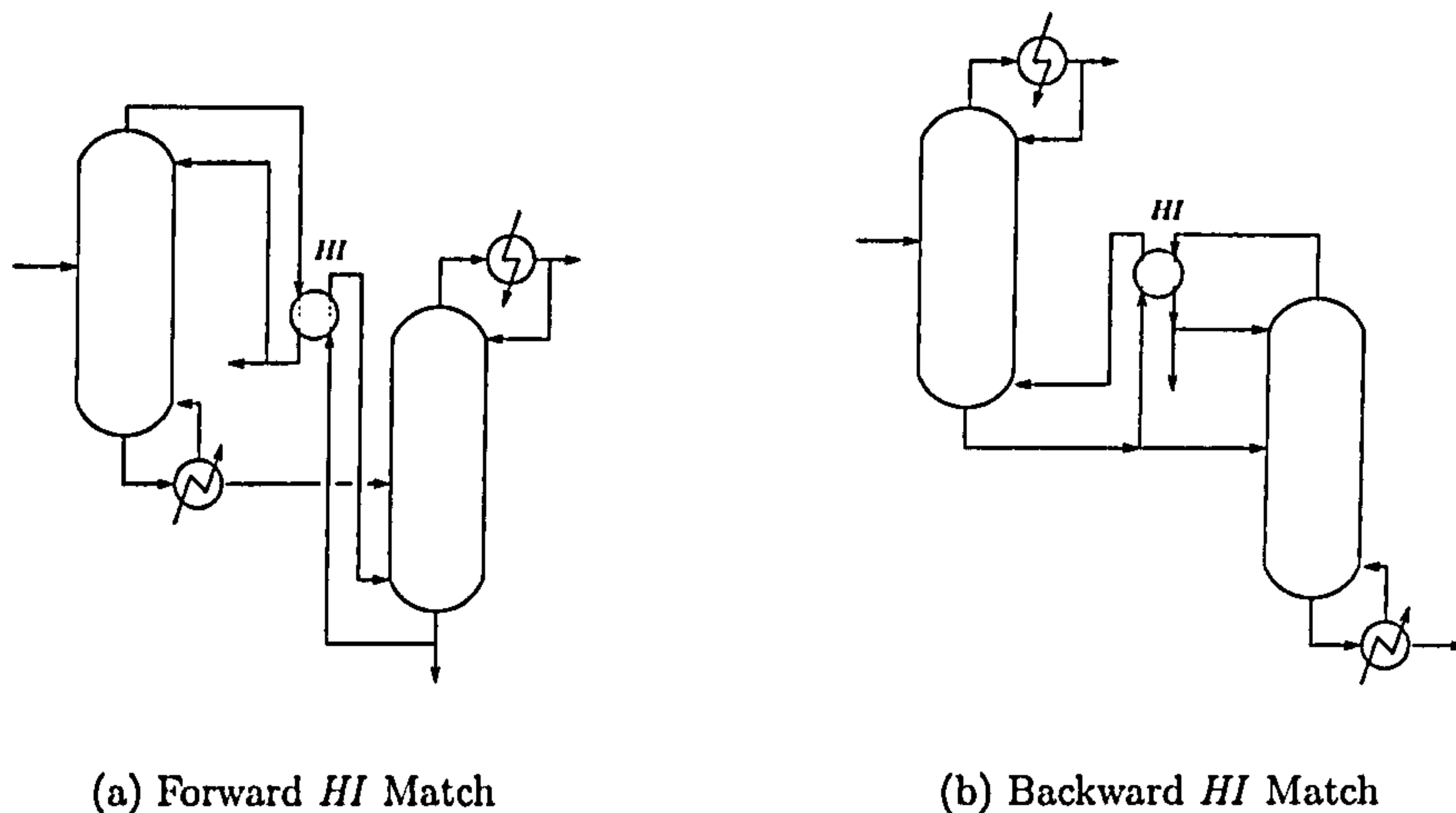


Figure 4.1: *HI* Illustration for a Ternary Direct Column Sequence

(for nonazeotropic and nonreacting mixtures, raising the column pressure, raises the column temperature). The operating cost savings achieved through *HI* have been reported of reaching ranges of 50% when compared to *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 has 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), 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. Here, we focus 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.

4.1.1 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 the *HI* distillation sequencing problem. Andreovich 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 flowrate. The *HI* possibilities were incorporated using the HEN Transportation (Cerdea *et al.*, 1983) and the Transshipment (Papoulias and Grossmann, 1983) problem formulations. However, in the above approach an invalid assumption was used, namely 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, Westerberg and Andreovich (1985) removed this assumption. The results generated the same *HI* sequences as previously, but the calculated utility targets were improved.

The *HI* column sequencing superstructure method of Westerberg and Andreovich (1985) 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 Transshipment/Transportation formulations. The distillation columns were modelled assuming sharp separations and total mass balances, generating a MILP problem, solved for the minimization of the TAC. The capital costing functions were based on a fixed charge part and on a feed flowrate dependent part and the column heat duties were also given as simple functions of the feed flowrate.

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 Andreovich and Westerberg (1985a). In the *HI* sequencing problem, columns of sharp splits were represented through the temperatures of their reboilers and condensers. In contrast with the *HI* method of Andreovich and Westerberg (1985a), the reboiler and condenser temperatures were not considered constant but were incorporated as variables. The columns were modelled operating at arbitrary pressures, as 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 flowrate dependant) model. In the operating cost model the heat loads of the reboilers and condensers were calculated by simple functions of the feed flowrate. The generated problem was solved incorporating 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 *et al.* (1990) (NLP) or of Yee and Grossmann (1990) (MINLP, in which binary variables were used for every potential heat match). The columns were modelled 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 (1986b) 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 (1986b) model and its disjunctive reformulation generated *HI* structures which were characterized by the same column sequencing but with different *HI* schemes. The Duran and Grossmann (1986b) model produced the worst solution, while its disjunctive reformulation and the Novak *et al* (1996) solution produced the best results which were quite close to each other.

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 vapour flowrates and heat of vapourization, 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 flowsheet optimization and the validation/analysis. A general separation problem posed in Aggarwal and Floudas (1990) was revisited incorporating also *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 2 feasible separation techniques were identified (flash and distillation). These 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, extended for the general separation case. *HI* was implemented in this model using the Yee and Grossmann (1990) HEN model. The columns were modelled using the Fenske-Gilliland-Underwood shortcut model and the *HI*

Table 4.1: Summary of Superstructure Methods for *HI* Simple Column Sequencing

Authors	Features
Simplified Methods (<i>Sharp Splits</i>)	
Andreovich & Westerberg (1985)	HEN Transportation/Transshipment, Fixed P Columns
Kakhu & Flower (1988)	Andreovich & Westerberg (1985b)-3 Complex Columns
Paules & Floudas (1988)	P via Condenser Temperature, Regression Analysis
Raman & Grossmann (1993)	Andreovich & Westerberg/Paules & Floudas, Logic BB
Novak <i>et al.</i> (1996)	HEN of Yee & Grossmann (1990)
Grossmann <i>et al.</i> (1998)	HEN of Duran & Grossmann (1986) and its GDP MILP
Yeomans & Grossmann (1999a,b)	<i>HI</i> of Raman & Grossmann (1993), GDP
Caballero & Grossmann (1999)	<i>HI</i> of Raman & Grossmann (1993), GDP
Hostrup <i>et al.</i> (2001)	Thermodynamic Insights & Novak <i>et al.</i> (1996)

results indicated 50% lower operating costs than those of the *non-HI* case.

Having covered the main principles behind the superstructure methods for *HI* distillation column synthesis found in the literature (a summary is given in Table 4.1), the following sections will focus on the proposed GMF *HI* Column Sequencing model, which is an extension of the GMF model proposed in Chapter 3 for the Simple Column Sequencing problem. In order to formally address the *HI* synthesis problem through the GMF, a *HI* block will be introduced, along with its structural and physical model components.

4.2 The GMF Heat Integration Block

So far, no formal heat integration techniques between distillation columns have been implemented in the GMF. In order to achieve this in a formal and systematic manner, a *HI* block has been introduced. The *HI* block is, in essence, a particular type of *He* module, where two *process* streams exchange heat without coming into mass active contact, providing there is an appropriate heat exchange driving force. The *HI* block must be appropriately modelled, structurally and physically, in order to be efficiently incorporated in the GMF, capturing the *HI* (structural) possibilities and their effects on the represented columns' operation.

4.2.1 HI Block Structural Representation

In Chapter 3, the vapour effluent of an Upper M/H module's Upper Auxiliary block exchanged heat with a cold utility in the module's associated Cooler. A similar heat exchange occurred between the liquid effluent of a Lower M/H module's Lower Auxiliary block and a hot utility in the module's associated Heater. In order to allow the HI of the aforementioned liquid and vapour effluent streams with each other, a HI block has been introduced, along with the necessary interconnections between the streams' origin modules. The HI block is presented in Figure 4.2.

Figure 4.2 shows the Lower Auxiliary block of a M/H module e , along with its associated Heater module (also numbered as e), the Upper Auxiliary block of a M/H module ea , along with its associated Cooler (ea) and the HI block between modules e and ea . In order to express mathematically the existence of a HI block, a primary binary variable, $y_{e,ea}^{HI}$, has been introduced (taking the value of 1 when the HI block exists).

The existence of most of the interconnections between the GMF Building Blocks illustrated in Figure 4.2, is mathematically translated using the HI block primary binary variable ($y_{e,ea}^{HI}$). The only streams that require the introduction of new secondary binary variables are those leaving the intermediate product and liquid interconnection mixers at the Hot Side of each Cooler/ HI block combination. For that purpose, the secondary binary variables $y_{ea,p}^{HIP}$ and $y_{ea,ea}^{HIL}$ have been introduced.

Finally, in order to ensure that meaningful HI structures are generated and to facilitate the

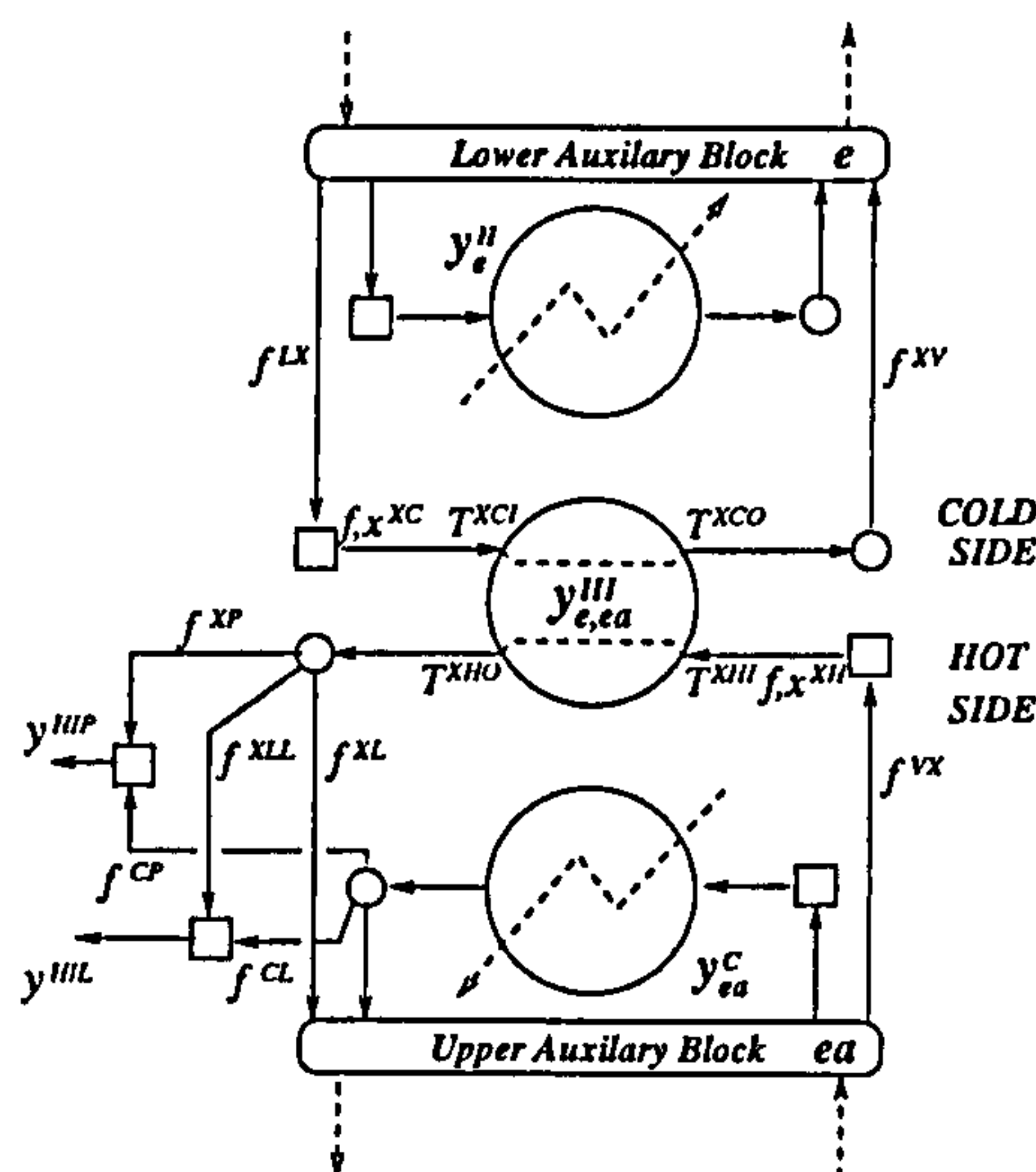


Figure 4.2: HI Block and its Interconnections

construction of the GMF Synthesis Model, the following *HI* Structural Sets are introduced:

$$\begin{aligned} E^X &= \{(e, ea) \mid \text{HI between modules } e (e \in E^L) \text{ and } ea (ea \in E^U), (ea \neq e + 1)\} \\ E_e^{XH} &= \{ea \mid \text{module } ea (ea \in E^L) \text{ that can be HI with module } e (e \in E^U), (ea \neq e - 1)\} \\ E_e^{XC} &= \{ea \mid \text{module } ea (ea \in E^U) \text{ that can be HI with module } e (e \in E^L), (ea \neq e + 1)\} \end{aligned}$$

Set E^{HI} defines all the allowable *HI* blocks between Lower and Upper *M/H* modules. E_e^{XH} and E_e^{XC} denote the sets of modules that can be heat integrated with the Hot and Cold Side modules, respectively. All these sets incorporate engineering knowledge, not allowing the heat integration of modules belonging to the same column.

4.2.2 *HI* Block Physical Representation

Beyond its structural model, the *HI* block is also accompanied by a physical model, incorporating appropriate *HI* physical modelling principles. These will affect the operation of the represented column sequences and will ensure that physically meaningful *HI* schemes are obtained.

In essence, as already noted, each *HI* block is a *He* module between two process streams. Therefore, *HI* blocks are modelled physically as the Cooler and Heater modules of Section 2.3.3, incorporating appropriately defined *HI* feasibility constraints. At the same time, the balances of other GMF Building Blocks receiving interconnections from *HI* blocks must be adjusted in order to incorporate the new *HI* terms. Furthermore, since column pressure is incorporated as a variable, which has an impact on the column operation and its heat integration, it must be modelled in such a way that modules belonging organically to the same column operate at the same pressure (under the assumption of uniform pressure profiles within each column, which is valid for the separations examined).

HI Block Physical Model

Additional sets are introduced for the automatic construction of the *HI* Physical Model for each chosen structure. These sets participate only in the GMF Physical Model.

$$\begin{aligned} E^{XE} &= \{(e, ea) \mid \text{existing HI blocks } (y_{e,ea}^{HI} = 1)\}, \quad \text{where } E^{XE} \subseteq E^X \\ E_e^{XHE} &= \{ea \mid \text{existing HI blocks } (y_{e,ea}^{HI} = 1)\}, \quad \text{where } E_e^{XHE} \subseteq E_e^{XH} \end{aligned}$$

Hot Side

- Mass, Component and Energy Balances (including the product and liquid interconnection mixers)

$$f_{e,ea}^{XH} - f_{e,ea}^{VX} = 0, \quad e, ea \in E^{XE} \quad (4.1)$$

$$f_{e,ea}^{XL} + f_{e,ea}^{XLL} + f_{e,ea}^{XP} - f_{e,ea}^{XH} = 0, \quad e, ea \in E^{XE} \quad (4.2)$$

$$f_{e,ea}^{XH} x_{e,ea,c}^{XH} - f_{e,ea}^{VX} x_{e,ea,c}^{VA} = 0, \quad e, ea \in E^{XE}, c \in C \quad (4.3)$$

$$f_{e,ea}^{XH} h_{e,ea}^{XHI} - f_{e,ea}^{VX} h_{e,ea}^{VA} = 0, \quad e, ea \in E^{XE} \quad (4.4)$$

$$Q_{e,ea}^{HI} - f_{e,ea}^{XH} (h_{e,ea}^{XHI} - h_{e,ea}^{XHO}) = 0, \quad e, ea \in E^{XE} \quad (4.5)$$

$$\sum_{p \in E_{ea}^{CPo}} f_{ea,p}^{HIP} - \sum_{e \in E_{ea}^{XHE}} f_{e,ea}^{XP} - \sum_{p \in E_{ea}^{CPo}} f_{ea,p}^{CP} = 0, \quad ea \in E^U, ea \in E^E \quad (4.6)$$

$$\sum_{eaa \in E_{ea}^{CLo}} f_{ea,eaa}^{HIL} - \sum_{e \in E_{ea}^{XHE}} f_{e,ea}^{XLL} - \sum_{eaa \in E_{ea}^{CLo}} f_{ea,eaa}^{CL} = 0, \quad ea \in E^U, ea \in E^E \quad (4.7)$$

$$\sum_{p \in E_{ea}^{CPo}} f_{ea,p}^{HIP} x_{ea,c}^{HIP} - \sum_{e \in E_{ea}^{XHE}} f_{e,ea}^{XP} x_{e,ea,c}^{XH} - \sum_{p \in E_{ea}^{CPo}} f_{ea,p}^{CP} x_{ea,c}^C = 0, \quad ea \in E^U, ea \in E^E, c \in C \quad (4.8)$$

$$\sum_{eaa \in E_{ea}^{CLo}} f_{ea,eaa}^{HIL} x_{ea,c}^{HIL} - \sum_{e \in E_{ea}^{XHE}} f_{e,ea}^{XLL} x_{e,ea,c}^{XH} - \sum_{eaa \in E_{ea}^{CLo}} f_{ea,eaa}^{CL} x_{ea,c}^C = 0, \quad ea \in E^U, ea \in E^E, c \in C \quad (4.9)$$

$$\sum_{p \in E_{ea}^{CPo}} f_{ea,p}^{HIP} h_{ea}^{HIP} - \sum_{e \in E_{ea}^{XHE}} f_{e,ea}^{XP} h_{e,ea}^{XHO} - \sum_{p \in E_{ea}^{CPo}} f_{ea,p}^{CP} h_{ea,c}^{CO} = 0, \quad ea \in E^U, ea \in E^E \quad (4.10)$$

$$\sum_{eaa \in E_{ea}^{CLo}} f_{ea,eaa}^{HIL} h_{ea}^{HIL} - \sum_{e \in E_{ea}^{XHE}} f_{e,ea}^{XLL} h_{e,ea}^{XHO} - \sum_{eaa \in E_{ea}^{CLo}} f_{ea,eaa}^{CL} h_{ea}^{CO} = 0, \quad ea \in E^U, ea \in E^E \quad (4.11)$$

- Phase Defining Constraints

$$\sum_{c \in C} (x_{e,ea,c}^{XH} / K_{e,ea,c}^{XHI}) - 1 \leq 0, \quad e, ea \in E^{XE} \quad (4.12)$$

$$\sum_{c \in C} (x_{e,ea,c}^{XH} K_{e,ea,c}^{XHO}) - 1 \leq 0, \quad e, ea \in E^{XE} \quad (4.13)$$

$$\sum_{c \in C} (x_{ea,c}^{HIP} K_{ea,c}^{HIP}) - 1 \leq 0, \quad ea \in E^U, ea \in E^E \quad (4.14)$$

$$\sum_{c \in C} (x_{ea,c}^{HIL} K_{ea,c}^{HIL}) - 1 \leq 0, \quad ea \in E^U, ea \in E^E \quad (4.15)$$

- Thermodynamic Properties

$$h_{e,ea}^{XHI} - h_c(x_{e,ea,c}^{XH}, T_{e,ea}^{XHI}) = 0, \quad e, ea \in E^{XE} \quad (4.16)$$

$$h_{e,ea}^{XHO} - h_c(x_{e,ea,c}^{XH}, T_{e,ea}^{XHO}) = 0, \quad e, ea \in E^{XE} \quad (4.17)$$

$$h_{ea}^{HIP} - h_c(x_{ea,c}^{HIP}, T_{ea}^{HIP}) = 0, \quad ea \in E^U, ea \in E^E \quad (4.18)$$

$$h_{ea}^{HIL} - h_c(x_{ea,c}^{HIL}, T_{ea}^{HIL}) = 0, \quad ea \in E^U, ea \in E^E \quad (4.19)$$

$$K_{e,ea,c}^{XHI} - K_c(x_{e,ea,c}^{XH}, T_{e,ea}^{XHI}, P_{ea}) = 0, \quad e, ea \in E^{XE}, c \in C \quad (4.20)$$

$$K_{e,ea,c}^{XHO} - K_c(x_{e,ea,c}^{XH}, T_{e,ea}^{XHO}, P_{ea}) = 0, \quad e, ea \in E^{XE}, c \in C \quad (4.21)$$

$$K_{ea,c}^{HIP} - K_c(x_{ea,c}^{HIP}, T_{ea}^{HIP}, P_{ea}) = 0, \quad ea \in E^U, ea \in E^E, c \in C \quad (4.22)$$

$$K_{ea,c}^{HIL} - K_c(x_{ea,c}^{HIL}, T_{ea}^{HIL}, P_{ea}) = 0, \quad ea \in E^U, ea \in E^E \quad (4.23)$$

- Mixed Integer Physical-Structural Constraints

$$f_{e,ea}^{XH} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.24)$$

$$f_{e,ea}^{VX} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.25)$$

$$f_{e,ea}^{XL} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.26)$$

$$f_{e,ea}^{XLL} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.27)$$

$$f_{e,ea}^{XP} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.28)$$

$$Q_{e,ea}^{HI} - y_{e,ea}^{HI} Q^{max} \leq 0, \quad e, ea \in E^X \quad (4.29)$$

$$f_{ea,p}^{HIP} - y_{ea,p}^{HIP} \mathcal{F}^{max} \leq 0, \quad p \in E_{ea}^{CPo}, ea \in E^U \quad (4.30)$$

$$f_{ea,aaa}^{HIL} - y_{ea,aaa}^{HIL} \mathcal{F}^{max} \leq 0, \quad aaa \in E_{ea}^{CLo}, ea \in E^U \quad (4.31)$$

Cold Side

- Mass, Component and Energy Balances

$$f_{e,ea}^{XC} - f_{e,ea}^{LX} = 0, \quad e, ea \in E^{XE} \quad (4.32)$$

$$f_{e,ea}^{XV} - f_{e,ea}^{XC} = 0, \quad e, ea \in E^{XE} \quad (4.33)$$

$$f_{e,ea}^{XC} x_{e,ea,c}^{XC} - f_{e,ea}^{LX} x_{e,c}^{LA} = 0, \quad e, ea \in E^{XE}, c \in C \quad (4.34)$$

$$f_{e,ea}^{XC} h_{e,ea}^{XCI} - f_{e,ea}^{LX} h_e^{LA} = 0, \quad e, ea \in E^{XE} \quad (4.35)$$

$$Q_{e,ea}^{HI} - f_{e,ea}^{XC} (h_{e,ea}^{XCO} - h_{e,ea}^{XCI}) = 0, \quad e, ea \in E^{XE} \quad (4.36)$$

- Phase Defining Constraints

$$\sum_{c \in C} (x_{e,ea,c}^{XC} K_{e,ea,c}^{XCI}) - 1 \leq 0, \quad e, ea \in E^{XE} \quad (4.37)$$

$$\sum_{c \in C} (x_{e,ea,c}^{XC} / K_{e,ea,c}^{XCO}) - 1 \leq 0, \quad e, ea \in E^{XE} \quad (4.38)$$

- Thermodynamic Properties

$$h_{e,ea}^{XCI} - h_c(x_{e,ea,c}^{XC}, T_{e,ea}^{XCI}) = 0, \quad e, ea \in E^{XE} \quad (4.39)$$

$$h_{e,ea}^{XCO} - h_c(x_{e,ea,c}^{XC}, T_{e,ea}^{XCO}) = 0, \quad e, ea \in E^{XE} \quad (4.40)$$

$$K_{e,ea,c}^{XCI} - K_c(x_{e,ea,c}^{XC}, T_{e,ea}^{XCI}, P_e) = 0, \quad e, ea \in E^{XE}, c \in C \quad (4.41)$$

$$K_{e,ea,c}^{XCO} - K_c(x_{e,ea,c}^{XC}, T_{e,ea}^{XCO}, P_e) = 0, \quad e, ea \in E^{XE}, c \in C \quad (4.42)$$

- Mixed Integer Physical-Structural Constraints

$$f_{e,ea}^{XC} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.43)$$

$$f_{e,ea}^{LX} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.44)$$

$$f_{e,ea}^{XV} - y_{e,ea}^{HI} \mathcal{F}^{max} \leq 0, \quad e, ea \in E^X \quad (4.45)$$

Cold-Hot Side HI Feasibility Constraints

$$(T_{e,ea}^{XCO} - T_{e,ea}^{XHI}) + EMTA - \mathcal{M}^{HI} (1 - y_{e,ea}^{HI}) \leq 0, \quad e, ea \in E^X \quad (4.46)$$

$$(T_{e,ea}^{XCI} - T_{e,ea}^{XHO}) + EMTA - \mathcal{M}^{HI} (1 - y_{e,ea}^{HI}) \leq 0, \quad e, ea \in E^X \quad (4.47)$$

The last two constraints ensure that, on both sides of the *HI* block of Figure 4.2, there is a temperature gradient, providing the driving force for heat exchange. These constraints will have an impact on the column pressures which should be shifted appropriately so that the column temperatures satisfy the above *HI* feasibility constraints. *EMTA* stands for the Exchange Minimum Temperature Approach. This big-*M* formulation is the same one used in Paules and Floudas (1988). The value of $\mathcal{M}^{HI}$ must be large enough so that the constraints do not become active when the *HI* block is not chosen (when $y_{e,ea}^{HI} = 0$), so that it has no negative effect on the system. However, the above value should not be extremely large as this will lead to very loose bounds, hampering the efficient solution of the problem and leading to potential convergence problems. Since this big-*M* refers to temperature, which in turn depends on column pressure, the upper and lower bounds of the latter must be accounted for when choosing a value for $\mathcal{M}^{HI}$. The utilized function for the estimation of $\mathcal{M}^{HI}$ is given below.

$$\mathcal{M}^{HI} = (T_h^{BPmax} - T_l^{BPmin}) + EMTA \quad (4.48)$$

In the above T_h^{BPmax} and T_l^{BPmin} are the boiling point temperatures of the heaviest component (*h*) calculated at the maximum allowed column pressure (pressure upper bound) and of the

lightest component (l) at the minimum allowed column pressure, respectively. This calculation of the value of $\mathcal{M}^{HI}$ is required since the pressure is a variable that affects temperature (and boiling point) levels. Moreover, a similar calculation for $\mathcal{M}$ must be applied also for the He GMF modules (Coolers and Heaters). Therefore, in the GMF Physical Model of Section 2.3.3, $\mathcal{M}^C$ and $\mathcal{M}^H$ of equations (2.48), (2.49), (2.60) and (2.61), for the Coolers and Heaters should be estimated by the following functions:

$$\mathcal{M}^C = (T^{cw} - T_l^{BPmin}) + EMTA \quad (4.49)$$

$$\mathcal{M}^H = (T_h^{BPmax} - T^{st}) + EMTA \quad (4.50)$$

Modified GMF Physical Model Constraints

The mass and energy balances of the Upper and Lower Auxiliary blocks and Product mixers must be modified in order to incorporate the potential interconnections from and to the Cooler/Heater/ HI block combinations. A new Structural Set, E_e^{XCE} , is also introduced for the automatic construction of the physical problems during the solution procedure.

$$E_e^{XCE} = \{ea | \text{existing HI blocks } (y_{e,ea}^{HI} = 1)\}, \quad \text{where } E_e^{XCE} \subseteq E_e^{XC}$$

- Upper Auxiliary block Balances (replacing equations (2.8),(2.9) and (2.10), respectively).

$$\begin{aligned} f_e^{LI} + f_{e,e}^{VC} + \sum_{ea \in E_e^{VV_0}} f_{e,ea}^{VV} + \sum_{ea \in E_e^{XHE}} f_{ea,e}^{VX} - f_e^{VO} - \sum_{i \in E_e^{FL}} f_{i,e}^{FL} - \sum_{ea \in E_e^{LLi}} f_{ea,e}^{LL} \\ - \sum_{ea \in E_e^{XHE}} f_{ea,e}^{XL} - \sum_{ea \in E_e^{CLi}} f_{ea,e}^{HIL} = 0, \quad e \in E^E \end{aligned} \quad (4.51)$$

$$\begin{aligned} f_e^{LI} x_{e,c}^{LI} + \left(f_{e,e}^{VC} + \sum_{ea \in E_e^{VV_0}} f_{e,ea}^{VV} + \sum_{ea \in E_e^{XHE}} f_{ea,e}^{VX} \right) x_{e,c}^{VA} - f_e^{VO} x_{e,c}^{VO} - \sum_{i \in E_e^{FL}} f_{i,e}^{FL} x_{i,c}^F - \sum_{ea \in E_e^{LLi}} f_{ea,e}^{LL} x_{ea,c}^{LA} \\ - \sum_{ea \in E_e^{XHE}} f_{ea,e}^{XL} x_{ea,c}^{XH} - \sum_{ea \in E_e^{CLi}} f_{ea,e}^{HIL} x_{ea,c}^{HIL} = 0, \quad e \in E^E, c \in C \end{aligned} \quad (4.52)$$

$$\begin{aligned} f_e^{LI} h_e^{LI} + \left(f_{e,e}^{VC} + \sum_{ea \in E_e^{VV_0}} f_{e,ea}^{VV} + \sum_{ea \in E_e^{XHE}} f_{ea,e}^{VX} \right) h_e^{VA} - f_e^{VO} h_e^{VO} - \sum_{i \in E_e^{FL}} f_{i,e}^{FL} h_i^F - \sum_{ea \in E_e^{LLi}} f_{ea,e}^{LL} h_{ea}^{LA} \\ - \sum_{ea \in E_e^{XHE}} f_{ea,e}^{XL} h_{ea,e}^{XHO} - \sum_{ea \in E_e^{CLi}} f_{ea,e}^{HIL} h_{ea}^{HIL} = 0, \quad e \in E^E \end{aligned} \quad (4.53)$$

- Lower Auxiliary block Balances (replacing equations (2.28),(2.29) and (2.30), respectively).

$$f_e^{VI} + f_{e,e}^{LH} + \sum_{ea \in E_e^{XCE}} f_{e,ea}^{LX} + \sum_{ea \in E_e^{LLo}} f_{e,ea}^{LL} + \sum_{p \in E_e^{LP_0}} f_{e,p}^{LP} - f_e^{LO} - f_{e,e}^{HV} - \sum_{ea \in E_e^{XCE}} f_{e,ea}^{XV} - \sum_{ea \in E_e^{VV_i}} f_{ea,e}^{VV} = 0, \quad e \in E^E \quad (4.54)$$

$$f_e^{VI} x_{e,c}^{VI} + \left(f_{e,e}^{LH} + \sum_{ca \in E_e^{XCE}} f_{e,ca}^{LX} + \sum_{ea \in E_e^{LLO}} f_{e,ea}^{LL} + \sum_{p \in E_e^{LPO}} f_{e,p}^{LP} \right) x_{e,c}^{LA} - f_e^{LO} x_{e,c}^{LO} - f_{e,e}^{HV} x_{e,c}^H - \sum_{ca \in E_e^{XCE}} f_{e,ca}^{XV} x_{e,ca,c}^{XC} - \sum_{ea \in E_e^{VVI}} f_{ea,e}^{VV} x_{ea,c}^{VA} = 0, \quad e \in E^E, c \in C \quad (4.55)$$

$$f_e^{VI} h_e^{VI} + \left(f_{e,e}^{LH} + \sum_{ca \in E_e^{XCE}} f_{e,ca}^{LX} + \sum_{ea \in E_e^{LLO}} f_{e,ea}^{LL} + \sum_{p \in E_e^{LPO}} f_{e,p}^{LP} \right) h_e^{LA} - f_e^{LO} h_e^{LO} - f_{e,e}^{HV} h_e^{HO} - \sum_{ca \in E_e^{XCE}} f_{e,ca}^{XV} h_{e,ca}^{XCO} - \sum_{ea \in E_e^{VVI}} f_{ea,e}^{VV} h_{ea}^{VA} = 0, \quad e \in E^E \quad (4.56)$$

- Product Mixer Balances (replacing equations (2.62),(2.63) and (2.64), respectively).

$$f_p^P - \sum_{e \in E_p^{LPI}} f_{e,p}^{LP} - \sum_{e \in E_p^{CPI}} f_{e,p}^{HIP} = 0, \quad p \in P \quad (4.57)$$

$$f_p^P x_{p,c}^P - \sum_{e \in E_p^{LPI}} f_{e,p}^{LP} x_{e,c}^{LA} - \sum_{e \in E_p^{CPI}} f_{e,p}^{HIP} x_{e,c}^{HIP} = 0, \quad p \in P, c \in C \quad (4.58)$$

$$f_p^P h_p^P - \sum_{e \in E_p^{LPI}} f_{e,p}^{LP} h_e^{LA} - \sum_{e \in E_p^{CPI}} f_{e,p}^{HIP} h_e^{HIP} = 0, \quad p \in P \quad (4.59)$$

- Column Pressure (imposing M/H modules that belong organically to the same column to operate in the same pressure).

$$P_e - P_{e+1} = 0, \quad e \in E^L \quad (4.60)$$

4.3 GMF Structural Model For *HI* Simple Column Sequences

The GMF Structural Model for the *HI* simple distillation sequencing problem is based on the corresponding structural model for *non-HI* columns, maintaining most of its constraints. The constraints that are replaced are those related with the existence of *He* units and their interconnections (with particular attention to those of the Cooler modules). The classification of the structural constraints, as Superstructure Basis, Intra and Inter-Column is also maintained. The *HI* Structural Sets are added to those of the *non-HI* sequencing problem. According to the employed 3-stage procedure, the Propositional Logic Expressions are initially generated (Stage 1), which are then translated into their corresponding structural constraints (Stage 2). In the 3rd Stage the GMF Structural Sets are assigned for the problems examined.

4.3.1 GMF Propositional Logic Expressions - Stage 1

Superstructure Basis Logical Expressions

All the Superstructure Basis expressions of the simple column sequencing problem of Section 3.2.1 are valid for the *HI* sequencing structural model. An additional constraint is included enforcing a maximum number N of *HI* blocks allowed per structure (written for simplification in its pure integer form).

$$\sum_{e,ea \in E^X} y_{e,ea}^{HI} \leq N \quad (4.61)$$

The above constraint is included in order to reduce the complexity of the generated structures and is by no means limiting since it can be readily relaxed.

Intra-Column Logical Expressions

These expressions arrange the interconnections between *M/H* and potential *He* modules and *HI* blocks within the *same* column. In the *HI* column case, the existence of a *He* module is no longer necessary, since it could be replaced by an *HI* block. The GMF *HI* Structural Model is defined in such a way, that a *He* module can coexist with one or more *HI* blocks. The majority of the Intra-Column Logical Expressions of the *non-HI* simple columns (Section 3.2.1) are maintained for the *HI* case. Only expressions (3.5) and (3.6) are replaced by the following:

$$y_e \Leftrightarrow \bigvee_{ea \in E_e^{XC}} y_{e,ea}^{HI} \vee y_e^H, \quad e \in E^L \quad (4.62)$$

$$y_e \Leftrightarrow \bigvee_{ea \in E_e^{XH}} y_{ea,e}^{HI} \vee y_e^C, \quad e \in E^U \quad (4.63)$$

Inter-Column Logical Expressions

As in the Intra-Column case, the Inter-Column Logical Expressions for the *HI* column sequencing problem are based on those of the *non-HI* case, as given in Section 3.2.1. However, in expressions (3.13), (3.21), (3.23) and (3.24), y^{CP} and y^{CL} should be replaced by y^{HIP} and y^{HIL} , respectively, while maintaining the same indices. The newly added expressions and the ones that should be replaced are given below.

- If a *HI* block exists, then its participating *M/H* modules should also exist.

$$y_{e,ea}^{HI} \Rightarrow y_e \wedge y_{ea}, \quad e, ea \in E^X \quad (4.64)$$

- Two columns should not be allowed to be heat integrated to each other at both ends (no simultaneous Forward and Backward *HI* match).

$$y_{e,ea}^{HI} \Rightarrow \neg y_{ea-1,e+1}^{HI}, \quad e, ea \in E^X \quad (4.65)$$

- If an *Upper M/H* module exists *one and only one* interconnecting stream is allowed from its associated Cooler/*HI* block combinations, *either* to a product mixer *or* to a *M/H* module of *another* column ($ea \neq e$) (replaces expression (3.14)).

$$y_e = \{ \{ y_{e,p1}^{HIP}, \dots, y_{e,pn}^{HIP} \}_{p \in E_e^{CPo}}, \{ y_{e,ea1}^{HIL}, \dots, y_{e,ean}^{HIL} \}_{ea \in E_e^{CLo}} \}, \quad e \in E^U, ea \neq e \quad (4.66)$$

- A product stream leaves the Cooler/*HI* block combinations of an Upper Outer module *if and only if* no other module belonging to *another* column that receives this interconnection exists (replaces expression (3.16)).

$$y_{e,p}^{HIP} \Leftrightarrow (\bigvee_{ea \in E_e^{XII}} y_{eaa,e}^{HI} \vee y_e^C) \wedge \neg y_{ea}, \quad e \in E^{UO}, p \in E_e^{CPo}, ea \in E_e^{CLo}, ea \neq e \quad (4.67)$$

- A liquid interconnection leaves the Cooler/*HI* block combinations of an Upper Outer module towards *another* column *if and only if* the destination *M/H* module exists (replaces expression (3.17)).

$$y_{e,ea}^{HIL} \Leftrightarrow (\bigvee_{eaa \in E_e^{XII}} y_{eaa,e}^{HI} \vee y_e^C) \wedge y_{ea}, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (4.68)$$

- If a liquid interconnection leaves the Cooler/*HI* block combinations of an Upper Inner module, then the destination module also exists (replaces expression (3.20)).

$$y_{e,ea}^{HIL} \Rightarrow (\bigvee_{eaa \in E_e^{XII}} y_{eaa,e}^{HI} \vee y_e^C) \wedge y_{ea}, \quad e \in E^{UI}, ea \in E_e^{CLo}, ea \neq e \quad (4.69)$$

The remaining Inter-Column expressions of Section 3.2.1 should be included in their original form in the *HI* column sequencing Inter-Column logical expressions.

4.3.2 GMF Structural Integer Constraints - Stage 2

As mentioned earlier in the 2nd stage of the systematic procedure for the construction of the GMF Structural Models, the Propositional Logic Expressions are translated into their conjunctive normal form and then into their pure integer form defining the GMF Structural Constraints, while replacing the Boolean variables with their corresponding binary variables.

Superstructure Basis Structural Constraints

These constraints are identical to those of Section 3.2.2, with the addition of constraint (4.61).

Intra-Column Structural Constraints

The non-modified Intra-Column constraints of Section 3.2.2 should be used in their original form. The structural constraints of the new *HI* Intra-Column expressions, defined in Section 4.3.1, are given below:

$$1 - y_e + \sum_{ea \in E_e^{XC}} y_{e,ea}^{HI} + y_e^H \geq 1, \quad e \in E^L \quad (4.70)$$

$$1 - y_{e,ea}^{HI} + y_e \geq 1, \quad ea \in E_e^{XC}, e \in E^L \quad (4.71)$$

$$1 - y_e^H + y_e \geq 1, \quad e \in E^L \quad (4.72)$$

$$1 - y_e + \sum_{ea \in E_e^{XH}} y_{ea,e}^{HI} + y_e^C \geq 1, \quad e \in E^U \quad (4.73)$$

$$1 - y_{ea,e}^{HI} + y_e \geq 1, \quad ea \in E_e^{XH}, e \in E^U \quad (4.74)$$

$$1 - y_e^C + y_e \geq 1, \quad e \in E^U \quad (4.75)$$

Inter-Column Structural Constraints

Similarly to the Intra-Column constraints, the Inter-Column constraints are based on the corresponding constraints of the *non-HI* column sequencing model (Section 3.2.2), using the modifications for the *HI* case. The constraints corresponding to the unmodified logical expressions are used here as found in the aforementioned section, including the designated y^{CP} and y^{CL} to y^{HIP} and y^{HIL} transformations. For simplicity, below are given the structural constraints corresponding to the newly introduced and modified logical expressions of Section 4.3.1.

$$1 - y_{e,ea}^{HI} + y_e \geq 1, \quad e, ea \in E^X \quad (4.76)$$

$$1 - y_{e,ea}^{HI} + y_{ea} \geq 1, \quad e, ea \in E^X \quad (4.77)$$

$$1 - y_{e,ea}^{HI} + 1 - y_{ea-1,e+1}^{HI} \geq 1, \quad e, ea \in E^X \quad (4.78)$$

$$\sum_{p \in E_e^{CPo}} y_{e,p}^{HIP} + \sum_{ea \in E_e^{CLo}} y_{e,ea}^{HIL} = y_e, \quad e \in E^U, ea \neq e \quad (4.79)$$

$$1 - y_{e,p}^{HIP} + \sum_{eaa \in E_e^{XH}} y_{eaa,e}^{HI} + y_e^C \geq 1, \quad e \in E^{UO}, p \in E_e^{CPo} \quad (4.80)$$

$$1 - y_{e,p}^{HIP} + 1 - y_{ea} \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, p \in E_e^{CPo}, ea \neq e \quad (4.81)$$

$$y_{e,p}^{HIP} + 1 - y_{eaa,e}^{HI} + y_{ea} \geq 1, \quad e \in E^{UO}, eaa \in E_e^{XH}, p \in E_e^{CPo},$$

$$ea \in E_e^{CLo}, ea \neq e \quad (4.82)$$

$$y_{e,p}^{HIP} + 1 - y_e^C + y_{ea} \geq 1, \quad e \in E^{UO}, p \in E_e^{CPo}, ea \in E_e^{CLo}, ea \neq e \quad (4.83)$$

$$1 - y_{e,ea}^{HIL} + \sum_{eaa \in E_e^{XH}} y_{eaa,e}^{HI} + y_e^C \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (4.84)$$

$$1 - y_{e,ea}^{HIL} + y_{ea} \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (4.85)$$

$$y_{e,ea}^{HIL} + 1 - y_{eaa,e}^{HI} + 1 - y_{ea} \geq 1, \quad e \in E^{UO}, eaa \in E_e^{XH}, ea \in E_e^{CLo}, ea \neq e \quad (4.86)$$

$$y_{e,ea}^{HIL} + 1 - y_e^C + 1 - y_{ea} \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (4.87)$$

$$1 - y_{e,ea}^{HIL} + \sum_{eaa \in E_e^{XH}} y_{eaa,e}^{HI} + y_e^C \geq 1, \quad e \in E^{UI}, ea \in E_e^{CLo}, ea \neq e \quad (4.88)$$

$$1 - y_{e,ea}^{HIL} + y_{ea} \geq 1, \quad e \in E^{UI}, ea \in E_e^{CLo}, ea \neq e \quad (4.89)$$

The GMF Structural Model for the synthesis of *HI* simple column sequences consists of the GMF Structural Constraints of Stage 2 defined over the appropriate GMF Structural Sets (Stage 3), along with the appropriate GBD Integer Cuts. The above model, in conjunction with the GMF Physical Model (Section 2.3.3) and the additions and modifications for the introduction of the *HI* blocks, define the complete GMF synthesis model for the *HI* simple column sequencing problem for energy efficiency. Employing this model, the case studies of Chapter 3 will be revisited for enhanced energy savings through *HI* in the following sections.

4.4 Case Study: Ternary *HI* Simple Column Sequencing

4.4.1 Problem Statement

The case study of the Benzene, Toluene and o-Xylene distillation separation used for the evaluation of the proposed GMF Ternary Simple Column Sequencing synthesis model, was revisited incorporating Heat Integration possibilities. The problem data was based on Table 3.3, with modifications/additions associated with the pressure in the columns. The latter was no longer fixed to the 1 atm value and it was formally incorporated as a variable in the optimization problem. The lower and upper bounds for the *M/H* modules' pressure were taken equal to 1 and 10 atm, respectively. The same held for the pressure of the feed, which was assumed equal to

the pressure of its destination M/H module. Consequently, the temperature of the feed stream, which was assumed to be at its bubble point, was calculated at the pressure of the feed.

The objective to be optimized was the minimization of the Operating Cost, subject to the product purity specifications of Table 3.4. The only additional information regarded the available utilities, their temperatures and the necessary value of the Exchanger Minimum Temperature Approach ($EMTA$). These are given in Table 4.2. For simplicity, only a single hot and cold utility were used, namely the steam and the cooling water of the simple column sequencing problem with the same costing. More utilities can be readily incorporated. Moreover, the cost of pumps was considered negligible when compared to the heat units' operating cost (Novak *et al.*, 1996).

Table 4.2: Ternary HI Heat Exchange Data

Cooling Water Temperature (T^{cw})	300 (K)
Steam Temperature (T^{st})	500 (K)
$EMTA$	10 (K)

The temperature of the available utilities was assumed constant (which is a valid assumption, since due to the availability of large quantities of utilities, their bulk temperature can be assumed unchanged). For simplicity reasons, the same $EMTA$ was used for all types of exchangers (utility-process stream or Heat Integration process-process stream). However, if necessary, alternative $EMTA$'s can be assigned according to the heat exchanger unit type.

4.4.2 GMF Problem Formulation - Stage 3

In order to generate the GMF Synthesis Model for the examined ternary distillation sequencing problem the GMF Structural Model of Section 4.3.2 was initially defined, by appropriately assigning the GMF Structural Sets (Stage 3), and then coupled to the GMF Physical Model. The GMF Structural Sets' assignments were the same as those of the ternary simple column sequencing problem without Heat Integration (Table 3.5). The assignment of the additional HI Structural Sets is given in Table 4.3. As throughout this work, these sets were incorporated in GAMS as PARAMETERS.

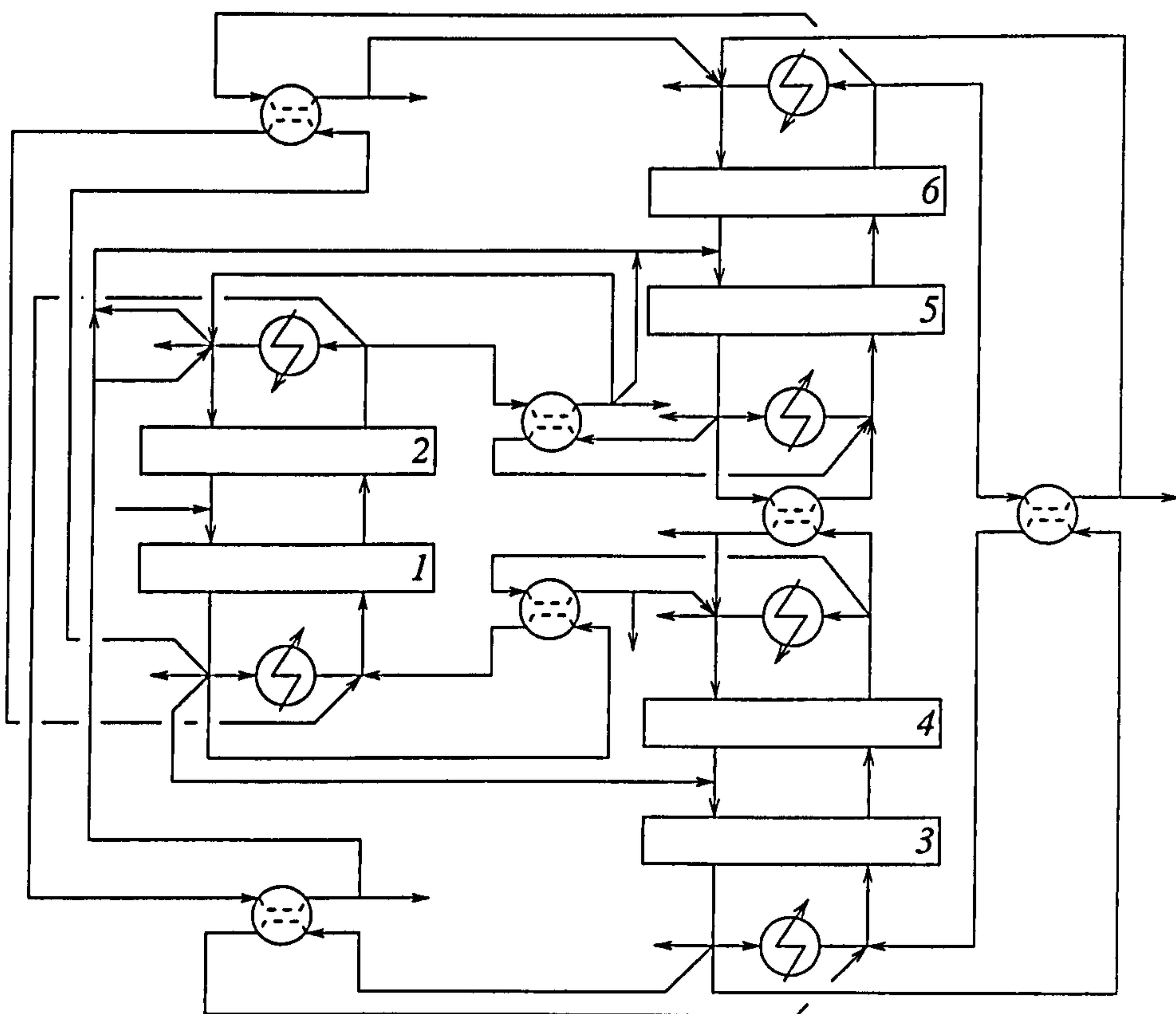
The GMF Structural Model was fully defined with the assignment of the maximum number of allowable HI blocks for each heat integrated structure. For the examined case study, this was set

Table 4.3: Ternary GMF *HI* Structural Sets (Stage - 3)

$E^X = \{(e, ea) e \in E^L, ea \in E^U, ea \neq e + 1\}$
$E_e^{XH} = \{ea ea \in E^L, ea \neq e - 1\}, e \in E^U$
$E_e^{XC} = \{ea ea \in E^U, ea \neq e + 1\}, e \in E^L$

to 2 ($N = 2$ for constraint (4.61)). The ternary sequencing problem, which in the *non-HI* case had only a small number of structural alternatives which allowed even enumeration techniques for its solution, in the *HI* case has become considerably more involved. As an illustration, the superstructure of the examined *HI* sequencing problem is shown in Figure 4.3.

In the GMF Physical Model, in order to facilitate convergence of the Primal subproblems and to find optimal solutions that represent the true energy efficiency potential of each sequence, appropriate bounds were provided for each column's pressure and temperatures. Pressure was bounded between the minimum allowable pressure for atmospheric operation (1 atm) and a large

Figure 4.3: GMF Ternary *HI* Simple Distillation Column Superstructure

upper bound, which was large enough so as to avoid cutting out a path towards the solution. An upper bound of 10 atm was thus imposed. However, from a closer observation of the separation's physics and the optimization problem being solved (minimization of operating cost), this upper bound was rather conservative, and could not become active, since the hot utility temperatures imposed a natural bound on the Heater temperatures (which are dependent on the pressures). The columns' temperature bounds were also adjusted to the fact that pressure was allowed to vary. Therefore, the temperature lower bound was set to the bubble point temperature of the lightest component calculated at the minimum allowed pressure, minus a $10^{\circ}C$ slack. The temperature upper bound was set to the bubble point temperature of the heaviest component at the maximum allowed pressure plus a $10^{\circ}C$ slack.

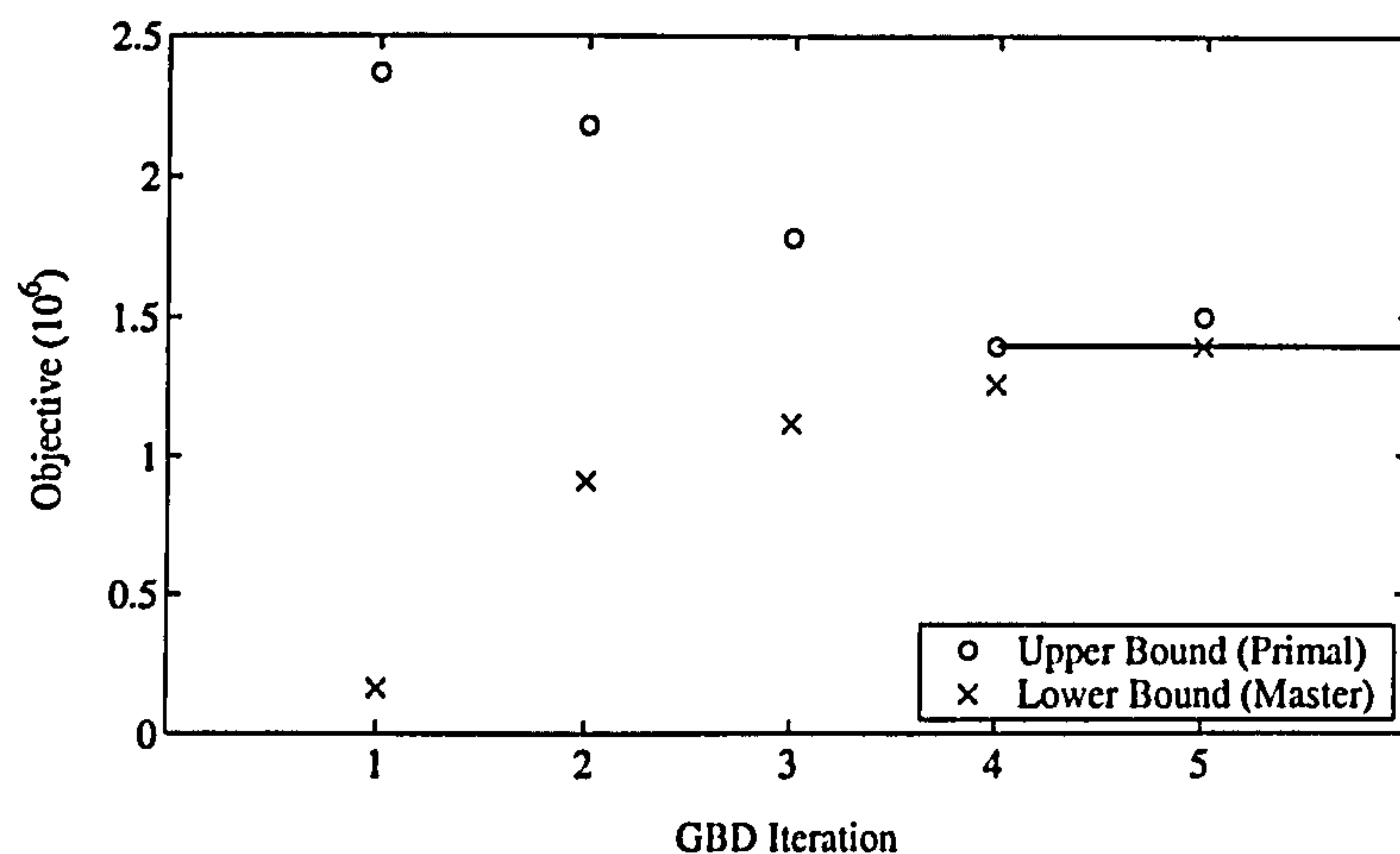
4.4.3 Problem Solution and Results

The complete GMF synthesis model generated an MINLP problem, which was implemented in GAMS and solved using the GBD/APROS methodology. The optimal solution corresponded to a heat integrated variant of the Direct Sequence. The optimal structure along with its operating conditions are shown in Table 4.4.

The Operating Cost in the optimal *HI* sequence was found equal to \$1,392,000/yr. From a comparison to the optimal *non-HI* simple column sequence for the same problem, it can be found that operating cost savings of \$977,000/yr have been achieved, corresponding to annual savings of 41%. This has been achieved by raising the pressure of the first column of the sequence from 1 to 5.78 atm, so that this column can be heat integrated with the second column, eliminating

Table 4.4: GMF *HI* Ternary Sequencing Optimal Structure and Operation

		F (kmol/hr)	x_{Benz}	x_{Tol}	$x_o - x_{yl}$
	$P1$	191	0.95	0.05	0
	S	394.75	0.04	0.95	0.01
	$P2$	414.25	0	0.05	0.95
		Column 1		Column 2	
	Q_e^H (kW)	8488.4		-	
	Q_e^C (kW)	-		10635.8	
	P_e (atm)	5.78		1	

Table 4.5: GMF Ternary *HI* Column Sequencing GBD Convergence

Iter.	<i>Primal</i>	<i>Master</i>
1	2.369 10^6	0.165 10^6
2	2.181 10^6	0.911 10^6
3	1.781 10^6	1.114 10^6
4	1.392 10^6	1.255 10^6
5	1.497 10^6	1.392 10^6

a Cooler and a Heater module, as shown in Table 4.4. From an optimization/physics point of view, this solution was obtained due to the economic potential of eliminating the second column's Heater and therefore its steam requirements. The latter would have been particularly high, since this end of the system was associated with the generation of the heaviest product (enriched in *o*-Xylene which has an enthalpy of vaporization 20% higher than the other components), thus requiring the use of more steam. Taking into consideration that steam is the most expensive utility, the elimination of the second column's Heater in the resulting *HI* scheme, led to the substantial energy consumption savings achieved.

From a computational point of view, convergence was achieved in 5 GBD iterations. Starting from the best *non-HI* simple column sequence (Direct Sequence), the optimal solution (corresponding to the best upper bound) was obtained in the 4th Primal subproblem. The generated and evaluated sequences at the 2nd and 3rd GBD iterations corresponded to *HI* variants of the Indirect Sequence, whereas those of the last two iterations corresponded to *HI* variants of the Direct Sequence. The GBD convergence history is given in Table 4.5.

4.5 Case Study: Quaternary *HI* Simple Column Sequencing

4.5.1 Problem Statement

The GMF synthesis model for the *HI* Simple Column Sequencing problem was applied for the solution of the Quaternary distillation separation case study of Section 3.4.1 (Novak *et al.*,

1996). The problem physical system data was taken from Table 3.7 with modifications for the feed temperature and pressure conditions. As far as the temperature of the feed is concerned, this corresponded to the bubble point at the pressure of M/H module 1 (where the feed enters the system). The pressure of each column was considered as a variable, bounded between 1 and 10 atm. The problem objectives and product specifications were the same as in the *non-HI* case and can be found in Table 3.8. For simplicity also in this case study only a single cold and hot utility was used, namely cooling water (at 300 K and at 0.159 \$/10⁶kJ) and high pressure steam (at 600 K and at 5.333 \$/10⁶kJ), both taken from Novak *et al.* (1996). As in the ternary *HI* case study, the temperatures of these utilities were assumed constant. Finally, the Exchanger Minimum Temperature Approach (*EMTA*), has been assumed equal to 10 K for all types of heat exchange units.

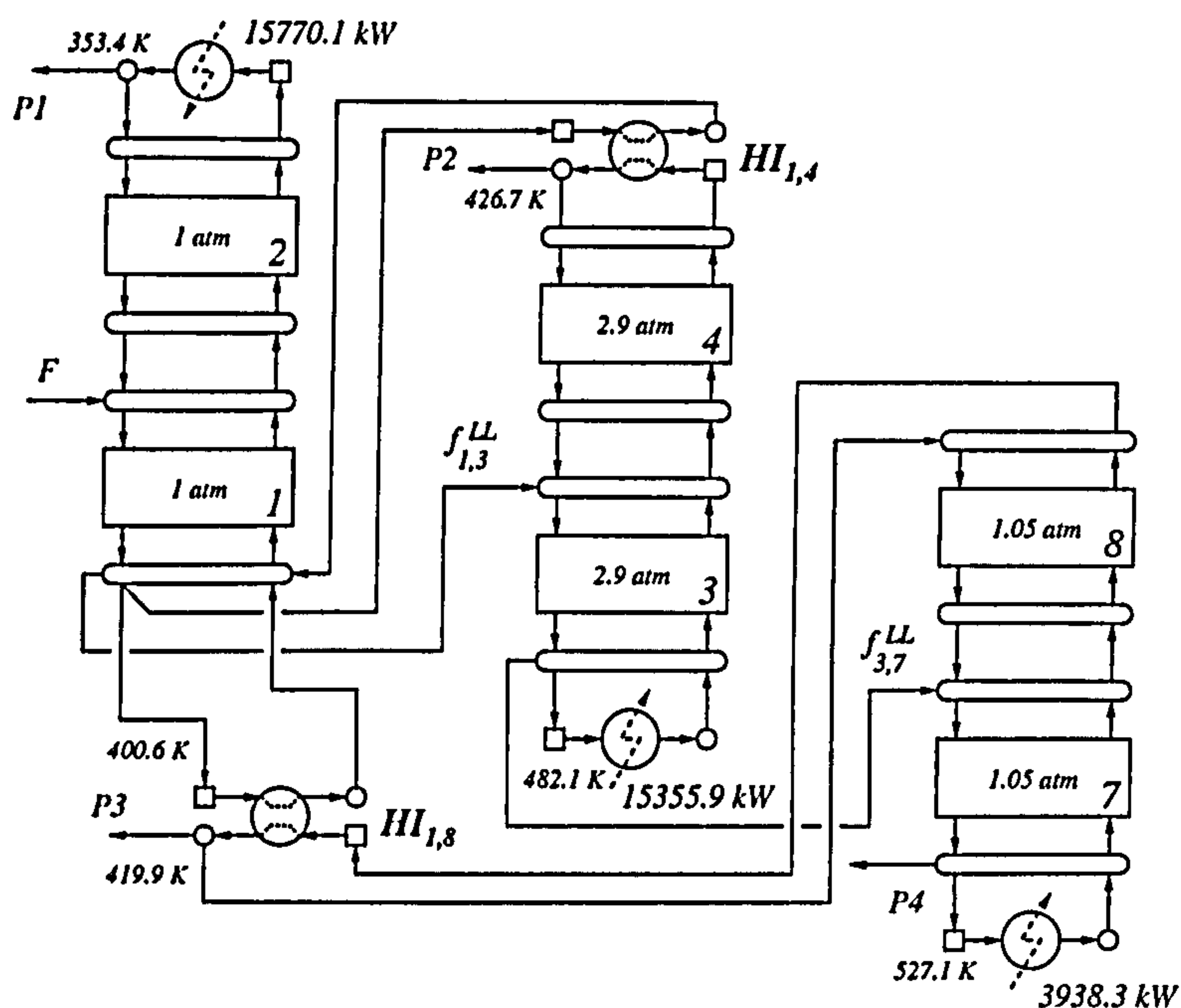
4.5.2 GMF Problem Formulation - Stage 3

In order to formulate the GMF Structural Model for the Quaternary *HI* column sequencing problem, the general structural model of Section 4.3 had to be defined appropriately for the quaternary case by assigning the members of the GMF Structural Sets. The latter were assigned as in the *non-HI* quaternary column sequencing case study (Table 3.9). The additional *HI* Structural Sets, were assigned as in the ternary *HI* sequencing case study (Table 4.3). The Quaternary *HI* structural model was considerably more involved than that of the ternary problem and for this reason the generated superstructure was far too complicated to be presented schematically. For simplification of the solution procedure, a maximum of 2 *HI* blocks was also imposed ($N = 2$ in constraint (4.61)).

Once the GMF Structural Model was fully defined, it was then coupled to the corresponding GMF Physical Model of Section 2.3.3 with the additions regarding the *HI* blocks, presented earlier in the current chapter. In order to facilitate the solution procedure, the pressure-related bounding procedure of the ternary *HI* sequencing problem, was also followed here.

4.5.3 Problem Solution and Results

The GMF Synthesis Model for the examined quaternary *HI* sequencing problem was implemented in GAMS and solved by employing the GBD/APROS methodology. The optimal sequence derived by the solution of the generated MINLP problem was a Heat Integrated variant

Figure 4.4: GMF *HI* Quaternary Sequencing Optimal Structure

of the Direct Sequence. The optimal structure, along with the column pressures, heat duties and temperature levels, are shown in Figure 4.4. Other results of the sequence's operating conditions are shown in Table 4.6.

From Figure 4.4 it is shown that the optimization resulted to a *HI* scheme involving 3 columns and 2 *HI* blocks. The latter heat integrated column 1 with columns 2 and 3, replacing Heater 1 and Coolers 4 and 8. The operating cost of this *HI* sequence was found equal to 3,092,500 \$/yr which, when compared to that of the optimal *non-HI* sequence, shows that savings of 2,241,500 \$/yr have been achieved (42% savings), which clearly demonstrate the energy efficiency of Heat Integrated schemes. The selection of this *HI* scheme and the above

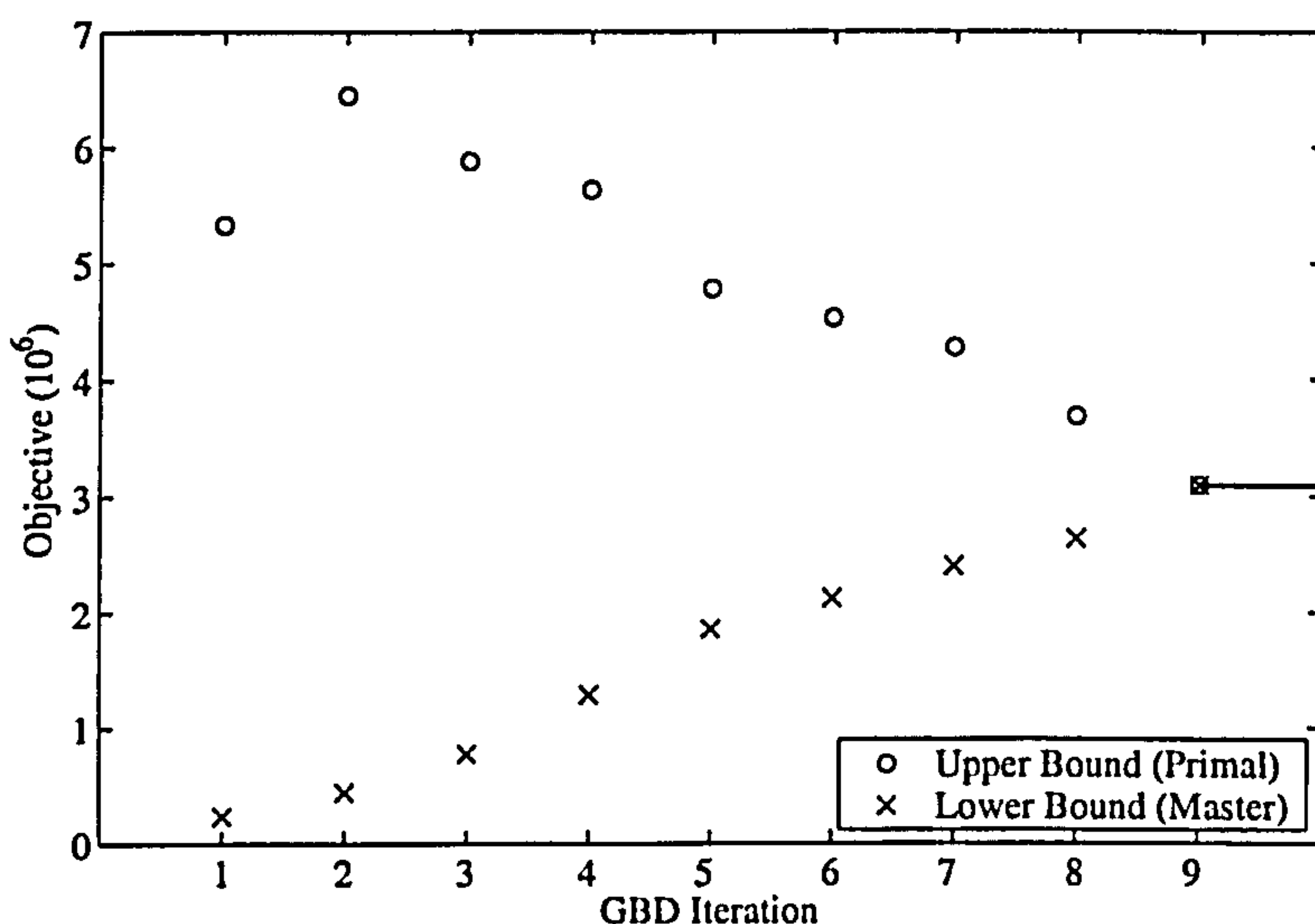
Table 4.6: GMF *HI* Quaternary Sequence Optimal Operating Conditions

	$F(\text{kmol/hr})$	$T(K)$	x_{Benz}	x_{Tol}	x_{o-Xyl}	x_{Diph}
$P1$	767.67	353.48	0.99	0.007	0.003	0
$f_{1,3}^{LL}$	1132.33	400.68	0	0.499	0.333	0.168
$P2$	570.67	426.74	0	0.99	0.01	0
$f_{3,7}^{LL}$	561.66	482.17	0	0	0.662	0.338
$P3$	373.5	419.97	0	0	0.99	0.01
$P4$	188.16	527.11	0	0	0.01	0.99

results can be also justified physically from an analysis of the sequence's operation. In the *non-HI* Direct Sequence, the Heater of the 1st column had the largest duty of all the other Heaters, and therefore, the highest contribution to the operating cost. Moreover, although Heater 7 operated at the highest temperatures, it had only a small duty (thus relatively small operating cost). This made the elimination of Heater 1 preferable from an economic point of view. In order to achieve this *HI* scheme, the pressure of the 2nd column increased from 1 to 2.9 atm, followed by a slight pressure increase of the pressure of the 3rd column, while the pressure of the 1st column remained at 1 atm.

From a computational point of view, convergence of the generated MINLP problem was achieved in 9 GBD iterations (the GBD convergence history is shown in Table 4.7). The initial structure in the GBD algorithm was the best *non-HI* simple column sequence (Direct Sequence). The following three GBD iterations evaluated *HI* variants of the Indirect Sequence, followed by the evaluation of three *HI* variants of a 3-Column Sequence (*M/H* modules 1-2, 3-4 and 9-10). The last 2 GBD iterations were *HI* variants of the Direct Sequence, while the best upper bound was obtained from the solution of the 9th Primal subproblem. An interesting remark is that the MINLP iterations generated and evaluated *HI* variants of the same column sequences that have been evaluated for the synthesis of quaternary simple column sequences (Section 3.4.3).

Table 4.7: GMF Quaternary *HI* Column Sequencing GBD Convergence



Iter.	Primal	Master
1	5.334 10 ⁶	0.239 10 ⁶
2	6.449 10 ⁶	0.448 10 ⁶
3	5.878 10 ⁶	0.776 10 ⁶
4	5.633 10 ⁶	1.289 10 ⁶
5	4.776 10 ⁶	1.854 10 ⁶
6	4.521 10 ⁶	2.117 10 ⁶
7	4.267 10 ⁶	2.392 10 ⁶
8	3.680 10 ⁶	2.630 10 ⁶
9	3.092 10 ⁶	3.092 10 ⁶

Remark

A note must be made here regarding the results obtained through the GMF and those of Novak *et al.* (1996). The latter also solved the problem for single utility (High Pressure Steam) and had the same specifications for the product purities. As remarked in Section 3.4.3, the only difference lied in the additional product specification of 99.5% recovery in all columns, which was necessary for the employed shortcut physical model. As in the *non-HI* case, the temperature levels in the Novak *et al.* (1996) solution were in agreement with those of the GMF. However, the column heat duties and, therefore, the objective function values were almost double from the ones obtained by the GMF. This could be only interpreted as a direct consequence of the mismatch that was observed in the *non-HI* sequencing case.

4.6 Conclusions

In this Chapter, the GMF method for the synthesis of simple distillation column sequences was extended to the incorporation of Heat Integration possibilities in order to obtain enhanced energy savings. This was achieved by introducing a *HI* block, which is essentially a *He* module between process-process streams instead of process streams-utilities. However, as it was shown, by including *HI* possibilities structurally, the number of alternatives, even for relatively simple problems such as the ternary column sequencing, has increased considerably, thus making the use of systematic methods for its solution mandatory. This was addressed through the introduction of a GMF *HI* column sequencing Structural Model, which provided a valid and systematic method for generating *HI* variants of distillation column sequences. Beyond the structural issues, the *HI* possibilities were also incorporated in the appropriately arranged GMF Physical Model. In the latter, particular attention was given to the *explicit* incorporation of the module (column) pressure as a variable, to be determined by the optimization problem.

In order to validate the GMF *HI* column sequencing method, the ternary and quaternary case studies of Chapter 3 were revisited allowing for *HI* possibilities. From the derived results it was found that, by applying Heat Integration techniques, the GMF managed to achieve significant energy savings, ranging around 40% when compared to the *non-HI* cases. At the same time, the results showed that the GMF Physical Model managed to capture accurately the physical phenomena and the effects of pressure in the various modules (column sections).

From a computational point of view, the complexity of the generated problem increased, due to the aforementioned combinatorial increase and to the increase of the nonlinearities in the continuous problem by to the incorporation of pressure as an additional degree of freedom. The combinatorial complexities were addressed through a tight structural model and rational assumptions, such as the incorporation of upper bounds on the number of potential *HI* blocks. The physical complexities were addressed through appropriate bounding procedures in order to obtain accurate optimal points which captured the actual physical behaviour and energy potential of the represented systems.

Chapter 5

Synthesis of Complex Distillation Column Sequences

5.1 Complex Distillation Column Sequencing

In the previous two chapters, the GMF was used for the distillation column sequencing problem, consisting only of simple columns. In Chapter 3 it was shown that choosing the most appropriate simple column sequence out of a set of possible alternatives can lead to substantial energy savings. In Chapter 4, these energy savings were extended by applying Heat Integration techniques on these simple column sequences. However, 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 chapter, the GMF is arranged for the Complex Distillation Column Sequencing problem, that is, the sequencing problem where both simple and complex columns are considered.

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 Figure 5.1. From those alternatives, the most common in both literature and industrial practice are those consisting of simple distillation columns, which are shown in Figures 5.1.a - c. However, the number of alternatives increases considerably when complex columns are considered (Figures 5.1.d - k). All these complex columns are either partially or fully thermally coupled. From these, the Fully Thermally Coupled (Petlyuk)

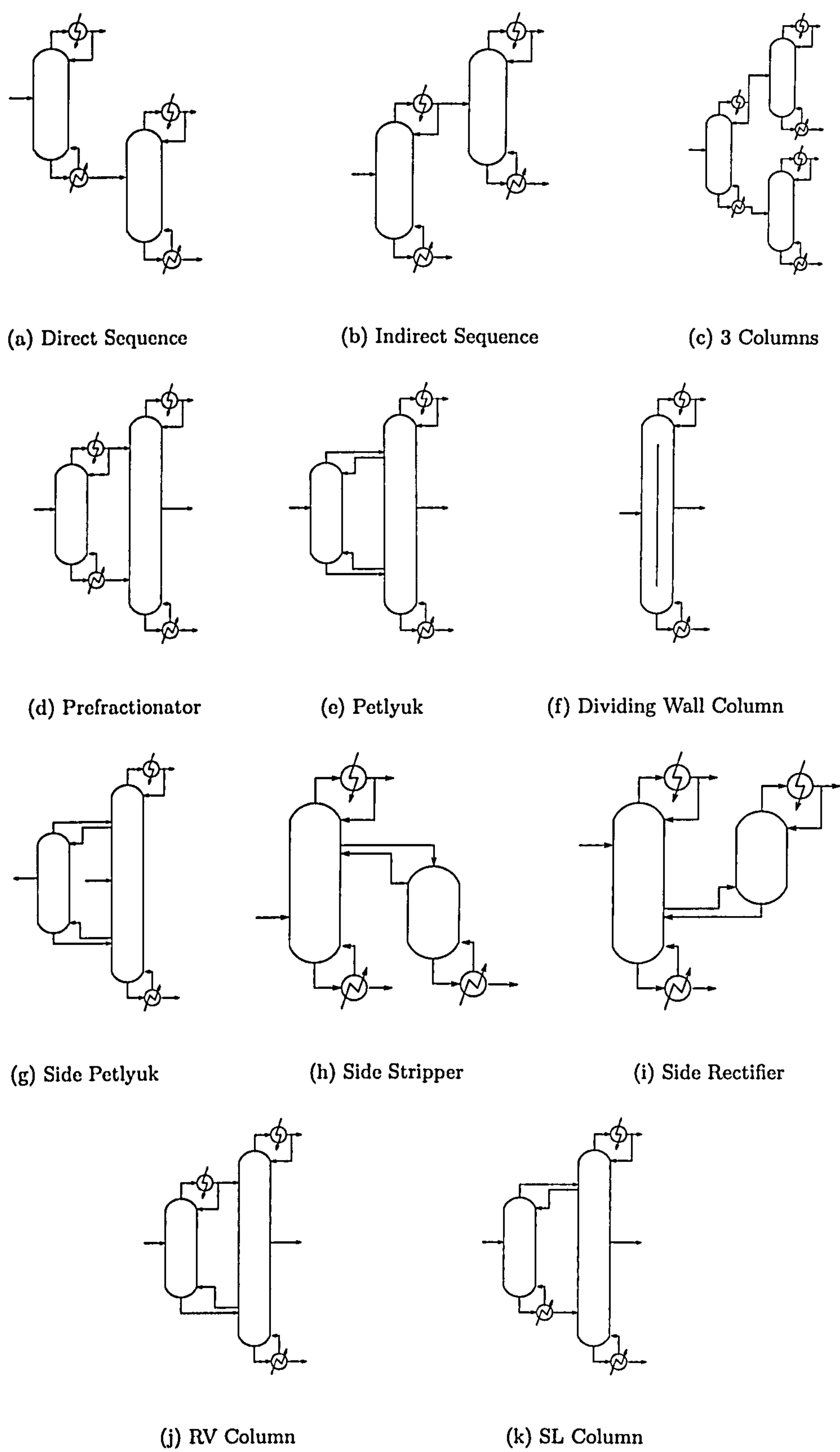


Figure 5.1: Alternative Configurations for the Distillation of a non-Azeotropic Ternary Mixture

Column (Figure 5.1.e) has been receiving increasing attention, as it has been found that it can exhibit energy consumption reductions even up to 40%, compared to conventional configurations (Fidkowski and Krolikowski (1986), Glinos and Malone (1988), Triantafyllou and Smith (1992), Annakou and Mizsey (1996), Dunnebir and Pantelides (1999)), which is due to its thermodynamic efficiency (minimization of losses due to unnecessary remixing). The Dividing Wall Column (Figure 5.1.f) 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 vapour 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 (Figure 5.2) (Agrawal, 2000b). As indicated in Figure 5.2, 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 in the columns' vapour interconnections. In the alternatives of Figure 5.2, one or more 'problematic' vapour 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 8 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.

5.1.1 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). 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

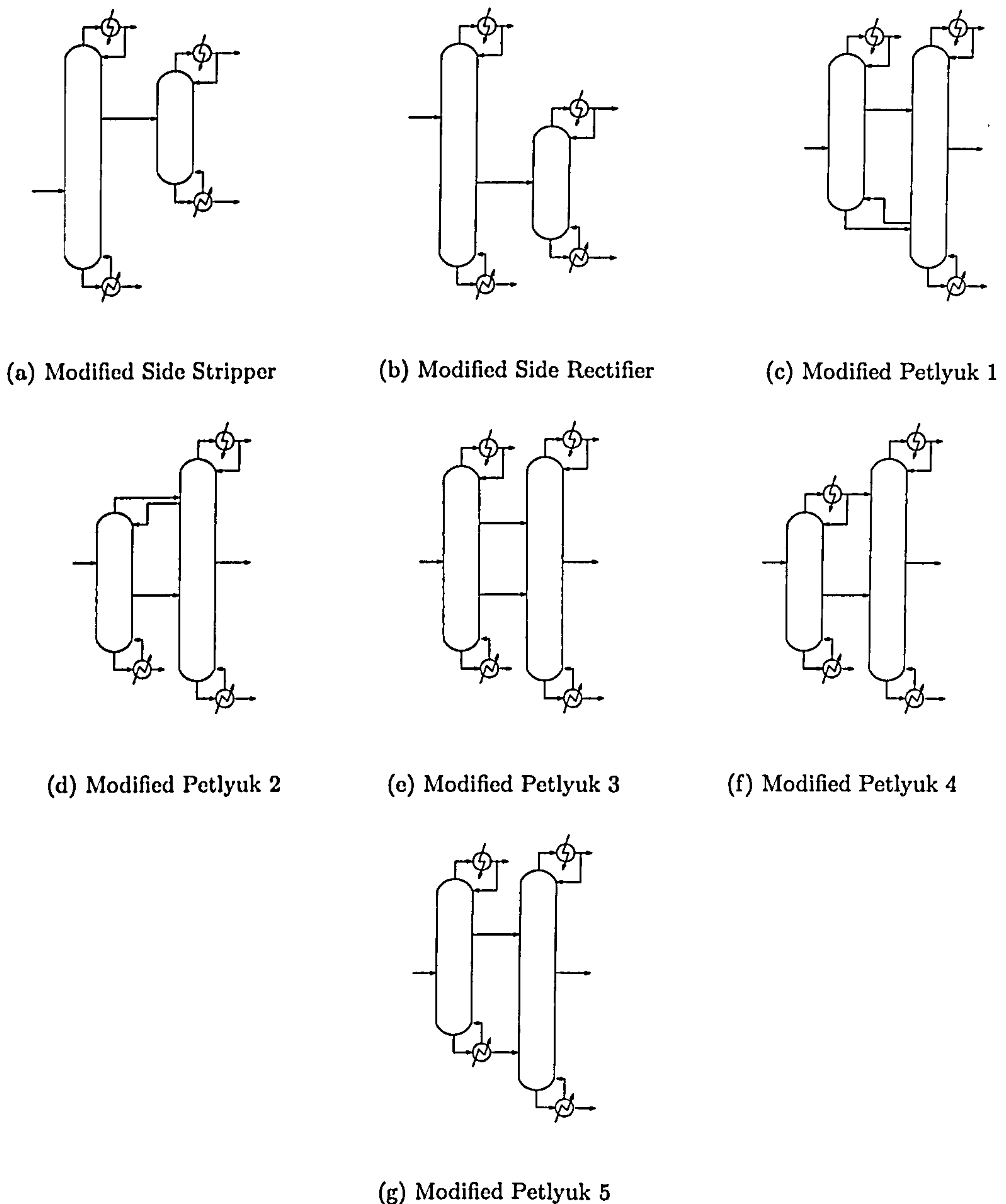


Figure 5.2: Modified Configurations for Operability Targets

column required the introduction of a large number of discrete variables, rendering the problem a large scale MINLP. The combinatorial complications were handled through treating the integers as continuous variables rounded off each time to the nearest integer variable, reducing eventually, the problem to a Nonlinear Programming (NLP) problem.

The work on the Sequential Column Superstructure was continued in Mei (1995), investigating the possibilities of aggregation and size reduction, by using as superstructure building

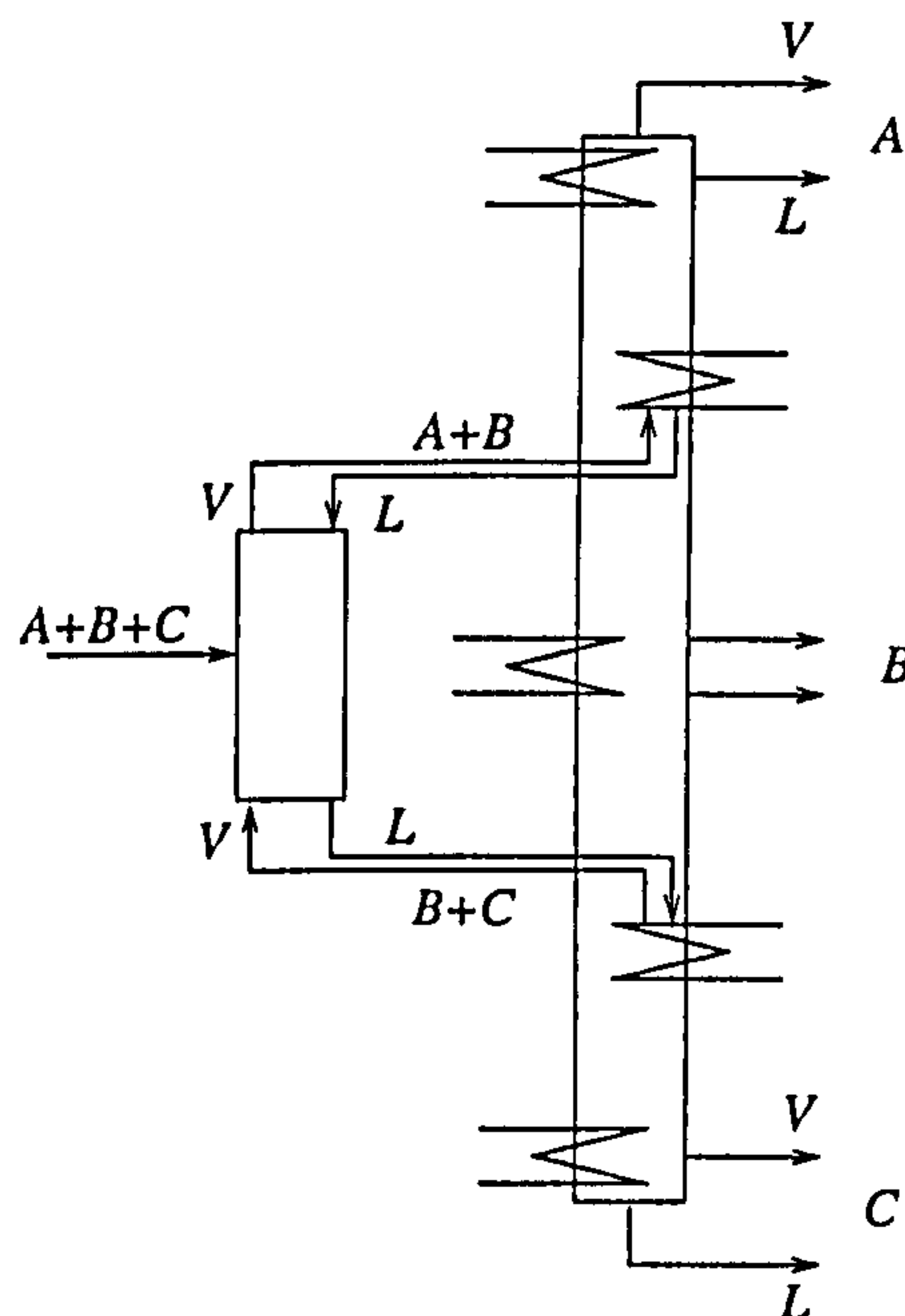


Figure 5.3: Sequential Column Superstructure (Eliceche and Sargent, 1981)

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 specified as an integer variable. Moreover, each building block was modelled as a modular simulator using as inputs a guess of the number of trays, the flowrates and the intensive variables characterizing each input stream and generating outputs of the calculated flowrates 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 fewer than 100 variables and equations.

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 (FC) 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 for the generation of all the other feasible partially or non-thermally 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 pro-

cedure 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 also proposed for the generation of feasible distillation column sequences was the State Task Network (Sargent, 1998) and 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 modelled 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. The authors included some very useful comments regarding the convergence complexities of the examined problem, while stressing the importance of complex arrangements for energy efficiency and of 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

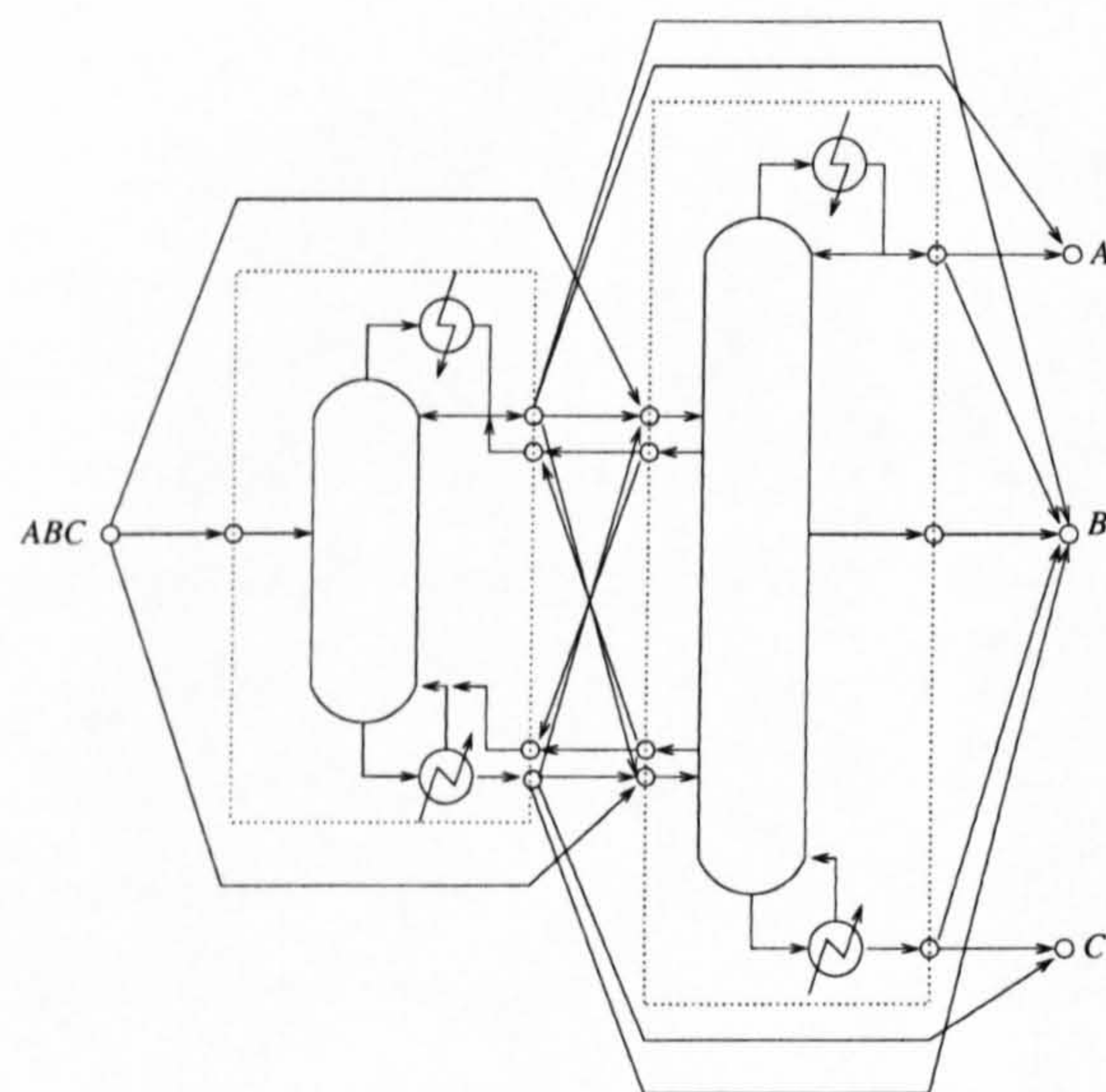


Figure 5.4: SON Superstructure for Ternary Distillation (Dünnebier and Pantelides, 1999)

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 vapour flows taking a value of zero, 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 the Fully Thermally Coupled (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 non-thermally coupled column sequences. The superstructure was modelled structurally using propositional logic expressions (Raman and Grossmann, 1991) and each column was modelled physically using 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 modelled using GDP and solved using a modified version of the logic-based Outer Approximation algorithm.

In a recent paper (Agrawal, 2003), an improved systematic procedure has been proposed for the generation of basic and thermally coupled column sequences. As basic columns were designated columns with a condenser and a reboiler at their top and bottom ends and no thermal coupling. 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, which 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’ in the literature 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 5.1: Summary of Superstructure Methods for Complex Column Sequencing

Authors	Features
Sargent & Gaminibandara (1976)	Sequential Column Superstructure, <i>MESH</i> Model
Eliceche & Sargent (1981)	Sequential Column Superstructure, <i>MESH</i> Model
Mei (1995)	Sequential Column Superst., <i>Pseudo</i> -Aggregated Model
Agrawal (1996), (2000), (2003)	Satellite Column Superstructure
Sargent (1998)	STN (Doherty & Malone (2001))
Dunnebier & Pantelides (1999)	SON Superstructure, <i>MESH</i> (Smith, 1996)
Yeomans & Grossmann (2000 <i>b</i>)	Sequential Column Superst., <i>MESH</i>
Caballero & Grossmann (2001)	Satellite Column Superstructure, GDP, Shortcut Model

Summarizing, it can be stated that the presented superstructure methods have contributed significantly to the efficient treatment of the distillation sequencing problem. It has been shown that the non-convexities and the 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 modelling 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. In the following sections, a GMF synthesis method will be proposed based on a structural model incorporating in a unified way both simple and complex column sequences.

5.2 GMF Structural Model For Ternary Complex Distillation Column Sequences

The GMF Structural Model for the ternary complex column sequencing problem is based on the GMF Building Blocks, in conjunction with appropriately defined Interconnection Principles. The GMF structural representation of the alternative sequences is given in Figures 5.5 and 5.6.

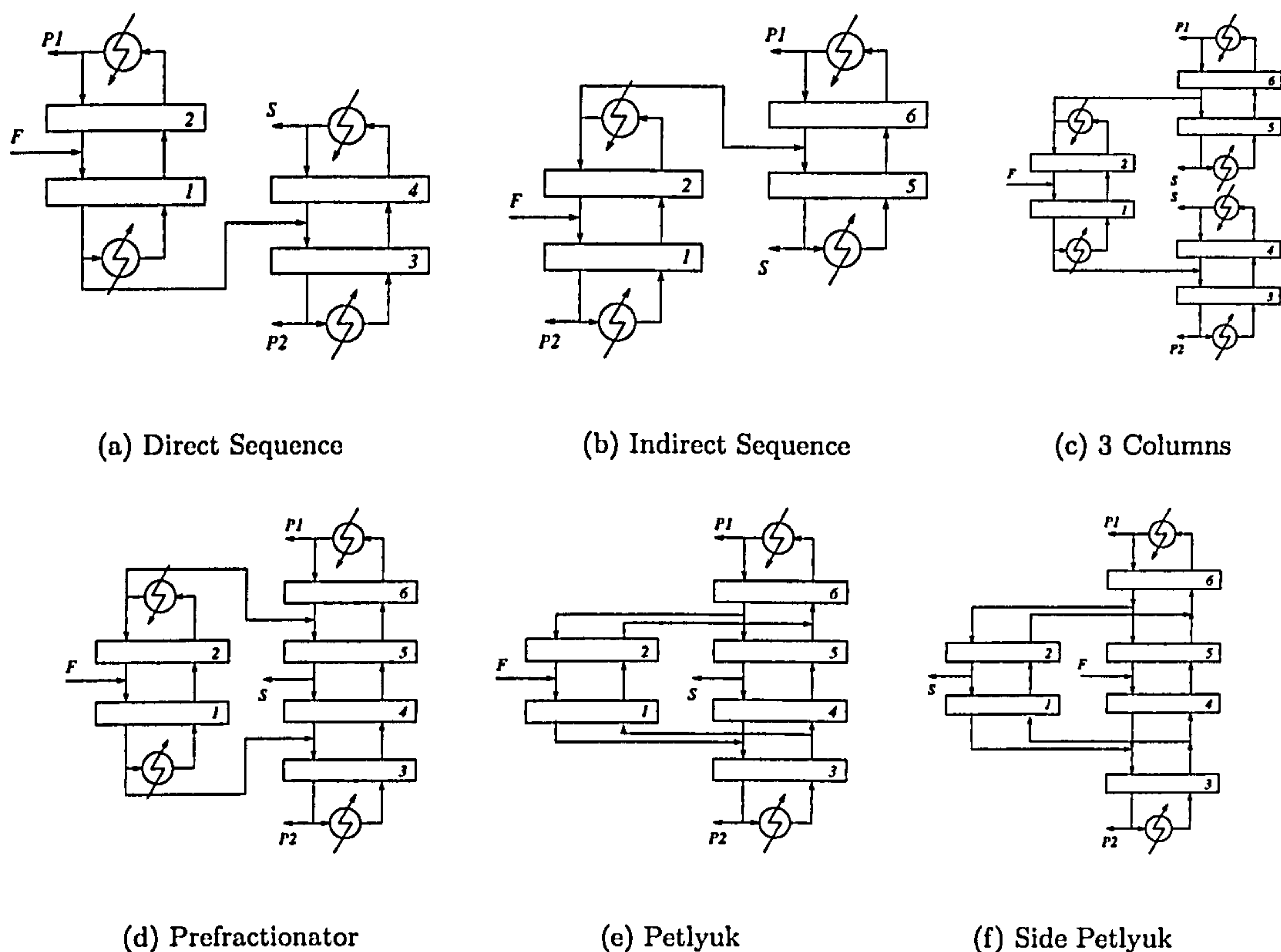
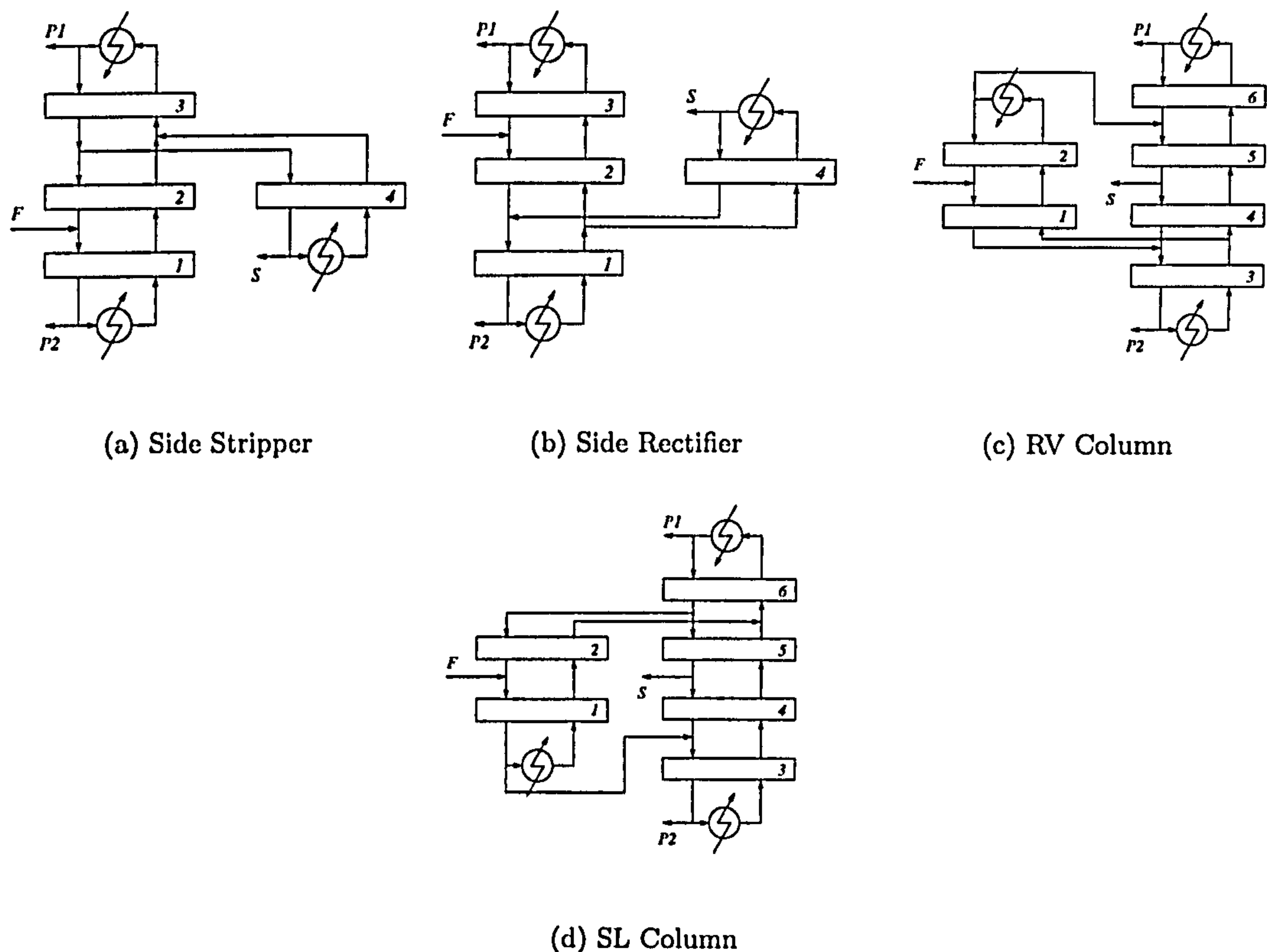


Figure 5.5: GMF Representation of Ternary (Complex) Distillation Sequences

Figure 5.6: GMF Representation of Ternary (Complex) Distillation Sequences (*cont.*)

5.2.1 GMF Module Rearrangement

In order to facilitate the construction of the superstructure for the ternary complex distillation sequencing problem particular attention must be given to the Side Petlyuk, Stripper and Rectifier alternatives (Figures 5.5.f, 5.6.a and 5.6.b, respectively). In conjunction with principles presented in Sargent and Gaminibandara (1976), the GMF Building Blocks of these three configurations can be positioned alternatively without, though, changing the operational characteristics of the represented sequences.

The Side Petlyuk Column (Figure 5.7) is a 'reverse' Petlyuk column where the feed enters the main column (at M/H module 4) and the side stream exits from the side column (M/H module 2). M/H modules 4 and 5 with their attached feed can be shifted structurally to the position of the side column and the M/H modules consisting the latter (M/H modules 1 and 2) with their attached side stream can take the position of M/H modules 4 and 5 in the main column (Figure 5.7). Then if M/H module 1 becomes module 4, module 2 becomes module 5, module

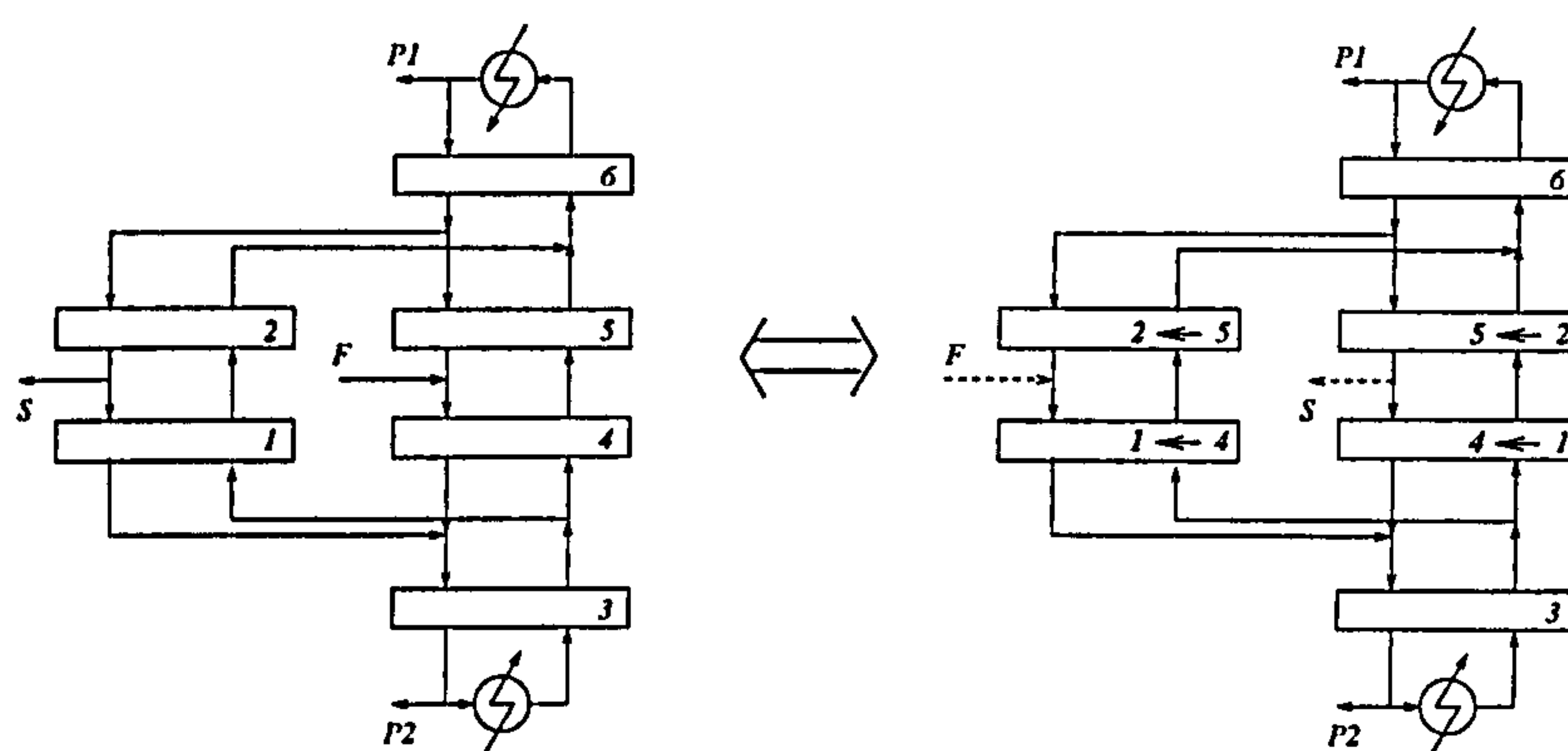


Figure 5.7: GMF Rearrangement of Side Petlyuk Column

4 becomes module 1 and module 5 becomes module 2, the Side Petlyuk Column becomes the Petlyuk Column. This rearrangement is allowed since the two columns are equivalent from an operation point of view (the M/H module interconnections are kept intact). The result of this rearrangement is the removal of the Side Petlyuk Column from the set of candidate alternatives for the examined problem (since it is represented by its equivalent Petlyuk Column).

A similar rearrangement is realized on the Side Stripper and Side Rectifier sequences (Figures 5.6.a and b, respectively). In the former, as shown in Figure 5.8, M/H module 3 is shifted structurally from the main column into the side stripper. To aid the consistent construction of the superstructure, M/H modules 3 and 4 become M/H modules 6 and 5, respectively. This repositioning does not alter the interconnections between the GMF Building Blocks, and consequently do not affect the physical phenomena taking place in the sequence. The same holds for the rearrangement of the M/H modules belonging to the Side Rectifier sequence, as

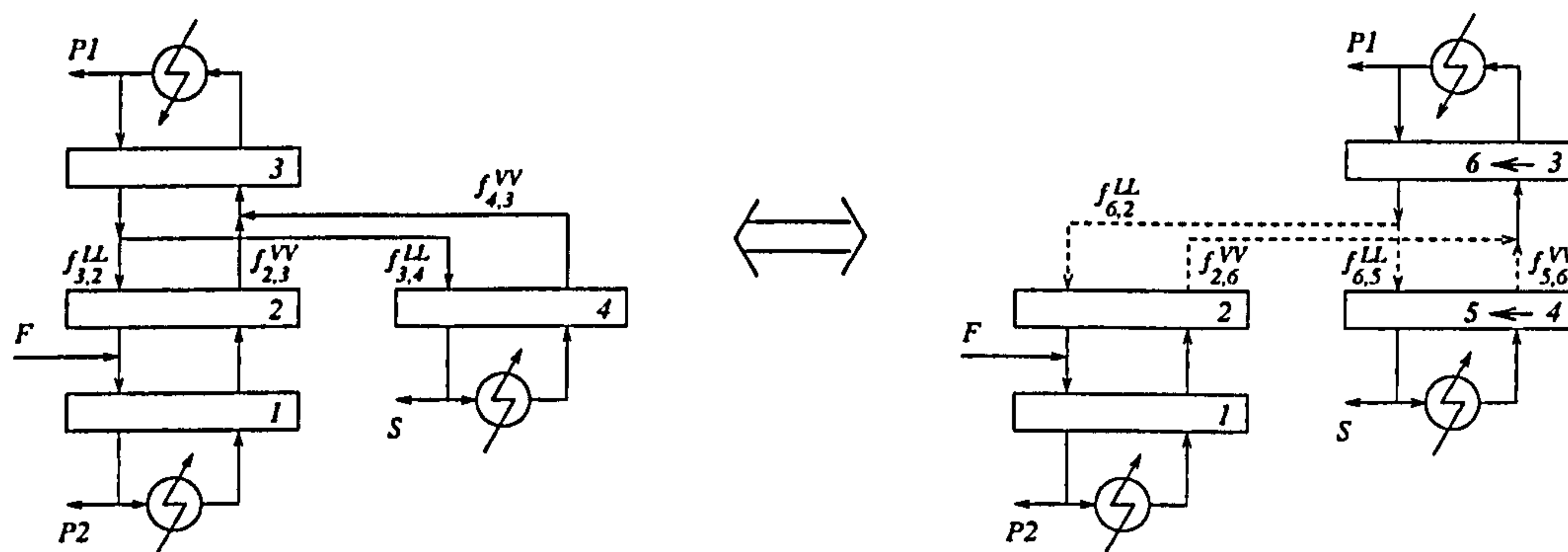


Figure 5.8: GMF Rearrangement of Side Stripper Column

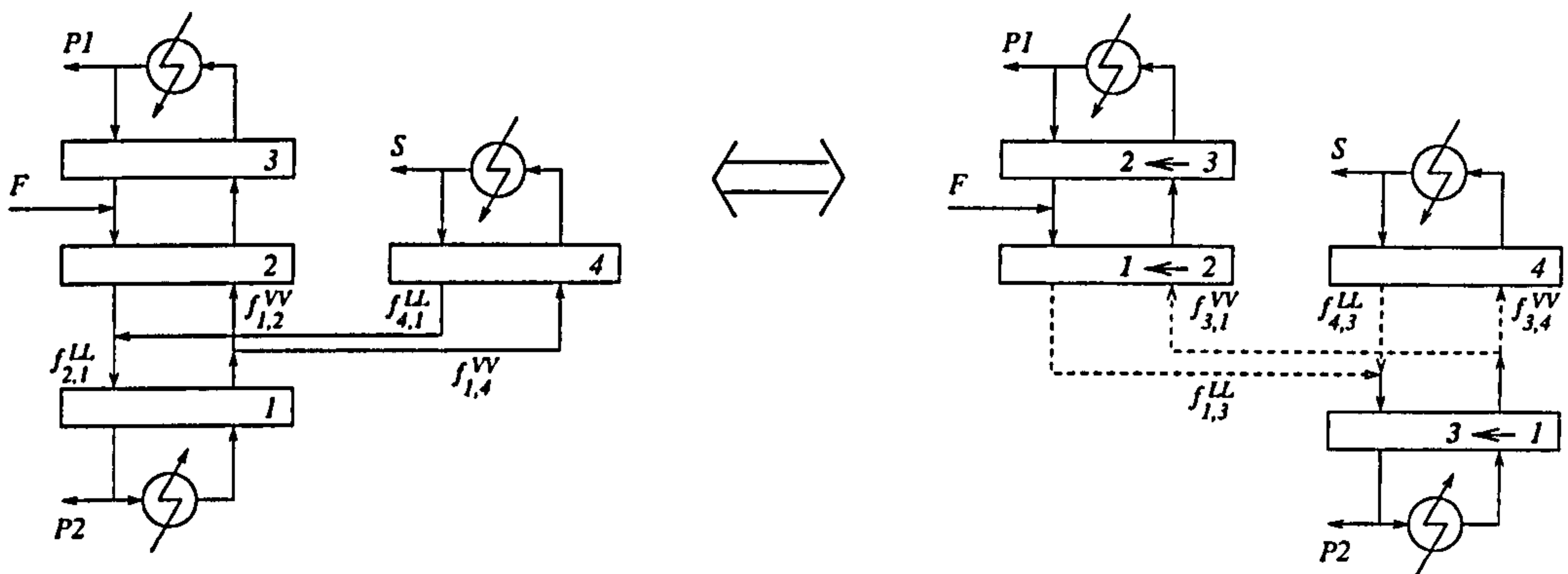


Figure 5.9: GMF Rearrangement of Side Rectifier Column

depicted in Figure 5.9. It must also be mentioned that in the above sequence rearrangements the only difference lies in the actual construction of the columns from a mechanical point of view which does not cause any implications in the search for the most energy efficient structure and, moreover, is beyond the scope of the GMF.

Note:

A note must be made here regarding the modified structures of Figure 5.2. These sequences, according to Agrawal (2000b) are modifications of the side stripper, side rectifier and Petlyuk columns proposed for the improvement of the ‘parent’ configurations’ operability and are thermally equivalent to the latter. However, since the focus of our study is the energy consumption of each configuration and not its operability, these modified columns are considered by the GMF in an implicit manner, by the representation and evaluation of their thermally equivalent structures. Similarly, the Dividing Wall Column, which cannot be explicitly represented by a combination of M/H modules, is implicitly considered through its thermodynamically equivalent Petlyuk column representation, under the assumption of no heat transfer through the dividing wall.

5.2.2 GMF Ternary Complex Distillation Column Superstructure

All the structural alternatives for the examined synthesis problem can be found in their final form (after their rearrangements of Section 5.2.1) in Figure B.1 (Appendix B.1). In the same Appendix, an STN representation of each modular alternative is provided. By observing the STNs, it is clear that the GMF is based on a *one-to-many* representation. However, the main difference of the GMF from other *one-to-many* representation methods (like the GDP-based

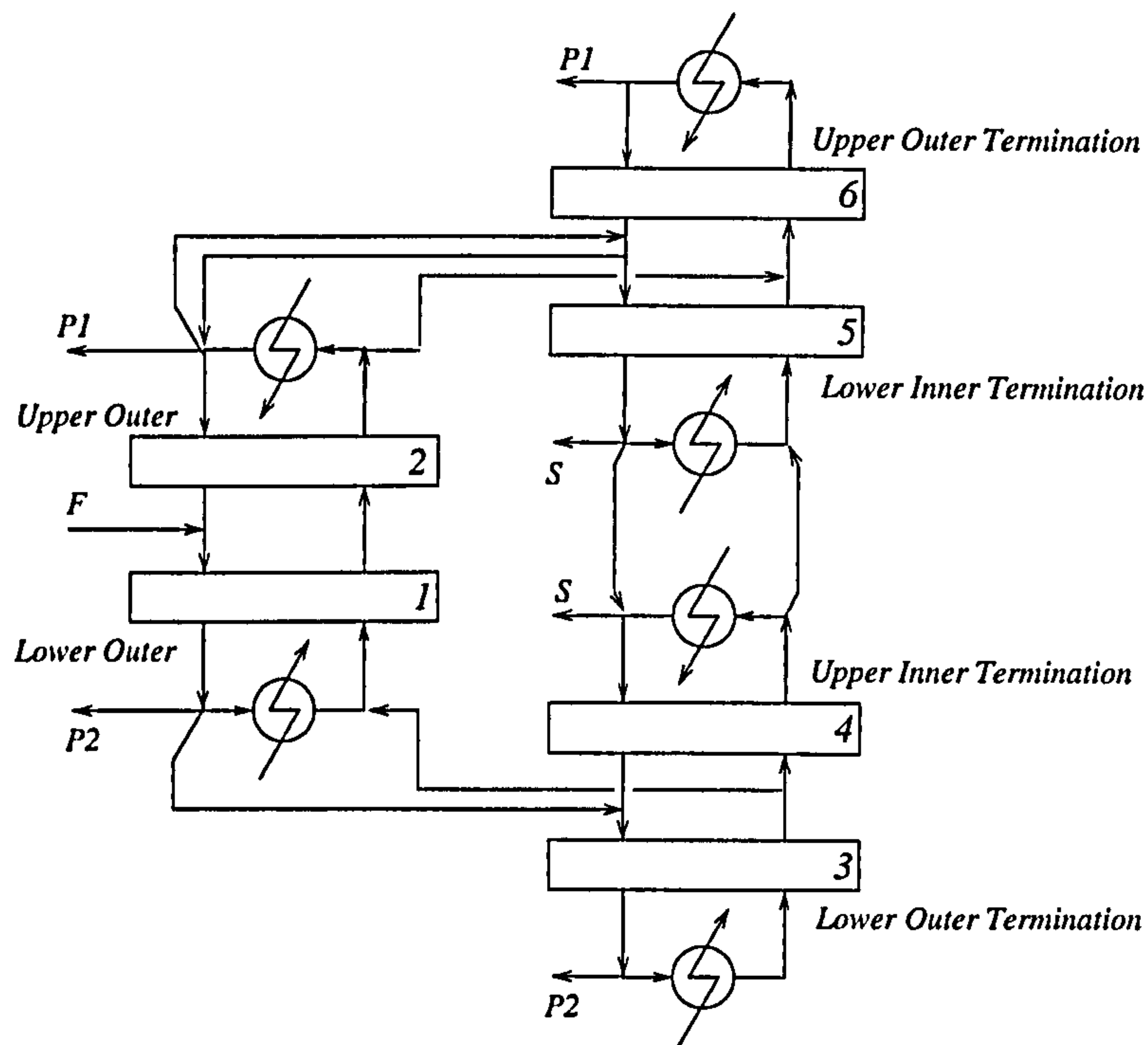


Figure 5.10: GMF Ternary Complex Distillation Column Superstructure

methods) is that the former solves a more general problem where each M/H module of the GMF superstructure is not assigned *a priori* to a task or to a set of tasks, but the association of building blocks and tasks will be derived by the solution of the optimization problem.

In order to generate a superstructure which can encompass all the aforementioned configurations 6 M/H modules have to be employed. The superstructure for the Ternary Complex Distillation Column Sequencing problem is shown in Figure 5.10.

In order to accommodate structurally the thermal coupling possibilities, new Structural Sets are *added* to those of Section 3.2, replacing the E^{UT} and E^{LT} sets and characterizing the terminating M/H modules according to their position in the superstructure. These sets, which participate only in the GMF Structural Model, are given below and are illustrated in Figure 5.10.

$$E^{UOT} = \{e | \text{Upper Outer Termination modules}\}$$

$$E^{LOT} = \{e | \text{Lower Outer Termination modules}\}$$

$$E^{UIT} = \{e | \text{Upper Inner Termination modules}\}$$

$$E^{LIT} = \{e | \text{Lower Inner Termination modules}\}$$

5.2.3 GMF Propositional Logic Expressions - Stage 1

Under the guidelines given in Section 3.2.1, in order to systematically derive the GMF Structural Constraints, the Propositional Logic Expressions have to be provided in Stage 1. The latter, according to their role, as before, are categorized into Superstructure Basis, Intra and Inter-Column Logical Expressions. These expressions are given below for the Complex Column Sequencing Problem.

Superstructure Basis Logical Expressions

- There must be an initial module.

$$y_1 : \text{true} \quad (5.1)$$

- There must be at least one termination column:

$$\sum_{e \in E^{LOT}} y_e + \sum_{e \in E^{LIT}} y_e \geq 1 \quad (5.2)$$

Intra-Column Logical Expressions

$$y_e \Leftrightarrow y_{e+1}, \quad e \in E^L \quad (5.3)$$

$$y_e \Leftrightarrow y_e^H, \quad e \in E^{LOT} \quad (5.4)$$

$$y_e \Leftrightarrow y_e^C, \quad e \in E^{UOT} \quad (5.5)$$

$$y_e^H \Rightarrow y_e, \quad e \in E^L, e \notin E^{LOT} \quad (5.6)$$

$$y_e^C \Rightarrow y_e, \quad e \in E^U, e \notin E^{UOT} \quad (5.7)$$

$$y_{e,e}^{LH} \Leftrightarrow y_e \wedge y_e^H, \quad e \in E^L \quad (5.8)$$

$$y_{e,e}^{HV} \Leftrightarrow y_e^H \wedge y_e, \quad e \in E^L \quad (5.9)$$

$$y_{e,e}^{VC} \Leftrightarrow y_e \wedge y_e^C, \quad e \in E^U \quad (5.10)$$

$$y_{e,e}^{CL} \Leftrightarrow y_e^C \wedge y_e, \quad e \in E^U \quad (5.11)$$

$$y_{e,e-1}^{LL} \Leftrightarrow y_e \wedge y_{e-1}, \quad e \in E^U \quad (5.12)$$

$$y_{e,e+1}^{VV} \Leftrightarrow y_e \wedge y_{e+1}, \quad e \in E^L \quad (5.13)$$

The above expressions provide the same information for the construction of each participating column in the superstructure as those of Section 3.2.1, with the exception of the changes made to encompass the particularities of the Upper and Lower Outer Termination modules, which should always be followed by their associated Coolers and Heaters, respectively.

Inter-Column Logical Expressions

- If a Cooler module exists, then *one and only one* external interconnection stream is allowed from it, *either* to a product mixer *or* to a M/H module of *another* column ($ea \neq e$). Coolers of Upper Termination modules, *if they exist*, have only product mixer interconnections.

$$y_e^C = \{\{y_{e,p1}^{CP}, \dots, y_{e,pn}^{CP}\}_{p \in E_e^{CPo}}, \{y_{e,ea1}^{CL}, \dots, y_{e,ean}^{CL}\}_{ea \in E_e^{CLo}}\}, \quad e \in E^C, ea \neq e \quad (5.14)$$

- If a Lower module exists, except from the Lower Inner Termination modules, then *one and only one* interconnection stream is allowed from it, *either* to a product mixer *or* to another M/H module.

$$y_e = \{\{y_{e,p1}^{LP}, \dots, y_{e,pn}^{LP}\}_{p \in E_e^{LPo}}, \{y_{e,ea1}^{LL}, \dots, y_{e,ean}^{LL}\}_{ea \in E_e^{LLo}}\}, \quad e \in E^L, e \notin E^{LIT} \quad (5.15)$$

- Along the same lines, if a Lower Inner Termination module exists, then it must always have a product stream leaving it and *one and only one* vapour interconnection stream entering it, *either* from its associated Heater *or* from another M/H module.

$$y_e \Leftrightarrow y_{e,p}^{LP}, \quad e \in E^{LIT}, p \in E_e^{LP} \quad (5.16)$$

$$y_e = \{y_{e,e}^{HV}, \{y_{ea1,e}^{VV}, \dots, y_{ean,e}^{VV}\}_{ea \in E_e^{VV}}\}, \quad e \in E^{LIT} \quad (5.17)$$

- A liquid interconnection leaves the Cooler of an Upper Outer module towards *another* column *if and only if* the destination M/H module exists.

$$y_{e,ea}^{CL} \Leftrightarrow y_e^C \wedge y_{ea}, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (5.18)$$

- A liquid interconnection leaves a Lower Outer module *if and only if* the destination M/H module also exists.

$$y_{e,ea}^{LL} \Leftrightarrow y_e \wedge y_{ea}, \quad e \in E^{LO}, ea \in E_e^{LLo} \quad (5.19)$$

- *Thermal Coupling*: A liquid interconnection leaves an Upper Outer Termination module *if and only if* the destination M/H module exists and its associated Cooler has been removed. If this liquid interconnection exists, then its corresponding vapour interconnection is also imposed in order to enforce Thermal Coupling between the columns.

$$y_{e,ea}^{LL} \Leftrightarrow y_e \wedge y_{ea} \wedge \neg y_{ea}^C, \quad e \in E^{UOT}, ea \in E_e^{LLo} \quad (5.20)$$

$$y_{e,ea}^{LL} \Leftrightarrow y_{ea,e}^{VV}, \quad e \in E^{UOT}, ea \in E_e^{LLo} \quad (5.21)$$

- *Thermal Coupling*: A liquid interconnection leaves a Lower Inner Termination module towards another M/H module *if and only if* its associated Heater has been eliminated,

the destination M/H module exists and the latter's associated Cooler has been removed. Thermal Coupling is enforced by imposing the corresponding vapour interconnection.

$$y_{e,ea}^{LL} \Leftrightarrow y_e \wedge y_{ea} \wedge \neg y_e^H \wedge \neg y_{ea}^C, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.22)$$

$$y_{e,ea}^{LL} \Leftrightarrow y_{ea,e}^{VV}, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.23)$$

- *Thermal Coupling:* A vapour interconnection leaves a Lower Outer Termination module towards the M/H module of another column *if and only if* the destination M/H module exists and its associated Heater has been removed.

$$y_{e,ea}^{VV} \Leftrightarrow y_e \wedge y_{ea} \wedge \neg y_{ea}^H, \quad e \in E^{LOT}, ea \in E_e^{VVo}, ea \neq e + 1 \quad (5.24)$$

- *Thermal Coupling:* If an Upper Outer module is thermally coupled from its top (eliminating its associated Cooler), then the Upper Inner Termination modules, if they exist, must be thermally coupled from their top (their associated Coolers eliminated).

$$\neg y_e^C \Rightarrow \neg y_{ea}^C, \quad e \in E^{UO}, ea \in E^{UIT} \quad (5.25)$$

- *Thermal Coupling:* If a Lower Outer module is thermally coupled from its bottom (eliminating its associated Heater), then the Lower Inner Termination modules, if they exist, must also be thermally coupled from their bottom (their associated Heaters eliminated).

$$\neg y_e^H \Rightarrow \neg y_{ea}^H, \quad e \in E^{LO}, ea \in E^{LIT} \quad (5.26)$$

- *Thermal Coupling:* Upper Inner Termination and Lower Inner Termination modules can belong, either to non-coupled columns (thus retaining their associated He modules), or to thermally coupled columns (thus eliminating their associated Coolers and Heaters).

$$y_e \wedge y_{ea} \Leftrightarrow (y_e^H \wedge y_{ea}^C) \vee y_{e,ea}^{LL}, \quad e \in E^{LIT}, ea \in E^{UIT} \quad (5.27)$$

- Every product mixer should receive *at least* one interconnection from a cooler or M/H module:

$$\bigvee_{e \in E_p^{CPi}} y_{e,p}^{CP} \bigvee_{e \in E_p^{LPi}} y_{e,p}^{LP}, \quad p \in P \quad (5.28)$$

5.2.4 GMF Structural Integer Constraints - Stage 2

The following constraints are generated from their corresponding Logical Expressions in the systematic procedure described in Section 3.2.2. These constraints constitute the GMF Structural Model for the Ternary Complex Distillation Sequencing problem.

Superstructure Basis Structural Constraints

$$y_1 = 1 \quad (5.29)$$

$$\sum_{e \in E^{LOT}} y_e + \sum_{e \in E^{LIT}} y_e \geq 1 \quad (5.30)$$

Intra-Column Structural Constraints

$$y_e - y_{e+1} = 0, \quad e \in E^L \quad (5.31)$$

$$y_e - y_e^H = 0, \quad e \in E^{LOT} \quad (5.32)$$

$$y_e - y_e^C = 0, \quad e \in E^{UOT} \quad (5.33)$$

$$y_e - y_e^H \geq 0, \quad e \in E^L, e \notin E^{LOT} \quad (5.34)$$

$$y_e - y_e^C \geq 0, \quad e \in E^U, e \notin E^{UOT} \quad (5.35)$$

$$1 - y_{e,e}^{LH} + y_e \geq 1, \quad e \in E^L \quad (5.36)$$

$$1 - y_{e,e}^{LH} + y_e^H \geq 1, \quad e \in E^L \quad (5.37)$$

$$y_{e,e}^{LH} + 1 - y_e + 1 - y_e^H \geq 1, \quad e \in E^L \quad (5.38)$$

$$1 - y_{e,e}^{HV} + y_e^H \geq 1, \quad e \in E^L \quad (5.39)$$

$$1 - y_{e,e}^{HV} + y_e \geq 1, \quad e \in E^L \quad (5.40)$$

$$y_{e,e}^{HV} + 1 - y_e^H + 1 - y_e \geq 1, \quad e \in E^L \quad (5.41)$$

$$1 - y_{e,e}^{VC} + y_e \geq 1, \quad e \in E^U \quad (5.42)$$

$$1 - y_{e,e}^{VC} + y_e^C \geq 1, \quad e \in E^U \quad (5.43)$$

$$y_{e,e}^{VC} + 1 - y_e + 1 - y_e^C \geq 1, \quad e \in E^U \quad (5.44)$$

$$1 - y_{e,e}^{CL} + y_e^C \geq 1, \quad e \in E^U \quad (5.45)$$

$$1 - y_{e,e}^{CL} + y_e \geq 1, \quad e \in E^U \quad (5.46)$$

$$y_{e,e}^{CL} + 1 - y_e^C + 1 - y_e \geq 1, \quad e \in E^U \quad (5.47)$$

$$1 - y_{e,e-1}^{LL} + y_e \geq 1, \quad e \in E^U \quad (5.48)$$

$$1 - y_{e,e-1}^{LL} + y_{e-1} \geq 1, \quad e \in E^U \quad (5.49)$$

$$y_{e,e-1}^{LL} + 1 - y_e + 1 - y_{e-1} \geq 1, \quad e \in E^U \quad (5.50)$$

$$1 - y_{e,e+1}^{VV} + y_e \geq 1, \quad e \in E^L \quad (5.51)$$

$$1 - y_{e,e+1}^{VV} + y_{e+1} \geq 1, \quad e \in E^L \quad (5.52)$$

$$y_{e,e+1}^{VV} + 1 - y_e + 1 - y_{e+1} \geq 1, \quad e \in E^L \quad (5.53)$$

Inter-Column Structural Constraints

$$\sum_{p \in E_e^{CPo}} y_{e,p}^{CP} + \sum_{ea \in E_e^{CLo}} y_{e,ea}^{CL} = y_e^C, \quad e \in E^C, ea \neq e \quad (5.54)$$

$$\sum_{p \in E_e^{LPo}} y_{e,p}^{LP} + \sum_{ea \in E_e^{LLo}} y_{e,ea}^{LL} = y_e, \quad e \in E^L, e \notin E^{LIT} \quad (5.55)$$

$$y_e - y_{e,p}^{LP} = 0, \quad e \in E^{LIT}, p \in E_e^{LPo} \quad (5.56)$$

$$y_{e,e}^{HV} + \sum_{ea \in E_e^{VVi}} y_{ea,e}^{VV} = y_e, \quad e \in E^{LIT} \quad (5.57)$$

$$1 - y_{e,ea}^{CL} + y_e^C \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (5.58)$$

$$1 - y_{e,ea}^{CL} + y_{ea} \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (5.59)$$

$$y_{e,ea}^{CL} + 1 - y_e^C + 1 - y_{ea} \geq 1, \quad e \in E^{UO}, ea \in E_e^{CLo}, ea \neq e \quad (5.60)$$

$$1 - y_{e,ea}^{LL} + y_e \geq 1, \quad e \in E^{LO}, ea \in E_e^{LLo} \quad (5.61)$$

$$1 - y_{e,ea}^{LL} + y_{ea} \geq 1, \quad e \in E^{LO}, ea \in E_e^{LLo} \quad (5.62)$$

$$y_{e,ea}^{LL} + 1 - y_e + 1 - y_{ea} \geq 1, \quad e \in E^{LO}, ea \in E_e^{LLo} \quad (5.63)$$

$$1 - y_{e,ea}^{LL} + y_e \geq 1, \quad e \in E^{UOT}, ea \in E_e^{LLo} \quad (5.64)$$

$$1 - y_{e,ea}^{LL} + y_{ea} \geq 1, \quad e \in E^{UOT}, ea \in E_e^{LLo} \quad (5.65)$$

$$1 - y_{e,ea}^{LL} + 1 - y_{ea}^C \geq 1, \quad e \in E^{UOT}, ea \in E_e^{LLo} \quad (5.66)$$

$$1 - y_e + 1 - y_{ea} + y_{ea}^C + y_{e,ea}^{LL} \geq 1, \quad e \in E^{UOT}, ea \in E_e^{LLo} \quad (5.67)$$

$$y_{e,ea}^{LL} - y_{ea,e}^{VV} = 0, \quad e \in E^{UOT}, ea \in E_e^{LLo} \quad (5.68)$$

$$1 - y_{e,ea}^{LL} + y_e \geq 1, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.69)$$

$$1 - y_{e,ea}^{LL} + y_{ea} \geq 1, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.70)$$

$$1 - y_{e,ea}^{LL} + 1 - y_e^H \geq 1, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.71)$$

$$1 - y_{e,ea}^{LL} + 1 - y_{ea}^C \geq 1, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.72)$$

$$1 - y_e + 1 - y_{ea} + y_e^H + y_{ea}^C + y_{e,ea}^{LL} \geq 1, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.73)$$

$$y_{e,ea}^{LL} - y_{ea,e}^{VV} = 0, \quad e \in E^{LIT}, ea \in E_e^{LLo} \quad (5.74)$$

$$1 - y_{e,ea}^{VV} + y_e \geq 1, \quad e \in E^{LOT}, ea \in E_e^{VV^o}, ea \neq e+1 \quad (5.75)$$

$$1 - y_{e,ea}^{VV} + y_{ea} \geq 1, \quad e \in E^{LOT}, ea \in E_e^{VV^o}, ea \neq e+1 \quad (5.76)$$

$$1 - y_{e,ea}^{VV} + 1 - y_{ea}^H \geq 1, \quad e \in E^{LOT}, ea \in E_e^{VV^o}, ea \neq e+1 \quad (5.77)$$

$$1 - y_e + 1 - y_{ea} + y_{ea}^H + y_{e,ea}^{VV} \geq 1, \quad e \in E^{LOT}, ea \in E_e^{VV^o}, ea \neq e+1 \quad (5.78)$$

$$y_e^C + 1 - y_{ea}^C \geq 1, \quad e \in E^{UO}, ea \in E^{UIT} \quad (5.79)$$

$$y_e^H + 1 - y_{ea}^H \geq 1, \quad e \in E^{LO}, ea \in E^{LIT} \quad (5.80)$$

$$1 - y_e + 1 - y_{ea} + y_e^H + y_{e,ea}^{LL} \geq 1, \quad e \in E^{LIT}, ea \in E^{UIT} \quad (5.81)$$

$$1 - y_e + 1 - y_{ea} + y_{ea}^C + y_{e,ea}^{LL} \geq 1, \quad e \in E^{LIT}, ea \in E^{UIT} \quad (5.82)$$

$$1 - y_{ea}^C + 1 - y_{e,ea}^{LL} + y_e \geq 1, \quad e \in E^{LIT}, ea \in E^{UIT} \quad (5.83)$$

$$1 - y_{ea}^C + 1 - y_{e,ea}^{LL} + y_{ea} \geq 1, \quad e \in E^{LIT}, ea \in E^{UIT} \quad (5.84)$$

$$1 - y_e^H + 1 - y_{e,ea}^{LL} + y_e \geq 1, \quad e \in E^{LIT}, ea \in E^{UIT} \quad (5.85)$$

$$1 - y_e^H + 1 - y_{e,ea}^{LL} + y_{ea} \geq 1, \quad e \in E^{LIT}, ea \in E^{UIT} \quad (5.86)$$

$$\sum_{e \in E_p^{CPi}} y_{e,p}^{CP} + \sum_{e \in E_p^{LPi}} y_{e,p}^{LP} \geq 1, \quad p \in P \quad (5.87)$$

The above GMF Structural Constraints defined over the appropriate Structural Sets constitute the GMF Structural Model for the complex column sequencing problem. The synthesis model is completed with the incorporation of the GMF Physical Model (Section 2.3.3).

5.3 Case Study: Ternary Complex Distillation Sequencing

5.3.1 Problem Statement

The proposed method for the Complex Column Sequencing problem was applied for the ternary separation case study of Benzene, Toluene and o-Xylene into 3 near-pure product streams, as posed in Section 3.3.1. The only difference is that here, the solution space is extended, since both simple and complex column sequences are incorporated in the synthesis framework.

5.3.2 GMF Problem Formulation - Stage 3

The superstructure for the ternary complex distillation column sequencing problem is given in Figure 5.10. As it can be seen 6 *M/H* modules are necessary in order to construct the

Table 5.2: Ternary GMF Complex Column Structural Sets (Stage - 3)

$I = \{F\}$	$E^L = \{1, 3, 5\}$
$C = \{Benz., Tol., o - Xyl.\}$	$E^U = \{2, 4, 6\}$
$P = \{P1, S, P2\}$	$E^{UO} = \{2\}$
$E = \{1, 2, 3, 4, 5, 6\}$	$E^{LO} = \{1\}$
$E^H = \{1, 3, 5\}$	$E^{UOT} = \{6\}$
$E^C = \{2, 4, 6\}$	$E^{LOT} = \{3\}$
	$E^{UIT} = \{4\}$
	$E^{LIT} = \{5\}$
$E_F^{FL} = \{1\}$	
$E_e^{VV^o} = \{ea ea = e + 1\}, e \in E^L$ and $E_2^{VV^o} = \{6\}, E_3^{VV^o} = \{1\}, E_4^{VV^o} = \{5\}$	$E_e^{VV^i} = \{ea ea = e - 1\}, e \in E^U$ and $E_1^{VV^i} = \{3\}, E_5^{VV^i} = \{4\}, E_6^{VV^i} = \{2\}$
$E_e^{LL^o} = \{ea ea = e - 1\}, e \in E^U$ and $E_1^{LL^o} = \{3\}, E_5^{LL^o} = \{4\}, E_6^{LL^o} = \{2\}$	$E_e^{LL^i} = \{ea ea = e + 1\}, e \in E^L$ and $E_2^{LL^i} = \{6\}, E_3^{LL^i} = \{1\}, E_4^{LL^i} = \{5\}$
$E_e^{CL^o} = \{ea ea = e\}, e \in E^U$ and $E_2^{CL^o} = \{5\}$	$E_e^{CL^i} = \{ea ea = e\}, e \in E^U$ and $E_5^{CL^i} = \{2\}$
$E_1^{LP^o} = \{P2\}, E_3^{LP^o} = \{P2\}, E_5^{LP^o} = \{S\}$	$E_{P2}^{LP^i} = \{1, 3\}, E_S^{LP^i} = \{5\}$
$E_2^{CP^o} = \{P1\}, E_4^{CP^o} = \{S\}, E_6^{CP^o} = \{P1\}$	$E_{P1}^{CP^i} = \{2, 6\}, E_S^{CP^i} = \{4\}$

superstructure. In order to construct the GMF Structural Model, which is the mathematical translation of the aforementioned superstructure, the GMF Structural Sets have to be assigned for the examined problem. The *non-zero* sets are defined in Table 5.2 (defining the Stage 3 of the construction of the GMF Structural Model for the synthesis of complex column sequences). Similarly to the practice used so far, for a GAMS implementation only I , C , P and E are included as GAMS SETS, whereas the remaining Structural Sets are included as GAMS PARAMETERS.

5.3.3 Solution Procedure

The problem generated by the GMF is an MINLP problem, solved using the GBD method which decomposes the problem into sequential Primal NLP and Master MILP subproblems. Due to the particular physical behaviour of the complex distillation columns examined, with their multiple interconnection streams, attention must be given to the solution procedure of the Primal NLP subproblems. Due to the nonconvexities, it was observed that during the solution procedure the solver tended to converge to local optima, depending on the initial point given.

This complication was overcome in this work by improving the solution techniques using better bounding and initialization procedures, as reported below.

Bounding and Initialization Procedure

The computational complexities caused by the nonlinearities encountered (located in the component and energy balances and in the Driving Force and Phase Defining Constraints) were tackled through a systematic initialization and bounding procedure, which provided initial guesses and bounds for the flowrates, temperatures and molar fractions of the components.

Flowrates: For the flowrates, it was essential that consistent initial guesses (closing at least the total mass balances) were given for the major flows, such as the product and the interconnection streams. The initialization of the flowrates was based on equimolar flowrates through each M/H module. Appropriate upper bounds were used for the flowrates.

Temperatures: The temperature bounding was based on the fact that, since fairly ideal mixtures without azeotropes were treated, the temperature was expected to be lower in the M/H modules which represented higher parts of a column (decreasing temperature profiles while ascending the column). The initial guesses for these highest and lowest temperatures were the boiling points of the heaviest and lightest components, respectively. The initial guesses for the intermediate M/H modules were derived by linear interpolation between the highest and lowest temperatures along the module sections. Sections corresponding to thermal coupling points were assigned to the same temperature initial guess. The temperature bounds were based on the heaviest and lightest components' boiling points slightly slackened (± 10 degrees).

Molar Fractions: Providing initial guesses for the molar fractions is relatively easy for binary mixtures. For the latter, initial guesses are obtained for one component through linear interpolation between the products purity specifications in the tops and bottoms. For the other component, the molar fractions are determined by subtracting the calculated values of the first component from 1. In the case of the examined ternary ideal distillation, deriving good initial guesses for the molar fractions is more involved, mainly, because of the lack of *a priori* knowledge of the medium components' distribution. In order to circumvent this complication, a logical approach was utilized based on the anticipated distribution of the components in the various parts of the represented configurations and on the specifications of the product stream purities. Based on the latter and on the assumption of sharp splits for initialization purposes,

some M/H modules were assumed to represent binary columns, others between the heaviest and middle and others between the middle and the lightest components. There, initial guesses were easily derived following the binary distillation procedure, as described above. In the modules' sections where the component distribution could not be predicted, the conservative approach of using molar fractions of $1/3$ for each component was applied.

5.3.4 Problem Results

The examined MINLP Ternary Complex Distillation Sequencing problem was solved employing the GBD algorithm and implemented in GAMS using the APROS methodology. From the solution of the MINLP problem, it was found that the most energy efficient configuration was the Petlyuk column achieving 30% savings in the operating cost, when compared to the Direct Sequence, the best conventional design. The optimization results for the operation of this column are shown in Table 5.3.

From a computational point of view, convergence was achieved in 4 GBD iterations. Starting from the Direct Sequence, the Petlyuk Column was generated by the solution of the 1st Master subproblem, while convergence was achieved with the lower bound crossing the current best

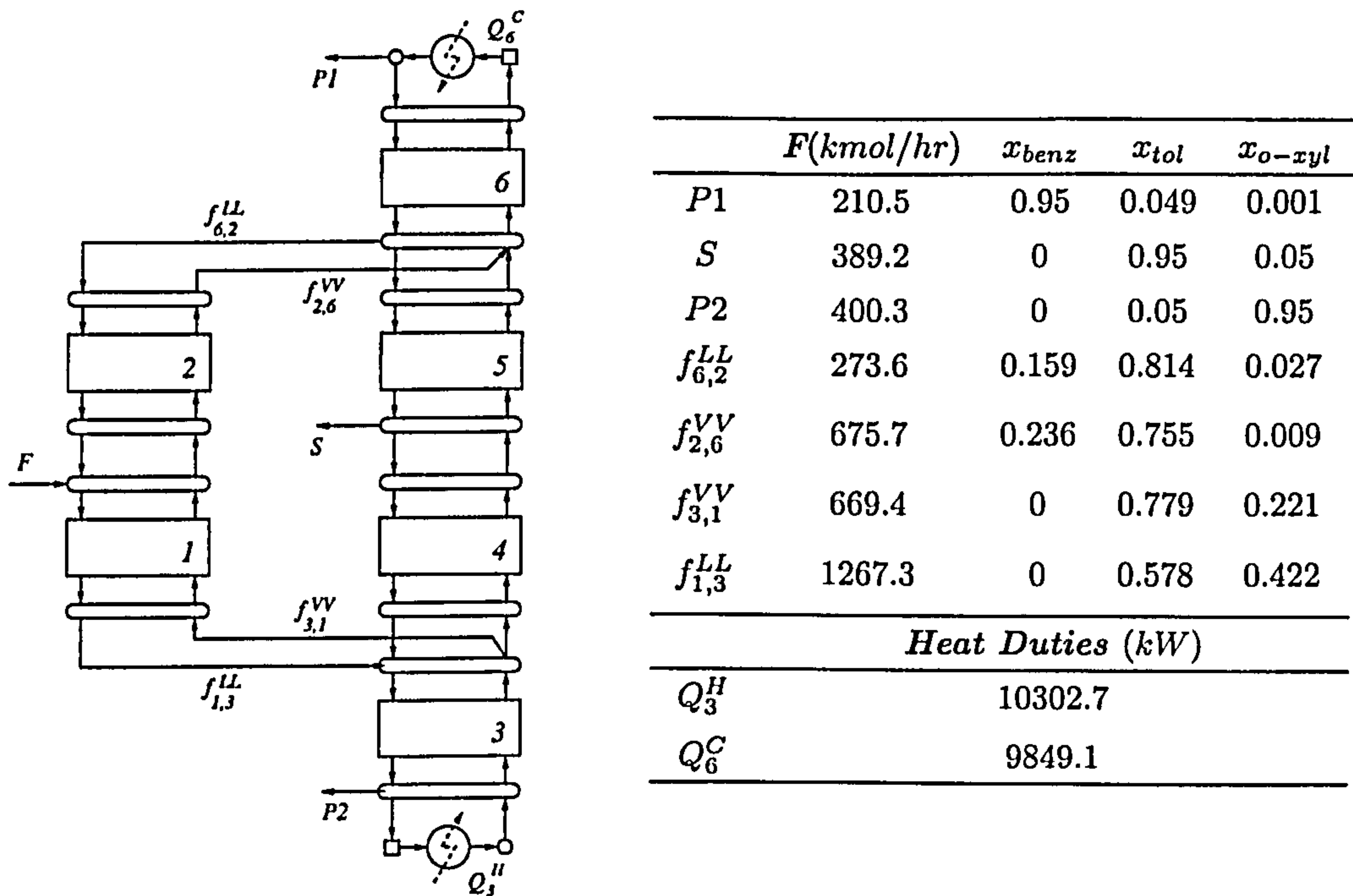
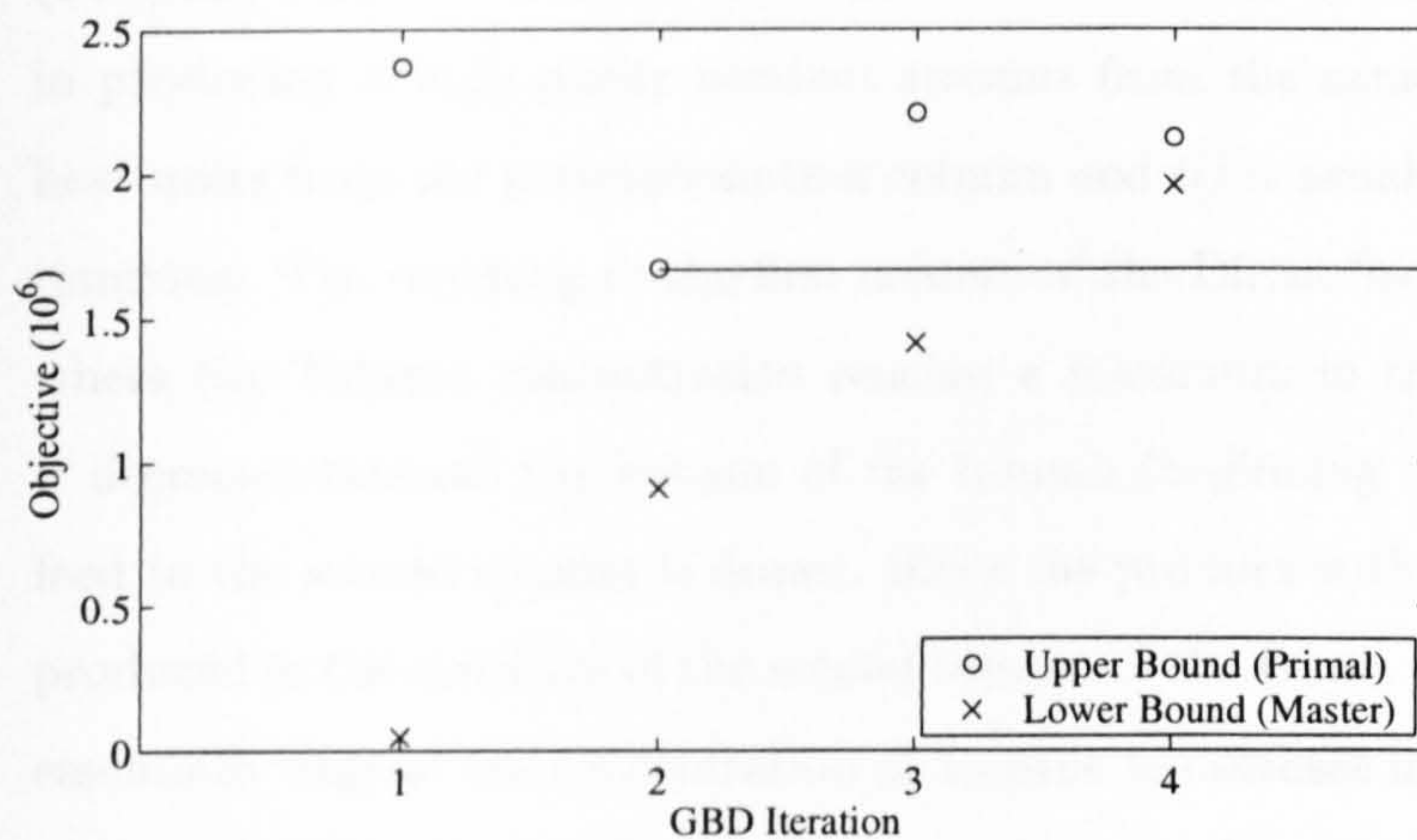


Table 5.3: GMF Complex Ternary Sequencing Optimal Structure and Operation

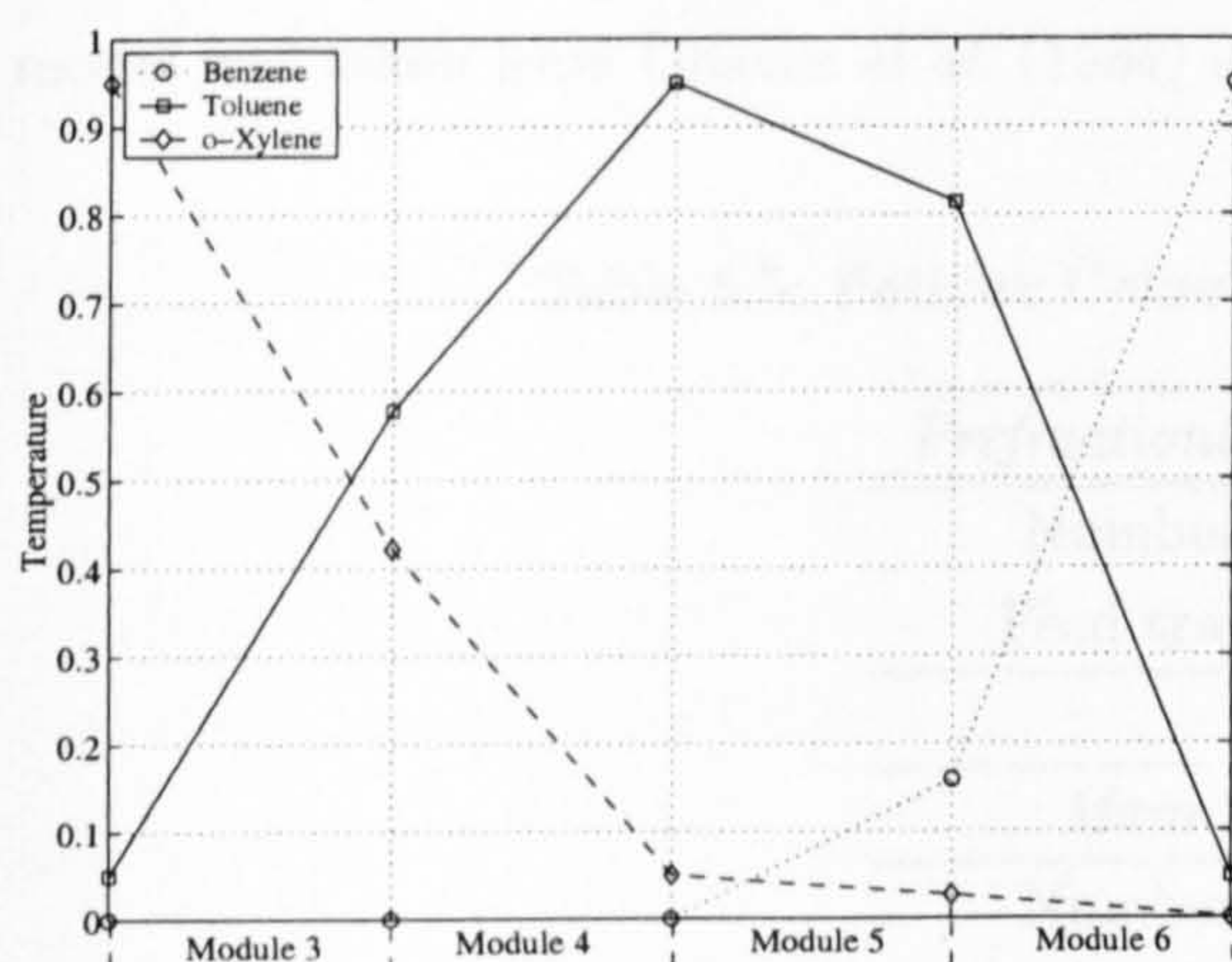
Table 5.4: GMF Ternary Complex Column Sequencing GBD Convergence



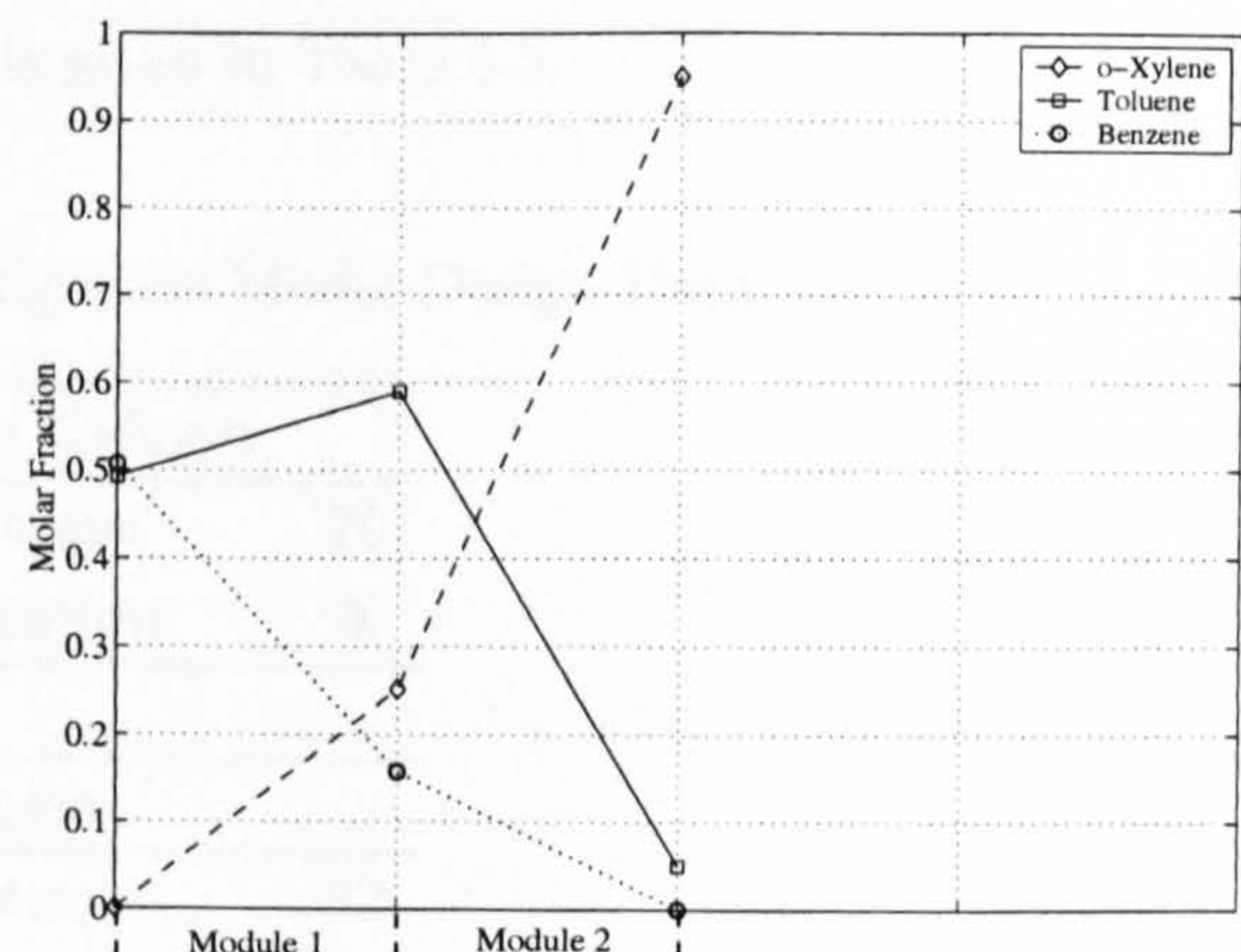
Iter.	Primal	Master
1	2.369 10^6	0.047 10^6
2	1.672 10^6	0.910 10^6
3	2.209 10^6	1.414 10^6
4	2.122 10^6	1.958 10^6

upper bound (the latter corresponding to the Petlyuk Column) after the solution of the 4th Master subproblem. The convergence history is given in Table 5.4.

Beyond the *quantitative* results (energy consumption), the GMF provided also a *qualitative* insight on the represented alternatives. Figures 5.11.a and 5.11.b. depict the distribution of the 3 components in the various sections of the GMF representation of the Petlyuk main column and of the first column of the Direct Sequence, respectively (for simplicity the details of only one input and output stream per *M/H* module are illustrated). In the *x*-axis are given the corresponding modules of the columns' representation.



(a) Petlyuk main column



(b) Direct Sequence first column

Figure 5.11: Ternary Distillation GMF Representations

These plots provide an insight on the (thermal) efficiency of the Fully Thermally Coupled (Petlyuk) column over simple columns. This is due to the following factors: *i*) it succeeds in producing 3 high purity product streams from the same column, while eliminating all the heat units from the prefractionation column and *ii*) it avoids thermal losses due to unnecessary remixing. The remixing in the first column of the Direct Sequence can be seen in Figure 5.11.b, where the Toluene concentration reaches a maximum in the middle of the column, and then it decreases towards the bottom of the column (beginning of *M/H* module 1), from where the feed to the second column is drawn. Since the product with high Toluene concentration will be produced in the distillate of the second column of the Direct Sequence, the current connectivities essentially impose the concentration of Toluene to decrease in the first column, before it is finally increased in the second column. This concentration decrease and subsequent increase leads to the undesired remixing and to the increased energy consumption. On the contrary, in the Petlyuk column the Toluene-enriched product is drawn, so that no such remixing occurs.

Modular Representation Validation

Due to the large energy savings of the Petlyuk Sequence and the complexity of its underlying mass and heat transfer over the fully thermally coupled sections, the GMF physical representation for this sequence was validated through a comparison to the rigorous model of Viswanathan and Grossmann (1993). The problem definition was the same as in Section 3.3.1, with the same objective to be minimized and the same process specifications. The design data for the rigorous model was taken from Chavez *et al.* (1986) and is given in Table 5.5.

Table 5.5: Petlyuk Column Rigorous Model Design Data

<i>Prefractionation Column</i>	
Number of trays	20
Feed tray location	9
<i>Main Column</i>	
Number of trays	32
Upper feed tray location	27
Lower feed tray location	6
Side stream tray location	17

The results of the optimization of the GMF and of the tray-by-tray model are shown in Table 5.6. As shown, the energy consumption levels in the reboiler and the condenser of the tray-by-tray model and in the heater and the cooler of the GMF are very close. As indicated also in Section 2.4.3, it can be seen that the GMF Physical Model solution provides a lower bound to the energy consumption of the Petlyuk column.

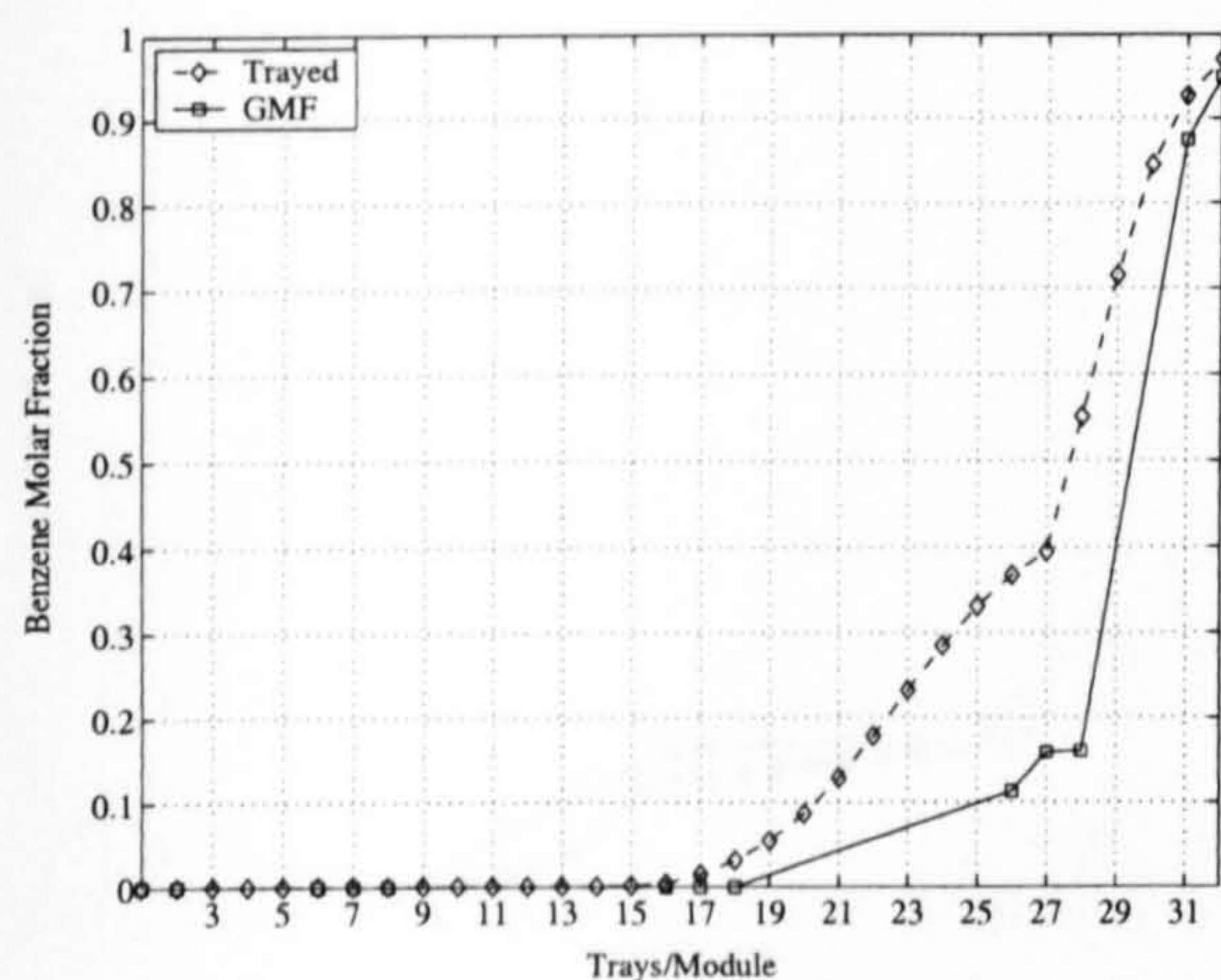
Table 5.6: GMF Quantitative Validation for Petlyuk Column

	$Q_{reboiler} (kW)$	$Q_{condenser} (kW)$
<i>GMF</i>	10302.7	9849.1
<i>Trayed Model</i>	12462.5	11919.4

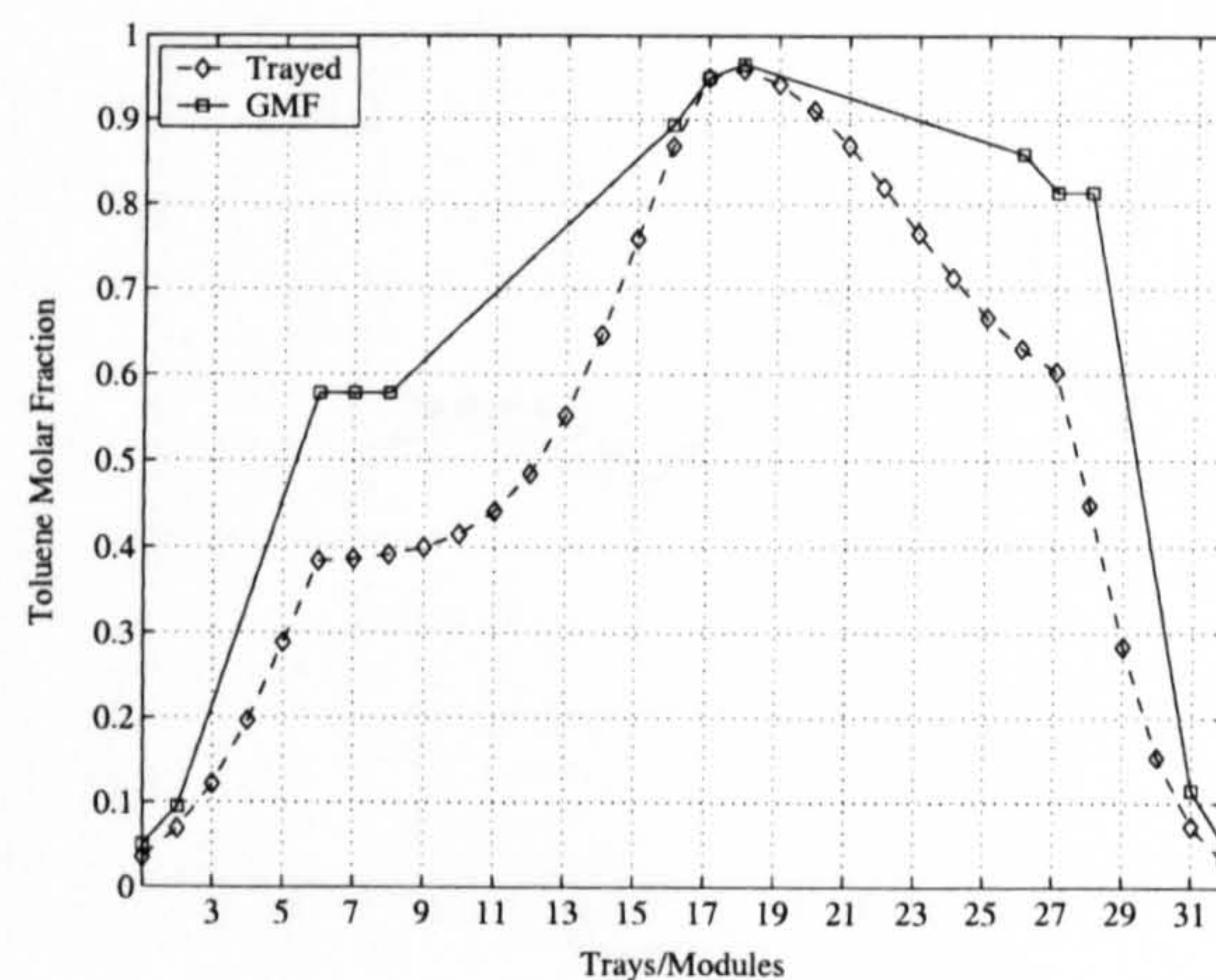
A qualitative comparison, *i.e.* of the general trends of the distribution of the components over the various sections of the column, was also carried out. In order to plot the results in the same graph the points of the feeds, of the interconnections and of the side streams of the GMF were placed on the corresponding tray locations of the rigorous model, so that a common x -axis could be obtained.

The results for the main column of the Petlyuk arrangement (Figure 5.12) show an agreement between the two models, although the GMF does not provide as much detail as the trayed model, it certainly captures the distribution of the components and the temperature profile in the examined parts of the column. The GMF results demonstrate the efficiency of the Fully Thermally Coupled column which provides 3 products of high purity from the same column (Benzene from the distillate, o-Xylene from the bottoms and Toluene from the side stream).

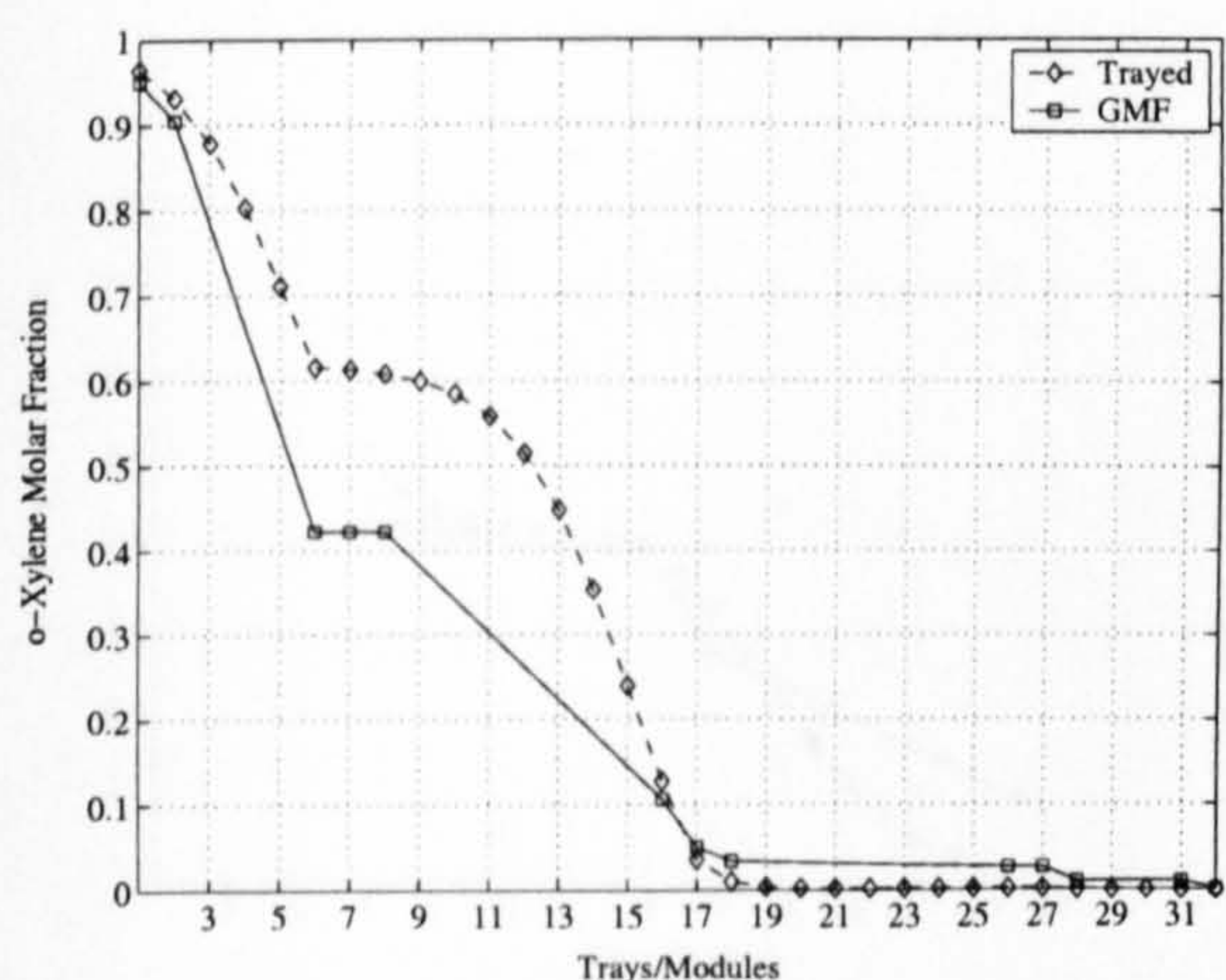
In the same manner, the profiles for the prefractionation column are showed in Figure 5.13. From this figure it is shown that the two models are in qualitative agreement in the prefractionation column, as well. Both models show that the prefractionation column essentially separates the mixture into a light and middle component stream in the top and into a heavy and middle component stream in the bottom, providing the feeds to the main column. From the presented figures and tables it is validated that the physical model of the GMF is capable of capturing efficiently the mass and heat transfer phenomena of the examined problem, generating valid and useful results for the operation and energy consumption of the Petlyuk Column.



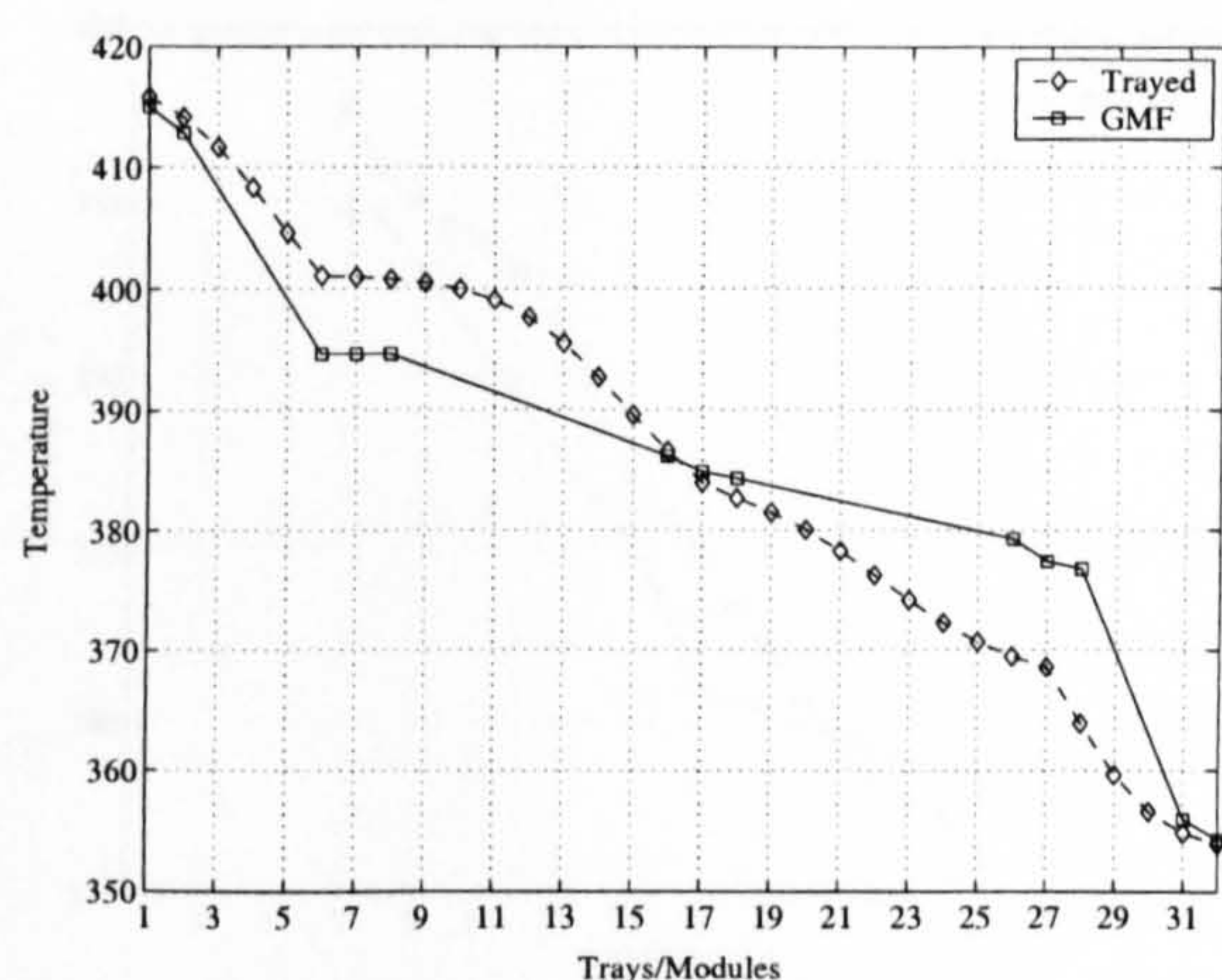
(a) benzene



(b) toluene



(c) o-xylene



(d) temperature

Figure 5.12: GMF Qualitative Validation for Petlyuk Main Column

5.4 Conclusions

As shown, the GMF provides a sound and useful tool for the generation and evaluation of distillation column sequences including complex columns, through its structural and physical models. Through an appropriate structural model it incorporated the complex structural possibilities of the thermally coupled columns, in a unified way along with conventional simple columns, thus generating all the reported alternative structures from within a superstructure. Moreover, it represented the underlying physical phenomena through a physical model providing insights on the energy efficiency of thermally coupling for the examined problem. A bounding and initial-

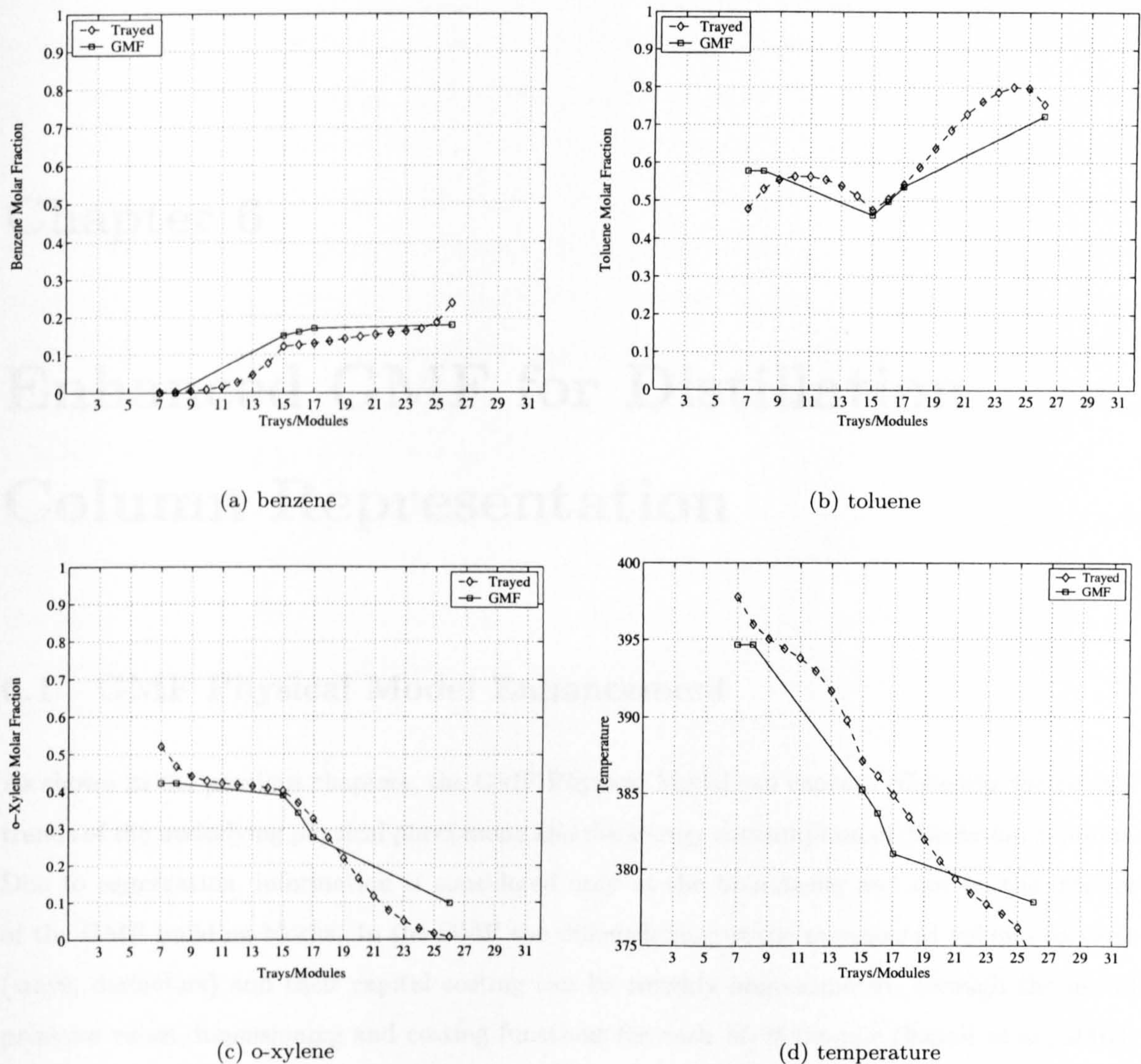


Figure 5.13: GMF Qualitative Validation for Petlyuk Prefractionation Column

ization procedure was also incorporated for the efficient solution of the generated Primal NLP problems in order to overcome the complexities due to the nonlinearities.

The GMF has been used for the ternary complex column sequencing problem which is a problem of industrial relevance and which can be used as the basis for higher separation sequencing methods. The results of the GMF for the particular synthesis problem were found valid through their comparison with well established methods and the obtained energy savings were in accord with those reported in the literature. Furthermore, the GMF results were derived using aggregated models, thus generating significantly compact optimization problems.

Chapter 6

Enhanced GMF for Distillation Column Representation

6.1 GMF Physical Model Enhancement

As shown in the previous chapters, the GMF Physical Model can capture efficiently the general trends of the underlying physical phenomena and the energy consumption of distillation columns. Due to aggregation, information is considered only at the boundaries and not on the interior of the GMF building blocks. In the GMF the dimensioning of the represented column sections (trays, diameters) and their capital costing can be roughly approximated, through the use of pressure vessel dimensioning and costing functions for each M/H module (Ismail *et al.*, 2001). Nevertheless, this does not affect the usefulness of the GMF for the distillation sequencing problems examined. This is due to the fact that no complex separation tasks, such as reactive or azeotropic distillation, take place within the M/H modules, that might require intra-module information. Moreover, it is well established (Douglas, 1988) that the capital cost contribution to the Total Annualized Cost (TAC) of distillation systems is significantly smaller than that of the operating cost. More specifically, Douglas indicated that the capital cost contribution in the distillation column TAC is around 20% as opposed to a 80% of the operating cost. In the GMF, a potential rough approximation of the capital cost is compensated and balanced by the accurate operating cost estimates (as determined over comparisons with rigorous models throughout this work).

However, it remains a challenge to enhance the GMF Physical Model so that it can incorporate intra-module information and improved capital cost estimates (and column dimensionality information) without sacrificing the GMF's main advantages of size compactness and representation efficiency and while avoiding the use of shortcut models or simplifying assumptions. The use of Kremser Group Methods cannot be employed for this purpose, since it is based on simplifying assumptions of equimolar flowrates, isothermal operation and linear phase equilibrium relations, assumptions that can be potentially limiting. At the same time, employing rigorous tray-by-tray MINLP models can provide accurate physical representations but at a substantial increase of the continuous and combinatorial size of the generated problem, leading to the loss of the GMF's advantage of compactness.

An approach that can guarantee the safeguarding of the aforementioned GMF physical representation advantages and can still achieve the GMF Physical Model enhancement, is the use of principles of Order Reduction Methods for distillation and namely those of Orthogonal Collocation (OC) and Orthogonal Collocation on Finite Elements (OCFE). The main principles of these methods and their coupling to the GMF will be presented in the following sections.

6.2 Principles of Collocation Methods For Distillation

Collocation methods were first proposed for distillation order reduction by Cho and Joseph (1983a), who proposed a method for steady state and dynamic distillation models based on the idea of approximating a staged distillation column as a distributed system in which the composition and flowrates were approximated by Lagrange polynomials, over collocation points. The latter were defined as the zeros of orthogonal Jacobi polynomials originally developed for continua. The method was developed for single gas absorption columns and was extended to simple distillation columns in Cho and Joseph (1983b) and to distillation columns with side streams in Cho and Joseph (1984).

Stewart *et al.* (1985) proposed an orthogonal collocation technique for steady state and dynamic simulations of distillation systems, based on the approximation of the system states (molar fractions and enthalpies) in each column section also by Lagrange polynomials, which were fitted to the process model at collocation points. In contrast with the Cho and Joseph (1983a) approach, the collocation points were chosen as the zeros of the Hahn family of polyno-

mials obeying orthogonality conditions. These polynomials had the property that, if their order took its maximum value (equal to the number of stages in each section), then the collocation points would fall exactly on the stages of that section. The authors through a number of case studies, where different types of Jacobi and Hahn polynomials were tested, demonstrated the accuracy of using Hahn polynomials, which were more appropriate for staged distillation than the Jacobi polynomials whose results converged towards continuum descriptions of the system rather than the desired staged solutions. Furthermore, the proposed method was proven more advantageous and consistent than other order reduction methods, such as the Laplace-Domain lumping (Wahl and Marriott, 1970), the Time-Domain lumping (Georgakis and Stoevers, 1982) and the Compartmental lumping (Benallou *et al.*, 1982).

Swartz and Stewart (1986) extended the above method to the distillation design problem, where the continuous number of stages (as incorporated in the collocation scheme) was determined directly by the optimization. The method approximated liquid and vapour enthalpies and component flowrates by Lagrange interpolation polynomials, defined over the zeros of orthogonal Hahn polynomials. The objectives to be minimized included the number of stages and the Total Annualized Cost for separations carried out in a single distillation column. The optimization results were found to be in a very good agreement with conventional distillation design methods. In Swartz and Stewart (1987) a Finite Element Collocation scheme was used in order to predict the phase boundaries of multiphase distillation systems. At the Element boundaries the approximation polynomials were made continuous and the forming or vanishing liquid phases were imposed to be at equilibrium with the other liquid phases at that location. An appropriate solution procedure was also proposed and evaluated over a number of case studies.

Seferlis and Hrymak (1994a), based on the above, proposed a systematic and detailed OC and OCFE design method for distillation columns. This provided more accuracy for cases where composition profiles were found to be steep and difficult to be approximated using the 'global' orthogonal collocation technique. At the boundaries of the Finite Elements zero-order continuity was enforced in the approximating polynomials. The method proved to be in excellent agreement with the rigorous models. Moreover, the authors provided an approximation error analysis, where different discretization schemes (combinations of different numbers of Finite Elements and Collocation Points) were compared for the minimization of the approximation error. The optimal Element length issue was further addressed in Seferlis and Hrymak (1994b) based on the approximation error equidistribution.

A collocation method for distillation was also proposed by Huss and Westerberg (1996a) who broke each column section into two Elements of two collocation ‘trays’. Lagrange approximation polynomials were used and the collocation points were the roots of appropriately weighted orthogonal Jacobi polynomials. In order to provide better approximations for large columns where difficult separations took place, the authors proposed an exponential transformation of the tray number variables and a hyperbolic tangent transformation of the mole fractions. This collocation model was applied in Huss and Westerberg (1996b), followed by a systematic solution procedure, for minimum reflux and Total Annualized Cost calculations and optimizations for single distillation columns.

More recently, Zhang and Linninger (2004) proposed a new minimum bubble point distance (MIDI) algorithm for addressing the feasibility problem of distillation separations. Based on the conversion of the tray-by-tray difference equations into ordinary differential equations (ODE) over the column height (Van Dongen and Doherty, 1985), the authors proposed a mapping of the column height into a dimensionless bubble point temperature, thus expressing the ODEs for the component compositions over the bubble point temperature instead of the column height. The ODEs were then converted into algebraic equations using orthogonal collocation on finite elements and Lagrange and Legendre base polynomials. The proposed algorithm was found effective for a wide variety of separation problems involving sharp and sloppy separations for minimum and maximum reflux ratio computations.

Table 6.1 summarizes the aforementioned OC and OCFE methods for distillation. A detailed

Table 6.1: Summary of OC and OCFE Methods for Distillation

Authors	Features
Cho & Joseph (1983a,b)(1984)	OC, Jacobi polynomials, simple and sidestream columns
Stewart <i>et al</i> (1985)	OC, Hahn polynomials, steady-state and dynamics
Swartz & Stewart (1986)	OC, Hahn polynomials, single column design
Swartz & Stewart (1987)	OCFE, Hahn polynomials, multiphase column design
Seferlis & Hrymak (1994a,b)	OCFE, Hahn polynomials, approximation error analysis
Huss & Westerberg (1996a,b)	OCFE, Jacobi polynomials, variable transformations
Zhang & Linninger (2004)	OCFE, Temperature Collocation Algorithm

analysis of the main principles of the collocation methods (OC and OCFE) for distillation as proposed by Seferlis and Hrymak (1994a) and its coupling to the GMF will be presented in the next sections.

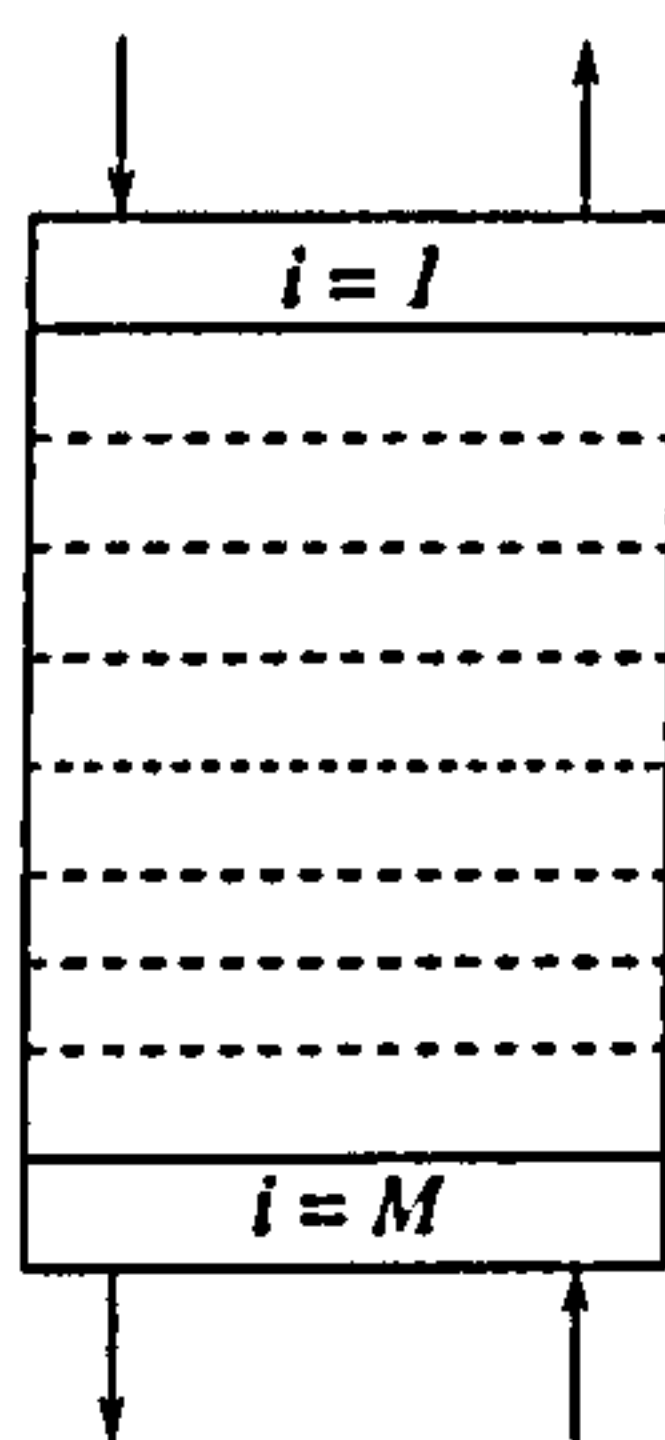
6.2.1 Orthogonal Collocation (OC)

A full order model for a distillation column considers information (variables and equations) at points which correspond to each column tray. This model corresponds to a rigorous tray-by-tray model (for instance, that of Viswanathan and Grossmann (1993)), which essentially ‘discretizes’ a column into discrete trays.

An order reduction model for distillation considers information at fewer points than the full order model, thus generating a problem with less variables and constraints. This can be achieved by approximating certain variables in each column section with Lagrange polynomials. The latter are defined at certain (collocation) points whose number depends on the order of the polynomials. The number of interior collocation points should be less than or equal to the number of trays in the section.

In the OC method of Seferlis and Hrymak (1994a) each column section of M trays corresponds to a single Element of ‘length’ $M + 1$ ($M + 1$ is the tray that provides the vapour inlet stream to the examined section, counting from top to bottom). According to the order of the approximating polynomials, the Element (section) is then discretized into $nc + 2$ collocation points ($j = 0, 1, \dots, nc, nc + 1$), as shown in Figure 6.1. The collocation points 0 and $nc + 1$ are called exte-

Full Order Column Section



OC Column Section

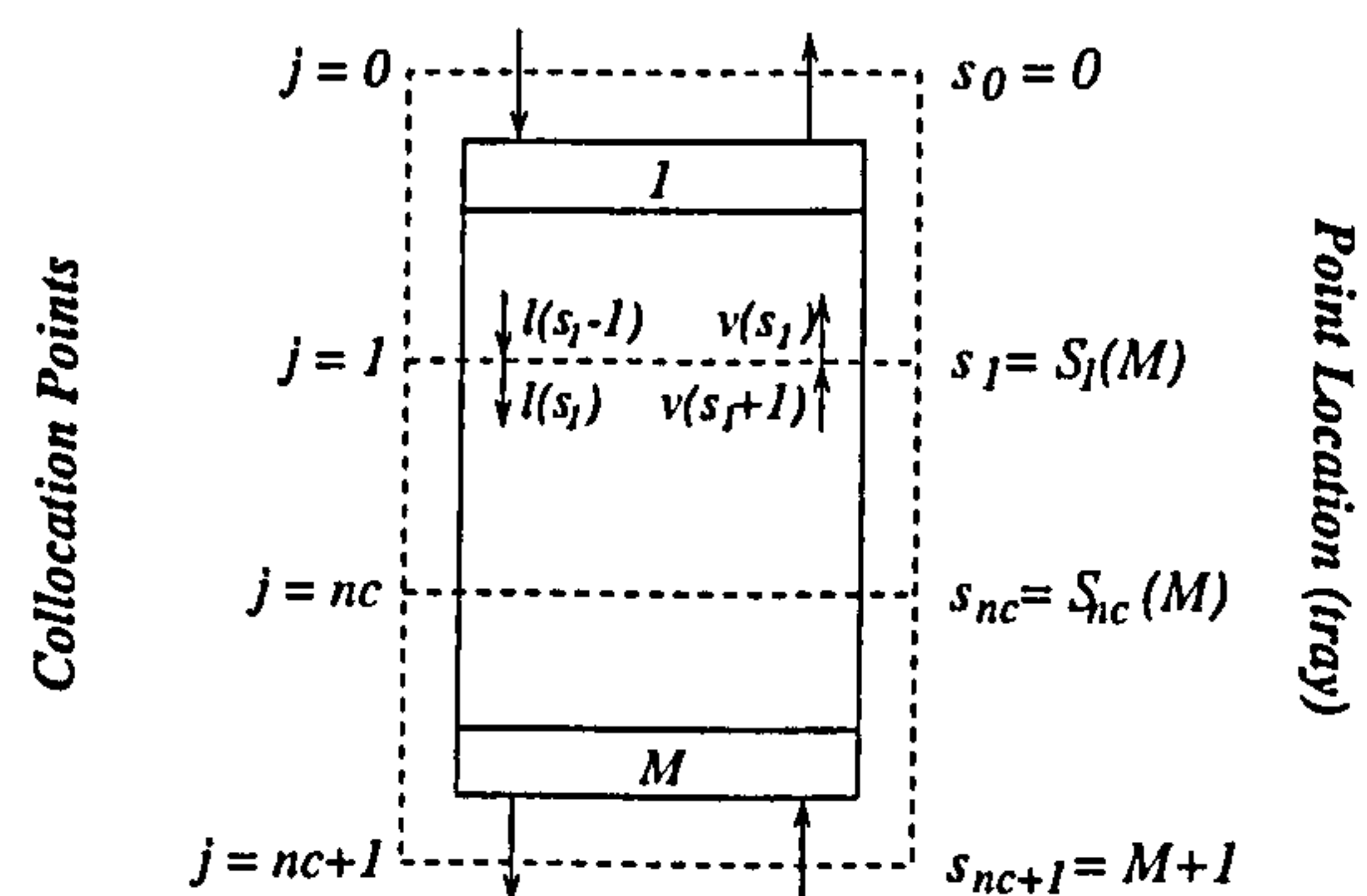


Figure 6.1: Full Order and OC Distillation Column Sections

rior collocation points and their locations are at the Element's origin ($s_{(j=0)} = s_0 = 0$) and at its end ($s_{(j=nc+1)} = s_{nc+1} = M+1$). The locations of the interior (remaining) collocation points are defined by the roots of appropriate polynomials obeying orthogonality conditions. For this purpose and based on the results reported in Stewart *et al.* (1985), appropriately weighted Hahn polynomials were employed. The resulting roots, which are explicit functions of the 'length' (number of trays) M , were provided in Stewart *et al.* (1985) for up to 4 interior collocation points. For illustration, the case of 1 ($nc = 1$) interior collocation point is shown below:

$$s_{(j=0)} = s_0 = 0 \quad (6.1)$$

$$s_{(j=nc)} = s_1 = \frac{M+1}{2} \quad (6.2)$$

$$s_{(j=nc+1)} = s_2 = M+1 \quad (6.3)$$

Once the order of the approximating polynomials is assigned (number of collocation points), the latter are used for the approximation of the liquid and vapour component molar flowrates and enthalpies. For illustration purposes, the Lagrange polynomial approximation expression for the liquid and vapour component flowrates for a location s in the Element, is given in equations (6.4) and (6.5). These are expressed in terms of the discretized liquid and vapour component flowrates $l_c(s_j)$ and $v_c(s_j)$ over the collocation points j .

$$l_c(s) = \sum_{j=0}^{nc} W_j^L(s) l_c(s_j), \quad c \in C \quad (6.4)$$

$$v_c(s) = \sum_{j=1}^{nc+1} W_j^V(s) v_c(s_j), \quad c \in C \quad (6.5)$$

The polynomial approximations for the enthalpies are written in an similar form. It must be noted that in the above expressions the liquid flowrates are defined over $nc+1$ collocation points ($l_c(s_0), \dots, l_c(s_{nc})$), whereas the vapour flowrates are defined over a different set of $nc+1$ collocation points ($v_c(s_1), \dots, v_c(s_{nc+1})$). The dependence of the approximating polynomials on the location of the examined point, s , and on the total 'length' (number of trays) of the Element is included in the Lagrange polynomials $W_j^L(s)$ and $W_j^V(s)$:

$$W_j^L(s) = \prod_{z=0, j}^{nc} \frac{s - s_z}{s_j - s_z}, \quad j = 0, \dots, nc \quad (6.6)$$

$$W_j^V(s) = \prod_{z=1, j}^{nc+1} \frac{s - s_z}{s_j - s_z}, \quad j = 1, \dots, nc+1 \quad (6.7)$$

Substituting the approximating polynomials into the *MESH* distillation column equations yields a corresponding set of residual functions continuous in s . The collocation equations of the OC model are then derived by setting these residual functions equal to zero at the *interior* collocation points $(s_1, \dots, s_{nc})$. Therefore, the number of OC model variables and equations depends exclusively on the number of sections in the column and on the number of collocation points per section. For illustration, the component mass balances are given below:

$$v_c(s_j) + l_c(s_j) - v_c(s_j + 1) - l_c(s_j - 1) = 0, \quad c \in C, j = 1, \dots, nc \quad (6.8)$$

In these balances the location, s_j , of each collocation point j corresponds to a tray number (which could be an integer or not). Therefore, the locations $s_j + 1$ and $s_j - 1$, correspond to the following and previous trays of tray s_j , which provide the inlet vapour and liquid streams to 'tray' s_j . However, since these locations do not correspond to collocation points, their respective component flowrates have to be interpolated using the polynomial approximations of equations (6.4) and (6.5). Thus, the component mass balances become:

$$v_c(s_j) + l_c(s_j) - \sum_{j'=1}^{nc+1} W_{j'}^V(s_j + 1) v_c(s_{j'}) - \sum_{j'=0}^{nc} W_{j'}^L(s_j - 1) l_c(s_{j'}) = 0, \quad c \in C, j = 1, \dots, nc \quad (6.9)$$

Index j' refers also to collocation points and is used as a separate interior counter in the summations. Using equations (6.6) and (6.7), the W functions over the locations $s_j + 1$ and $s_j - 1$, are given below:

$$W_{j'}^L(s_j - 1) = \prod_{z=0, j'}^{nc} \frac{(s_j - 1) - s_z}{s_{j'} - s_z}, \quad j = 1, \dots, nc \quad (6.10)$$

$$W_{j'}^V(s_j + 1) = \prod_{z=1, j'}^{nc+1} \frac{(s_j + 1) - s_z}{s_{j'} - s_z}, \quad j = 1, \dots, nc \quad (6.11)$$

In the OC representation of Seferlis and Hrymak (1994a), a simple distillation column consisted of two discretized sections, a feed tray and a condenser and a reboiler (Figure 6.2). The models of the condenser and reboiler were the same as in any rigorous model. The feed tray was modelled as an equilibrium stage using the rigorous *MESH* equations. A schematic of the feed location can be seen in Figure 6.3 and the corresponding component mass balances are given in equation (6.12).

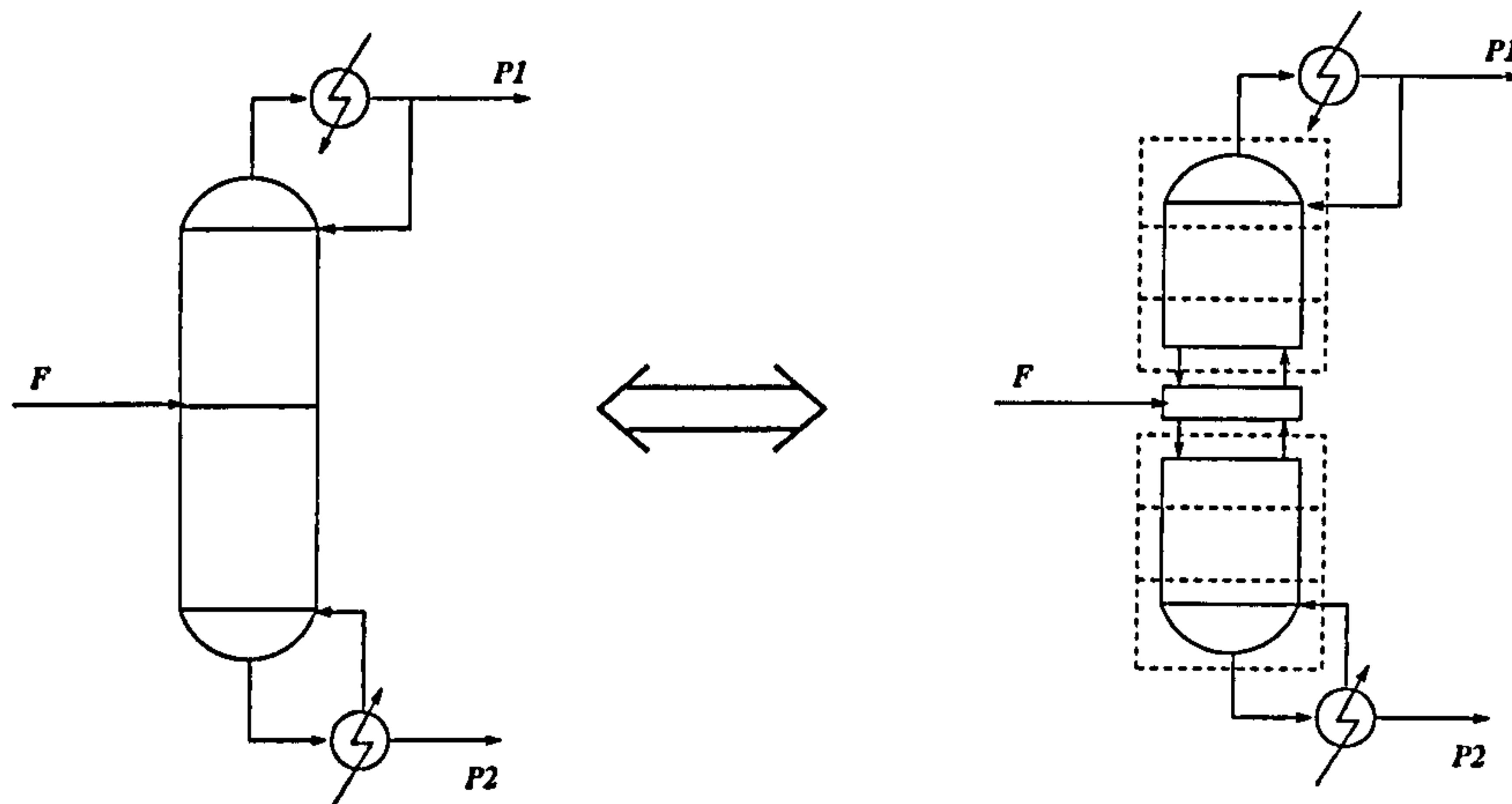


Figure 6.2: Conventional and OC Representations of a Simple Column

$$v_c(s_{nc^r+1}^r) + l_c(s_0^s) - \sum_{j=1}^{nc^s+1} W_j^V(1^s) v_c(s_j^s) - \sum_{j=0}^{nc^r} W_j^L(M^r) l_c(s_j^r) - f_c = 0, \quad c \in C \quad (6.12)$$

The superscripts r and s refer to the rectifier and stripper sections of the column. As shown in equation (6.12), the inlet streams to the feed tray are written in their polynomial form. This is because the origin of those streams does not correspond to collocation points (first tray of the stripper section for the vapour stream, $v_c^s(1)$, and last (M^r) tray of the rectifier section for the liquid stream, $l_c^r(M^r)$, as shown in Figure 6.3). The streams leaving the feed tray are essentially the inlet liquid and vapour streams to the stripper and rectifier, respectively, which correspond to these sections' exterior collocation points, thus not requiring a polynomial extrapolation.

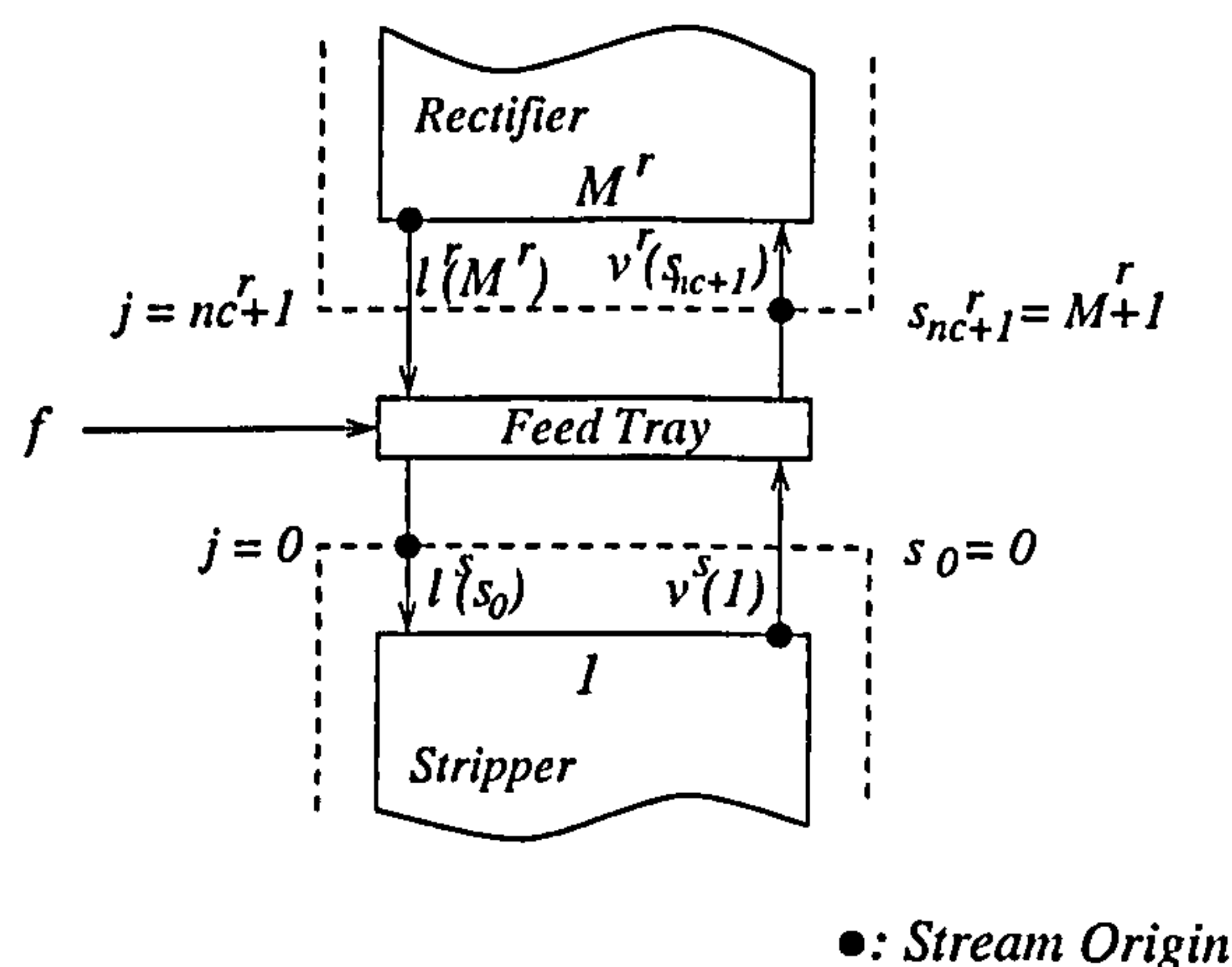


Figure 6.3: Feed Tray in OC Simple Column Representation

The OC method described above, was evaluated in Seferlis and Hrymak (1994a) over a number of case studies and its results showed remarkable accuracy and agreement with those of rigorous tray-by-tray models. However, the main advantage of the OC method for distillation is related to the continuous problem size. Similarly to the GMF for distillation, where the size of the generated problem does not depend on the number of trays in the column but on the number of column sections (M/H modules), in the OC method the problem size depends on the number of column sections and on the number of the collocation points used for the polynomial approximation, thus generating a significantly smaller problem. Another advantage of the OC method for distillation is that, for the calculation of the number of trays in each column section, no binary variables are required, thus not increasing the combinatorial size of a synthesis problem. The total number of trays per section (M) is a continuous variable calculated explicitly in the continuous optimization problem, thus allowing a simultaneous optimization of operating and capital cost and capturing more efficiently the interactions between the two.

Finally, the pre-specified number of collocation points per section should be sufficient for the accurate representation of the physical phenomena, but at the same time it should not be too high to lead to a substantial size increase or to numerical complexities (oscillatory behaviour). However, according to the OC principles, the number of collocation points should be less than the number of trays in a column (when the design is known and operation of the column is the objective). It must be noted that, in most studies, fewer than 6 interior collocation points per section were found adequate for an accurate representation.

6.2.2 Orthogonal Collocation On Finite Elements (OCFE)

In the Orthogonal Collocation method for distillation, each column section corresponds to a single Element, discretized into a number of collocation points. It has been noted though that it is possible to have profiles within the same column section which are fairly flat over a number of trays, thus requiring a small number of collocation points to capture the column behaviour and other parts which exhibit very steep profiles, thus requiring either a greater number of collocation points or collocation points more closely positioned. In order to achieve this, either a large number of collocation points can be used, or the column section can be broken into more than one Finite Element. The first case can be viewed as a rather crude approach which also increases the size of the problem without necessarily capturing the detail in the crucial parts of

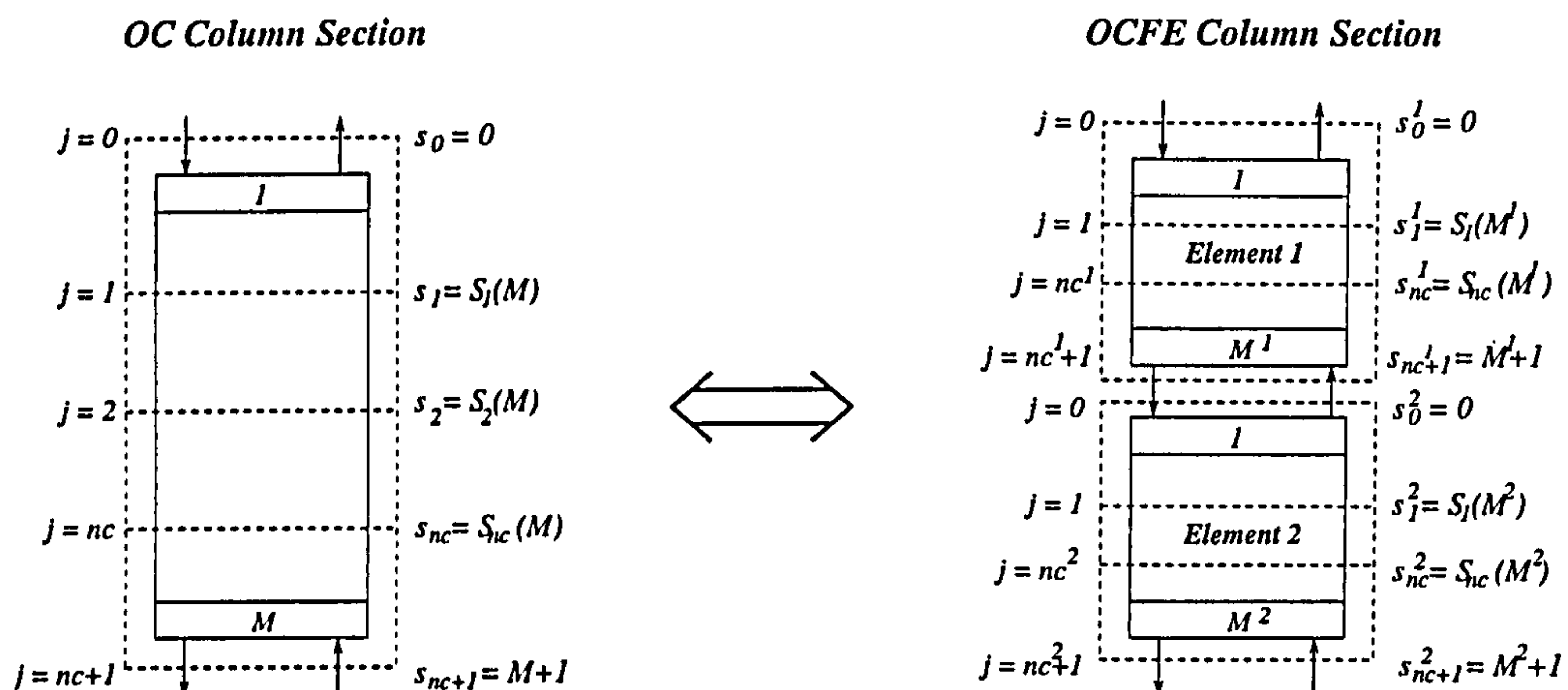


Figure 6.4: OC and OCFE Distillation Column Sections

each section. On the contrary, the second approach is the one recommended for this purpose. This method is called Orthogonal Collocation On Finite Elements (OCFE) and each column section now corresponds to l Finite Elements, each of a length M^l (number of trays) and each discretized into a specified number of collocation points (Figure 6.4). The flexibility of this method is that the column section can be broken into Finite Elements with fewer collocation points for regions with flat profiles and into Finite Elements with more collocation points or with smaller lengths for regions with steep profiles.

In the OCFE method, as proposed by Seferlis and Hrymak (1994a), each Finite Element is governed by the same conditions as the single Element of the OC method. The only additional condition is that of zero-order continuity between adjacent Finite Elements for the component liquid and vapour flowrates and enthalpies. The former is given below (the latter can be written in an equivalent form):

$$\sum_{j=0}^{nc^1} W_j^L(M^1) l_c(s_j^1) - l_c(s_0^2) = 0, \quad c \in C \quad (6.13)$$

$$v_c(s_{nc^1+1}^1) - \sum_{j=1}^{nc^2+1} W_j^V(1) v_c(s_j^2) = 0, \quad c \in C \quad (6.14)$$

In the above constraints nc^1 and nc^2 , refer to the number of interior collocation points of Finite Elements 1 and 2, respectively. For illustration, equation (6.15) shows the component mass balances in the feed tray of the column.

$$v_c(s_{nc^{r,2}+1}^{r,2}) + l_c(s_0^{s,1}) - \sum_{j=1}^{nc^{s,1}+1} W_j^V(1) v_c(s_j^{s,1}) - \sum_{j=0}^{nc^{r,2}} W_j^L(M^{r,2}) l_c(s_j^{r,2}) - f_c = 0, \quad c \in C \quad (6.15)$$

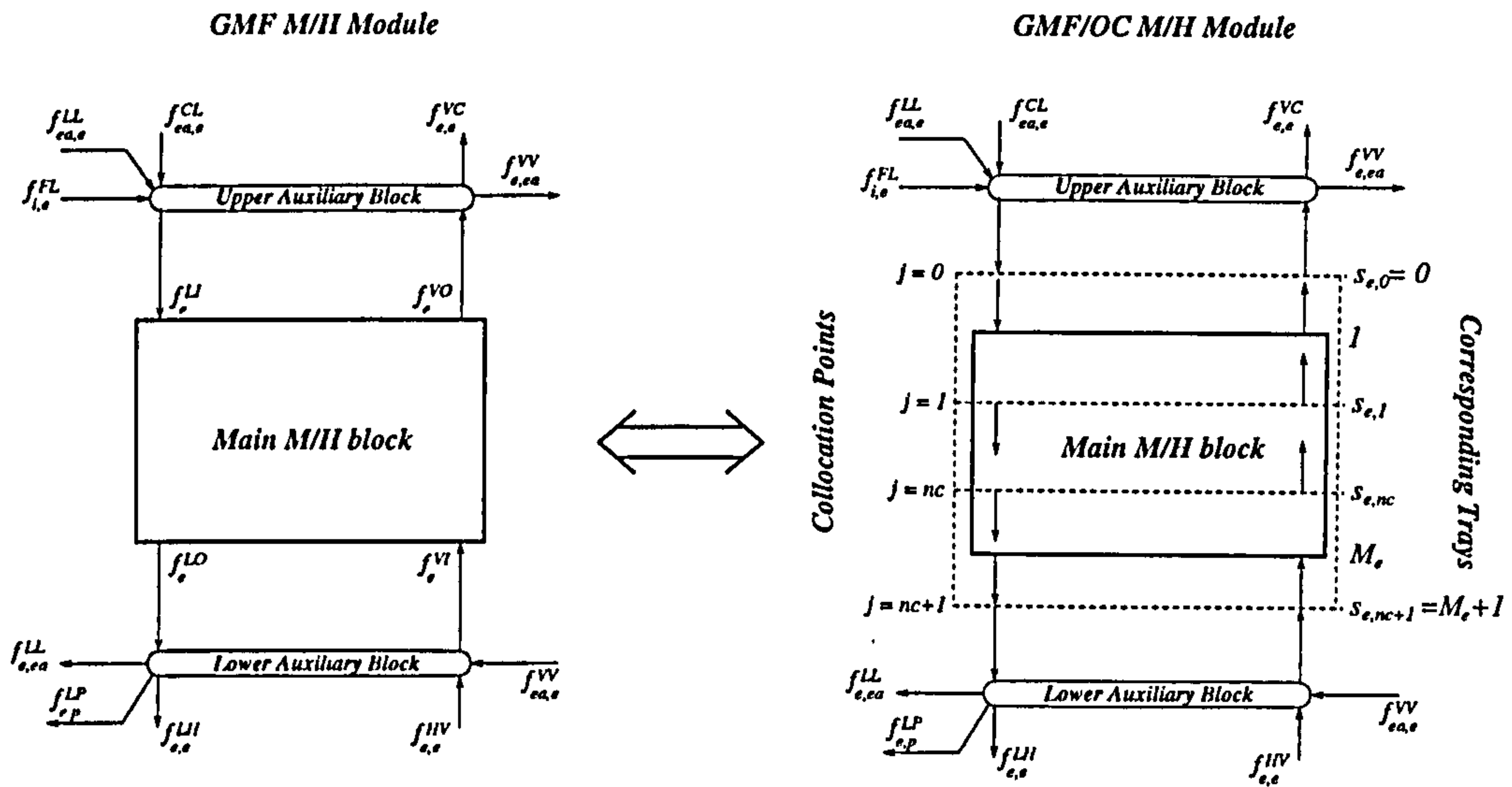
In the above, $nc^{r,2}$ denotes the number of collocation points of Element 2 of the rectifier.

6.3 Coupling GMF and OC For Distillation

As shown in Section 6.2.1, the OC method for distillation can provide valuable intra-section detail and tray number estimates, in a compact and modular way. This provided the key for the GMF Physical Model enhancement target. The GMF main M/H modules could effectively be discretized using the OC principles in order to provide a good estimate of the number of trays per column section (thus leading to greatly improved capital cost estimates and column design guidelines) and more intra-module detail (thus capturing even more accurately the represented physical phenomena). Moreover, this coupling of the GMF to OC ensures the preservation of the compactness of the GMF model, both in the combinatorial and continuous size, due to the fact that no binary variables are required for the estimation of the total number of trays per module and that the continuous problem size increase using the OC principles is small (due to the order reduction characteristics of the OC).

In accord with the OC principles of Seferlis and Hrymak (1994a), each main M/H block is discretized into nc interior and 2 exterior collocation points, as can be seen in Figure 6.5 (*note*: recall that a M/H module consists of the Upper and Lower Auxiliary blocks and the main M/H block). Within the main M/H block, Lagrange polynomials are used for the approximation of liquid and vapour component flowrates and enthalpies. The roots of the orthogonal Hahn polynomials are the locations of the collocation points over the main M/H block and are explicit functions of the number of trays, M_e , of the represented column section. The location, $s_{e,j}$, of each collocation point corresponds to a tray number, as shown in Figure 6.5. Once all the model variables have been discretized over the collocation points and the aforementioned variables approximated using the Lagrange polynomials, then the column *MESH* equations are enforced at the interior collocation points, in accord with the OC principles.

The GMF/OC Physical Model is based on the GMF model presented in Section 2.3.3. From the latter, the models of the Feed Splitter, Upper and Lower Auxiliary blocks, Cooler and

Figure 6.5: GMF and GMF/OC M/H Module For Distillation

Heater blocks and Product Mixer remain exactly the same (Common Model). The only part of the GMF Physical Model where the OC principles are employed is the main M/H block. Also, additional equality constraints are used in order to link the GMF/OC main M/H block model to the GMF Auxiliary block models. The GMF/OC constraints are characterized as *substituting* and *supplementary* depending on whether they substitute or are added to the constraints of the GMF model of Section 2.3.3.

GMF/OC Main M/H Block Physical Model (*Substituting*)

The presented model should effectively *substitute* the main M/H block Physical Model of Section 2.3.3. It consists of: the discretized *MESH* equations (enforced at the interior collocation points), the mixed integer physical-structural constraints and the equations that relate the collocation point locations, $s_{e,j}$, and the Lagrange polynomial weighting functions, $W_j^L(s)$ and $W_j^V(s)$, to the number of trays, M_e , per M/H block e .

- Collocation Point Locations and Weighting Functions

$$s_{e,0} - 1 = 0, \quad e \in E^E \quad (6.16)$$

$$s_{e,j} - s_j(M_e) = 0, \quad e \in E^E, \quad j = 1, \dots, nc_e \quad (6.17)$$

$$s_{e,nc_e+1} - (M_e + 1) = 0, \quad e \in E^E \quad (6.18)$$

$$W_{j'}^V(s) - \prod_{z=1,j'}^{nc_e+1} \frac{s - s_{e,z}}{s_{e,j'} - s_{e,z}} = 0, \quad e \in E^E, j' = 1, \dots, nc_e + 1 \quad (6.19)$$

$$W_{j'}^L(s) - \prod_{z=0,j'}^{nc_e} \frac{s - s_{e,z}}{s_{e,j'} - s_{e,z}} = 0, \quad e \in E^E, j' = 0, \dots, nc_e \quad (6.20)$$

- Component Mass and Energy Balances

$$\sum_{j'=1}^{nc_e+1} W_{j'}^V(s_{e,j} + 1) f_c^V(s_{e,j'}) + \sum_{j'=0}^{nc_e} W_{j'}^L(s_{e,j} - 1) f_c^L(s_{e,j'}) - f_c^V(s_{e,j}) - f_c^L(s_{e,j}) = 0, \quad e \in E^E, c \in C, j = 1, \dots, nc_e \quad (6.21)$$

$$\sum_{j'=1}^{nc_e+1} W_{j'}^V(s_{e,j} + 1) f^V(s_{e,j'}) h^V(s_{e,j'}) + \sum_{j'=0}^{nc_e} W_{j'}^L(s_{e,j} - 1) f^L(s_{e,j'}) h^L(s_{e,j'}) - f^V(s_{e,j}) h^V(s_{e,j}) - f^L(s_{e,j}) h^L(s_{e,j}) = 0, \quad e \in E^E, j = 1, \dots, nc_e \quad (6.22)$$

- Phase Equilibrium

$$\left[\frac{f_c^V(s_{e,j})}{f^V(s_{e,j})} \right] - K_c(s_{e,j}) \left[\frac{f_c^L(s_{e,j})}{f^L(s_{e,j})} \right] = 0, \quad e \in E^E, c \in C, j = 1, \dots, nc_e \quad (6.23)$$

- Molar Fraction Summations

$$\sum_{c \in C} \frac{f_c^V(s_{e,j})}{f^V(s_{e,j})} - 1 = 0, \quad e \in E^E, j = 1, \dots, nc_e \quad (6.24)$$

$$\sum_{c \in C} \frac{f_c^L(s_{e,j})}{f^L(s_{e,j})} - 1 = 0, \quad e \in E^E, j = 1, \dots, nc_e \quad (6.25)$$

- Mixed Integer Physical-Structural Constraints

$$f_e^{LO} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.26)$$

$$f_e^{LI} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.27)$$

$$f_e^{VO} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.28)$$

$$f_e^{VI} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.29)$$

$$f^L(s_{e,j}) - y_e \mathcal{F}^{max} \leq 0, \quad e \in E, j = 0, \dots, nc_e \quad (6.30)$$

$$f^V(s_{e,j}) - y_e \mathcal{F}^{max} \leq 0, \quad e \in E, j = 1, \dots, nc_e + 1 \quad (6.31)$$

Conditions Linking Upper Auxiliary Block (*Supplementary*)

The following *supplementary* equations should be *added* to the GMF Physical Model of Section 2.3.3. They link the Physical Model of the main M/H block (GMF/OC) to that of the Upper Auxiliary block (GMF). They represent a relation between the GMF/OC and GMF inputs and outputs in the top part of the M/H Module.

$$f_e^{VO} - \sum_{c \in C} \left(\sum_{j=1}^{nc_e+1} W_j^V(1) f c_c^V(s_{e,j}) \right) = 0, \quad e \in E^E \quad (6.32)$$

$$f_e^{LI} - f^L(s_{e,0}) = 0, \quad e \in E^E \quad (6.33)$$

$$f_e^{VO} x_{e,c}^{VO} - \sum_{j=1}^{nc_e+1} W_j^V(1) f c_c^V(s_{e,j}) = 0, \quad e \in E^E, c \in C \quad (6.34)$$

$$f_e^{LI} x_{e,c}^{LI} - f c_c^L(s_{e,0}) = 0, \quad e \in E^E, c \in C \quad (6.35)$$

$$f_e^{VO} h_e^{VO} - \sum_{j=1}^{nc_e+1} W_j^V(1) f^V(s_{e,j}) h^V(s_{e,j}) = 0, \quad e \in E^E \quad (6.36)$$

$$f_e^{LI} h_e^{LI} - f^L(s_{e,0}) h^L(s_{e,0}) = 0, \quad e \in E^E \quad (6.37)$$

Conditions Linking Lower Auxiliary Block (*Supplementary*)

Similarly to the Upper Auxiliary block, *supplementary* equations should be *added* to the GMF Physical Model of Section 2.3.3, relating the GMF Lower Auxiliary block Physical Model to that of the GMF/OC main M/H block (inputs and outputs in the lower part of the M/H module).

$$f_e^{LO} - \sum_{c \in C} \left(\sum_{j=0}^{nc_e} W_j^L(M_e) f c_c^L(s_{e,j}) \right) = 0, \quad e \in E^E \quad (6.38)$$

$$f_e^{VI} - f^V(s_{e,nc_e+1}) = 0, \quad e \in E^E \quad (6.39)$$

$$f_e^{LO} x_{e,c}^{LO} - \sum_{j=0}^{nc_e} W_j^L(M_e) f c_c^L(s_{e,j}) = 0, \quad e \in E^E, c \in C \quad (6.40)$$

$$f_e^{VI} x_{e,c}^{VI} - f c_c^V(s_{e,nc_e+1}) = 0, \quad e \in E^E, c \in C \quad (6.41)$$

$$f_e^{LO} h_e^{LO} - \sum_{j=0}^{nc_e} W_j^L(M_e) f^L(s_{e,j}) h^L(s_{e,j}) = 0, \quad e \in E^E \quad (6.42)$$

$$f_e^{VI} h_e^{VI} - f^V(s_{e,nc_e+1}) h^V(s_{e,nc_e+1}) = 0, \quad e \in E^E \quad (6.43)$$

Thermodynamic Functions (*Supplementary*)

These *supplementary* equations relate the discretized enthalpies and equilibrium constants to the discretized temperatures and vapour and liquid molar fractions. They should be *added* to the model of Section 2.3.3. Any thermodynamic model can be readily used for their calculation.

$$H^V(s_{e,j}) - H^V\left(\frac{f_c^V}{f^V}, T\right)_{(s_{e,j})} = 0, \quad e \in E^E, j = 1, \dots, nc_e + 1 \quad (6.44)$$

$$H^L(s_{e,j}) - H^L\left(\frac{f_c^L}{f^L}, T\right)_{(s_{e,j})} = 0, \quad e \in E^E, j = 0, \dots, nc_e \quad (6.45)$$

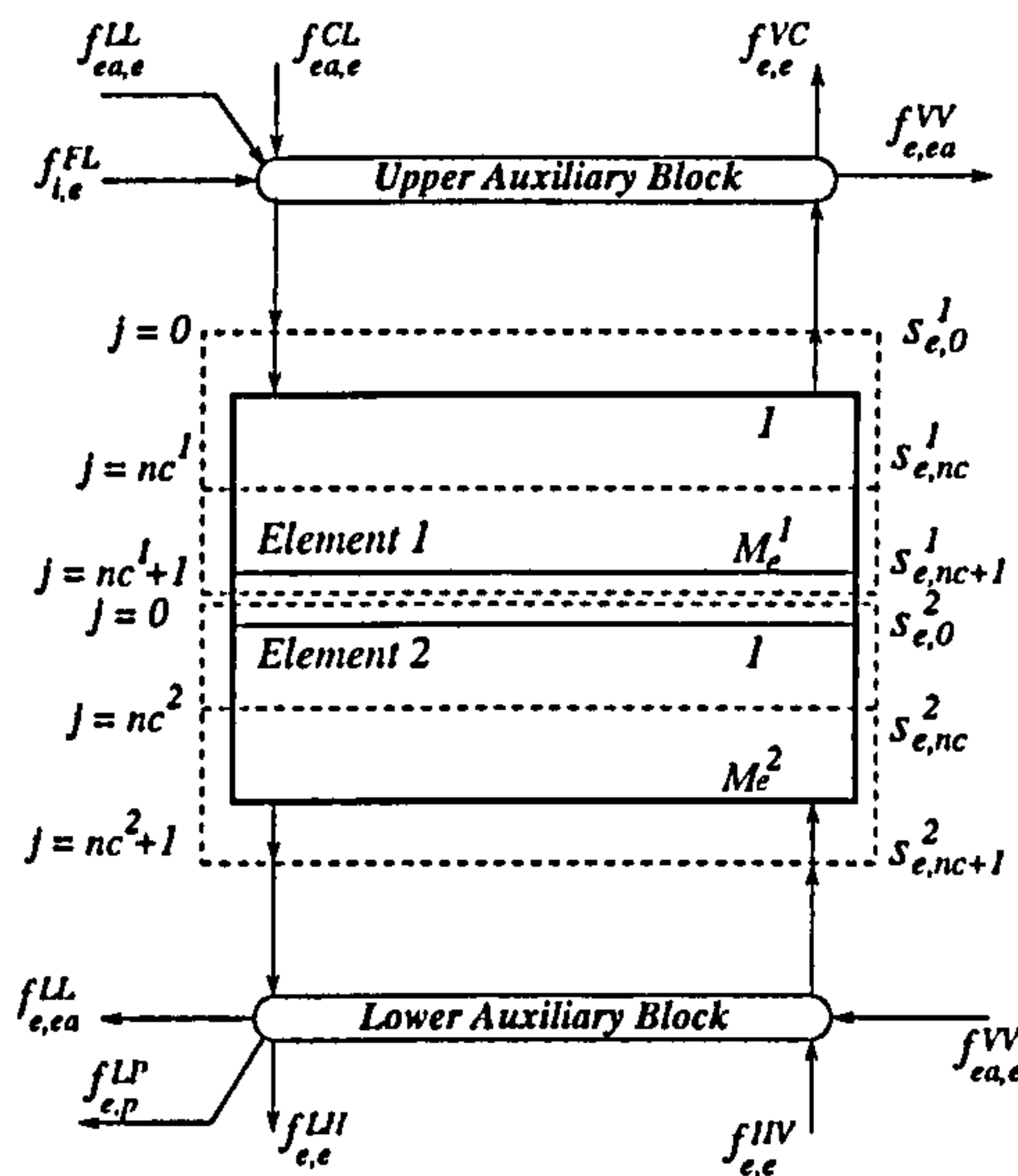
$$K_c(s_{e,j}) - K_c\left(\frac{f_c^L}{f^L}, \frac{f_c^V}{f^V}, T, P\right)_{(s_{e,j})} = 0, \quad e \in E^E, c \in C, j = 1, \dots, nc_e \quad (6.46)$$

OC Formulation Remarks

The modular characteristics of the OC method (which treats a distillation column section-wise) make it highly compatible to the GMF column representation. The GMF/OC Physical Model is structured in such a way that both the GMF and the GMF/OC models can be used according to the problem requirements. This is achieved by using the linking equations between the main M/H block and the Upper and Lower Auxiliary blocks of each M/H Module (*'supplementary'* equations above). This formulation creates a separability feature in the model writing, which ultimately allows the modeler to use either the *'conventional'* GMF or the GMF/OC Physical Models, by exchanging two blocks of constraints (illustrated in Figure 6.7, page 137). As mentioned above, most of the GMF Physical Model has remained intact. The OC additions have taken place in the model of the main M/H block (*'substituting'* and *'supplementary'* equations).

6.4 Coupling GMF and OCFE For Distillation

The GMF was also coupled to the representational principles of the Orthogonal Collocation on Finite Element method for distillation (presented in Section 6.2.2). In the GMF/OCFE the key feature is the representation of each main M/H block by more than one Finite Element, l , which are linked with each other through zero-order continuity conditions. The GMF/OCFE Physical Model is composed in the same way as the GMF/OC model, consisting of *substituting* and *supplementary* equations. Moreover, a new set L_e is introduced along with an additional index (l) in all the discretized variables denoting the Finite Element over which they are defined.


 Figure 6.6: GMF/OCFE Main M/H Block Discretization

$$L_e = \{l \mid \text{number of Finite Elements per module } e\}$$

GMF/OCFE Main M/H Block Physical Model (*Substituting*)

- Collocation Point Locations and Weighting Functions per Element

$$s_{e,l,0} - 1 = 0, \quad e \in E^E, l \in L_e \quad (6.47)$$

$$s_{e,l,j} - s_j(M_{e,l}) = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l} \quad (6.48)$$

$$s_{e,l,nc_{e,l}+1} - (M_{e,l} + 1) = 0, \quad e \in E^E, l \in L_e \quad (6.49)$$

$$W_{j'}^V(s) - \prod_{z=1,j'}^{nc_{e,l}+1} \frac{s - s_{e,l,z}}{s_{e,l,j'} - s_{e,l,z}} = 0, \quad e \in E^E, l \in L_e, j' = 1, \dots, nc_{e,l} + 1 \quad (6.50)$$

$$W_{j'}^L(s) - \prod_{z=0,j'}^{nc_{e,l}} \frac{s - s_{e,l,z}}{s_{e,l,j'} - s_{e,l,z}} = 0, \quad e \in E^E, l \in L_e, j' = 0, \dots, nc_{e,l} \quad (6.51)$$

- Component Mass and Energy Balances

$$\sum_{j'=1}^{nc_{e,l}+1} W_{j'}^V(s_{e,l,j} + 1) f_c^V(s_{e,l,j'}) + \sum_{j'=0}^{nc_{e,l}} W_{j'}^L(s_{e,l,j} - 1) f_c^L(s_{e,l,j'}) - f_c^V(s_{e,l,j}) - f_c^L(s_{e,l,j}) = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l}, c \in C \quad (6.52)$$

$$\sum_{j'=1}^{nc_{e,l}+1} W_{j'}^V(s_{e,l,j} + 1) f^V(s_{e,l,j'}) h^V(s_{e,l,j'}) + \sum_{j'=0}^{nc_{e,l}} W_{j'}^L(s_{e,l,j} - 1) f^L(s_{e,l,j'}) h^L(s_{e,l,j'}) - f^V(s_{e,l,j}) h^V(s_{e,l,j}) - f^L(s_{e,l,j}) h^L(s_{e,l,j}) = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l} \quad (6.53)$$

- Phase Equilibrium

$$\left[\frac{f c_c^V(s_{e,l,j})}{f^V(s_{e,l,j})} \right] - K_c(s_{e,l,j}) \left[\frac{f c_c^L(s_{e,l,j})}{f^L(s_{e,l,j})} \right] = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l}, c \in C \quad (6.54)$$

- Molar Fraction Summations

$$\sum_{c \in C} \frac{f c_c^V(s_{e,l,j})}{f^V(s_{e,l,j})} - 1 = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l} \quad (6.55)$$

$$\sum_{c \in C} \frac{f c_c^L(s_{e,l,j})}{f^L(s_{e,l,j})} - 1 = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l} \quad (6.56)$$

- Mixed Integer Physical-Structural Constraints

$$f_e^{LO} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.57)$$

$$f_e^{LI} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.58)$$

$$f_e^{VO} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.59)$$

$$f_e^{VI} - y_e \mathcal{F}^{max} \leq 0, \quad e \in E \quad (6.60)$$

$$f^L(s_{e,l,j}) - y_e \mathcal{F}^{max} \leq 0, \quad e \in E, l \in L_e, j = 0, \dots, nc_{e,l} \quad (6.61)$$

$$f^V(s_{e,l,j}) - y_e \mathcal{F}^{max} \leq 0, \quad e \in E, l \in L_e, j = 1, \dots, nc_{e,l} + 1 \quad (6.62)$$

Conditions Linking Adjacent Finite Elements (*Supplementary*)

$$\sum_{c \in C} \left(\sum_{j=0}^{nc_{e,l-1}} W_j^L(M_{e,l-1}) f c_c^L(s_{e,l-1,j}) \right) - f^L(s_{e,l,0}) = 0, \quad e \in E^E, l = 2, \dots, |L_e| \quad (6.63)$$

$$f^V(s_{e,l-1,nc_{e,l-1}+1}) - \sum_{c \in C} \left(\sum_{j=1}^{nc_{e,l}+1} W_j^V(1) f c_c^V(s_{e,l,j}) \right) = 0, \quad e \in E^E, l = 2, \dots, |L_e| \quad (6.64)$$

$$\sum_{j=0}^{nc_{e,l-1}} W_j^L(M_{e,l-1}) f c_c^L(s_{e,l-1,j}) - f c_c^L(s_{e,l,0}) = 0, \quad e \in E^E, l = 2, \dots, |L_e|, c \in C \quad (6.65)$$

$$f c_c^V(s_{e,l-1,nc_{e,l-1}+1}) - \sum_{j=1}^{nc_{e,l}+1} W_j^V(1) f c_c^V(s_{e,l,j}) = 0, \quad e \in E^E, l = 2, \dots, |L_e|, c \in C \quad (6.66)$$

$$\sum_{j=0}^{nc_{e,l-1}} W_j^L(M_{e,l-1}) f^L(s_{e,l-1,j}) H^L(s_{e,l-1,j}) - f^L(s_{e,l,0}) H^L(s_{e,l,0}) = 0, \quad e \in E^E, l = 2, \dots, |L_e| \quad (6.67)$$

$$f^V(s_{e,l-1,nc_{e,l-1}+1}) H^V(s_{e,l-1,nc_{e,l-1}+1}) - \sum_{j=1}^{nc_{e,l}+1} W_j^V(1) f^V(s_{e,l,j}) H^V(s_{e,l,j}) = 0, \quad e \in E^E, l = 2, \dots, |L_e| \quad (6.68)$$

Conditions Linking Upper Auxiliary Block to Uppermost Element ($l=1$) (*Supplementary*)

$$f_e^{VO} - \sum_{c \in C} \left(\sum_{j=1}^{nc_{e,l}+1} W_j^V(1) f c_c^V(s_{e,1,j}) \right) = 0, \quad e \in E^E \quad (6.69)$$

$$f_e^{LI} - f^L(s_{e,1,0}) = 0, \quad e \in E^E \quad (6.70)$$

$$f_e^{VO} x_{e,c}^{VO} - \sum_{j=1}^{nc_{e,l}+1} W_j^V(1) f c_c^V(s_{e,1,j}) = 0, \quad e \in E^E, c \in C \quad (6.71)$$

$$f_e^{LI} x_{e,c}^{LI} - f c_c^L(s_{e,1,0}) = 0, \quad e \in E^E, c \in C \quad (6.72)$$

$$f_e^{VO} h_e^{VO} - \sum_{j=1}^{nc_{e,l}+1} W_j^V(1) f^V(s_{e,1,j}) h^V(s_{e,1,j}) = 0, \quad e \in E^E \quad (6.73)$$

$$f_e^{LI} h_e^{LI} - f^L(s_{e,1,0}) h^L(s_{e,1,0}) = 0, \quad e \in E^E \quad (6.74)$$

Conditions Linking Lower Auxiliary Block to Lowermost Element ($l=|L_e|$) (*Supplementary*)

The last Finite Element of a M/H module is denoted by the cardinality, $|L_e|$, of set L_e .

$$f_e^{LO} - \sum_{c \in C} \left(\sum_{j=0}^{nc_{e,l}} W_j^L(M_{e,l}) f c_c^L(s_{e,l,j}) \right) = 0, \quad e \in E^E, l = |L_e| \quad (6.75)$$

$$f_e^{VI} - f^V(s_{e,l,nc_{e,l}+1}) = 0, \quad e \in E^E, l = |L_e| \quad (6.76)$$

$$f_e^{LO} x_{e,c}^{LO} - \sum_{j=0}^{nc_{e,l}} W_j^L(M_{e,l}) f c_c^L(s_{e,l,j}) = 0, \quad e \in E^E, l = |L_e|, c \in C \quad (6.77)$$

$$f_e^{VI} x_{e,c}^{VI} - f c_c^V(s_{e,l,nc_{e,l}+1}) = 0, \quad e \in E^E, l = |L_e|, c \in C \quad (6.78)$$

$$f_e^{LO} h_e^{LO} - \sum_{j=0}^{nc_{e,l}} W_j^L(M_{e,l}) f^L(s_{e,l,j}) h^L(s_{e,l,j}) = 0, \quad e \in E^E, l = |L_e| \quad (6.79)$$

$$f_e^{VI} h_e^{VI} - f^V(s_{e,l,nc_{e,l}+1}) h^V(s_{e,l,nc_{e,l}+1}) = 0, \quad e \in E^E, l = |L_e| \quad (6.80)$$

Thermodynamic Functions (*Supplementary*)

$$H^V(s_{e,l,j}) - H^V\left(\frac{f c_c^V}{f^V}, T\right)_{(s_{e,l,j})} = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l} + 1 \quad (6.81)$$

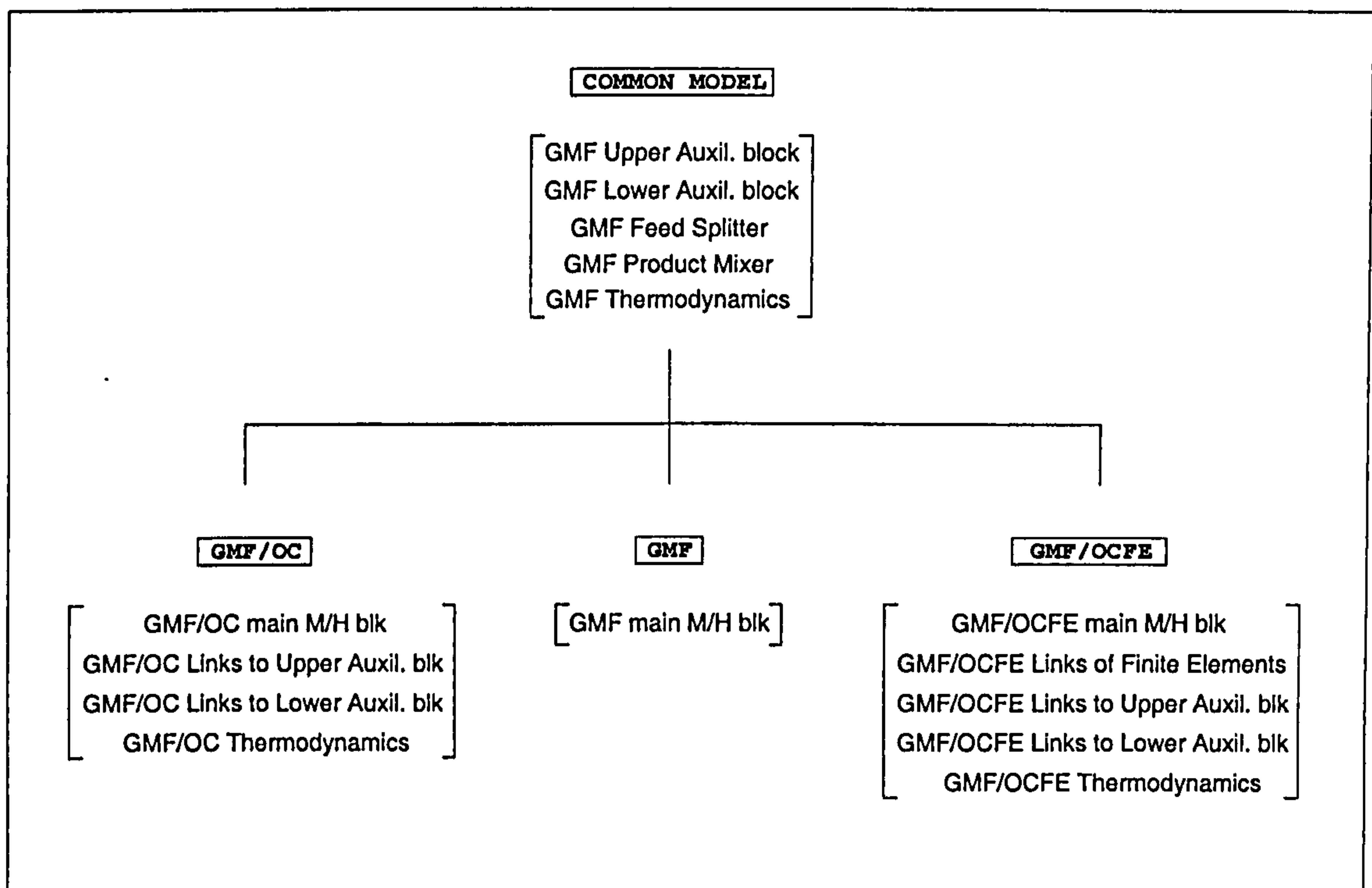


Figure 6.7: GMF, GMF/OC and GMF/OCFE Exchanging Equation Blocks

$$H^L(s_{e,l,j}) - H^L\left(\frac{fc_c^L}{f^L}, T\right)_{(s_{e,l,j})} = 0, \quad e \in E^E, l \in L_e, j = 0, \dots, nc_{e,l} \quad (6.82)$$

$$K(s_{e,l,j}) - K\left(\frac{fc_c^L}{f^L}, \frac{fc_c^V}{f^V}, T, P\right)_{(s_{e,l,j})} = 0, \quad e \in E^E, l \in L_e, j = 1, \dots, nc_{e,l} \quad (6.83)$$

OCFE Formulation Remarks

The GMF/OCFE Physical Model is formulated in the same way as the GMF/OC model, thus allowing the modeler the choice of using the ‘conventional’ GMF, the GMF/OC or the GMF/OCFE Physical Models, according to the level of physical representation accuracy desired. In the GMF/OCFE the new block of constraints, consists of the aforementioned ‘*substituting*’ and ‘*supplementary*’ equations. For clarification purposes, the interchanging blocks of constraints of the GMF, GMF/OC and GMF/OCFE Physical Models are illustrated in Figure 6.7.

6.5 Case Study: Enhanced GMF Binary Distillation Column

The binary distillation separation of Benzene-Toluene examined in Section 2.4 is revisited in this Section using the enhanced GMF/OC and GMF/OCFE formulations. The problem statement, objective and purity specifications are the same as the ones of Section 2.4.

6.5.1 GMF/OC Formulation and Results

The single simple distillation column was generated as in Section 2.4.2 using the GMF Structural Model for a simple column. The Structural Sets and the binary variables were assigned as specified in Table 2.3. For the GMF/OC representation, each M/H block was discretized using a pre-specified number of collocation points. For the type of mixture examined, 4 interior collocation points were used for the discretization of each M/H module. A schematic of the GMF versus the GMF/OC representation is given in Figure 6.8. For the physical representation of the column, the GMF/OC Physical Model was employed, utilizing the ‘conventional’ GMF Physical Models (Section 2.3.3) and the enhanced GMF/OC Physical Model for the main M/H block.

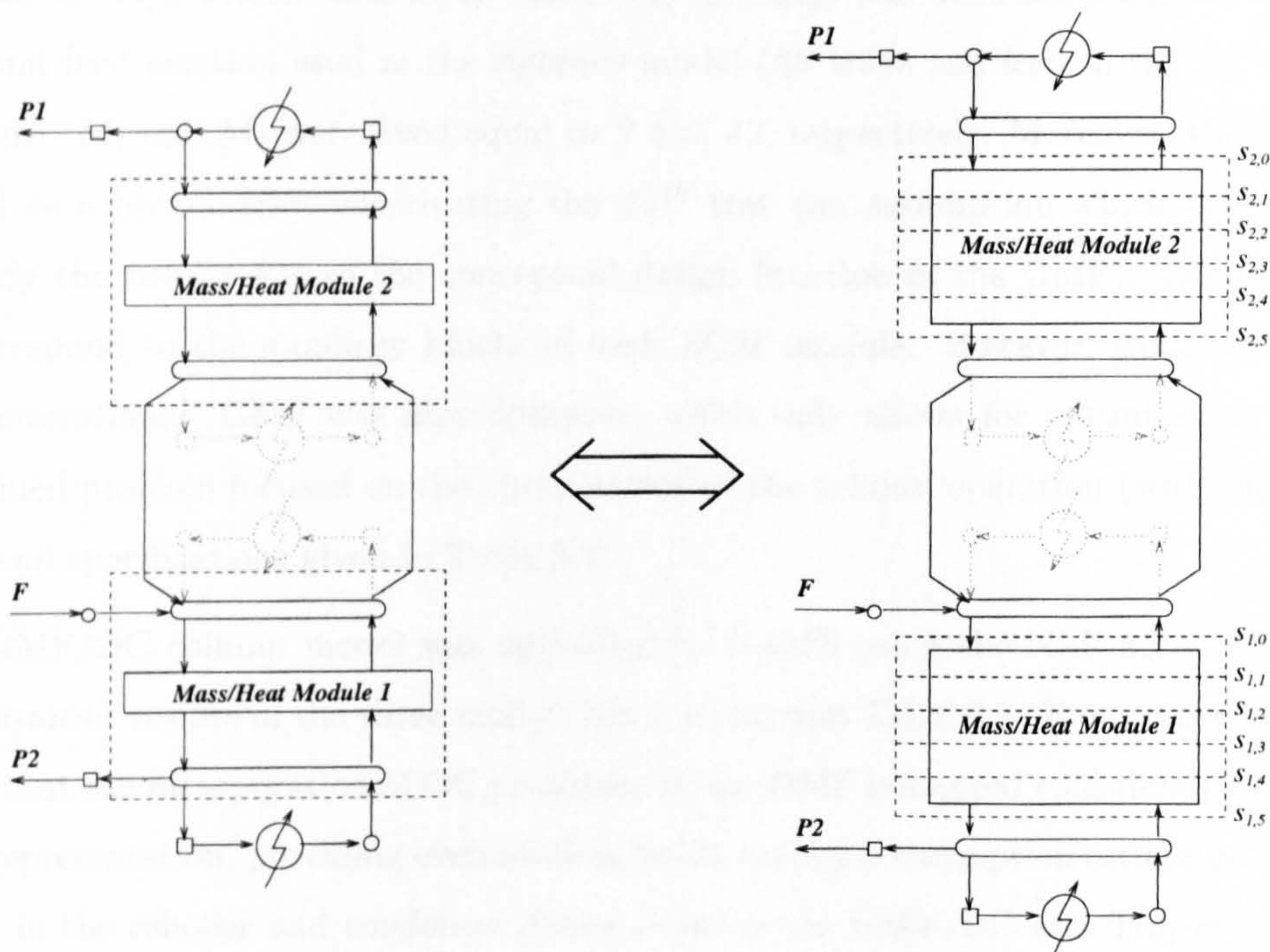


Figure 6.8: GMF and GMF/OC Representations of a Simple Column

Using the GMF/OC Physical Model for the representation of a single simple distillation column, a Degree of Freedom analysis was conducted (Appendix C.1). From the latter it was found that the simple column GMF/OC Physical Model has 4 degrees of freedom. These correspond to 2 operation-related degrees of freedom (which are the same as those of the rigorous model of Viswanathan and Grossmann (1993), for fixed design, that is, fixed number of trays) and 2 additional design-related degrees of freedom, corresponding to the number of trays per module e (M_e). For simulation (fixed design) purposes, a possible pair for the 2 operational degrees of freedom could be the reflux and the purity of a component in the column distillate. It must also be noted that by incorporating the OC into the GMF the inequality constraints of the latter are replaced with equality constraints, allowing simulations to be carried out, in contrast with the ‘conventional’ GMF which could only be used for optimization studies.

As practised throughout this work, in order to validate the GMF/OC Physical Model, a *quantitative* and *qualitative* comparison was conducted over the results of both the rigorous tray-by-tray model of Viswanathan and Grossmann (1993) and those of the ‘conventional’ GMF. Although, the GMF/OC can now be used for a formal optimization of the number of trays of the represented column, in order to provide a common comparison basis between the three models, the number of trays within each M/H block (M_1 and M_2) was fixed according to the number of trays and feed location used in the rigorous model (25 trays and feed in the 11th tray from the bottom). M_1 and M_2 were fixed equal to 9 and 11, respectively. Moreover, the Cooler was numbered as a pseudo-tray, constituting the 25th tray (an assumption which does not affect particularly the results due to the conceptual design function of the GMF). The remaining 4 trays correspond to the auxiliary blocks of each M/H module. However, since a comparison to the ‘conventional’ GMF was also desirable, which only allows for optimization problems, the examined problem focused on the optimization of the column operation (with the objective function and specifications given in Table 2.2).

The GMF/OC column model was optimized in GAMS using the NLP solver CONOPT2. The *quantitative* results of the three models are compared in Table 6.2. From these results, it is apparent that the incorporation of OC principles in the GMF enhanced considerably the GMF’s physical representation, providing even more accurate energy consumption estimates. The small difference in the reboiler and condenser duties between the GMF/OC and Trayed models (3% and 4%, respectively), is due to the fact that in the GMF/OC the reboiler is approximated through a Heater and the condenser through a Cooler which are pure heat modules, where no

Table 6.2: GMF/OC Quantitative Validation for Binary Distillation

	<i>Q</i> reboiler (kW)	<i>Q</i> condenser (kW)	<i>P</i> 1 (mol/s)	<i>r</i>
GMF	4194	4149.5	70.7	0.91
GMF/OC	4258	4216.8	69.6	0.96
Trayed Model	4401	4398.6	69.7	0.97

mass exchange takes place.

However, the main enhancement in the physical representation of the GMF by the incorporation of the OC principles is particularly evident when the results of the three alternative models are compared *qualitatively*. This comparison is depicted in Figure 6.9. From the latter, it is apparent that the GMF/OC and the Trayed models are in a remarkable agreement in the two sections/modules of the distillation column. The GMF enhanced with OC principles, no longer captures the *general* trends of mass and heat transfer as the ‘*conventional*’ GMF, but can provide a detailed representation of the physical behaviour of a distillation column. This is evident in both the Benzene distribution and the column temperature profiles, where the GMF/OC and Trayed results are virtually identical.

Another advantage of the GMF/OC model that needs to be stressed is that the above results have been obtained by a model which still remains compact in the combinatorial and continuous

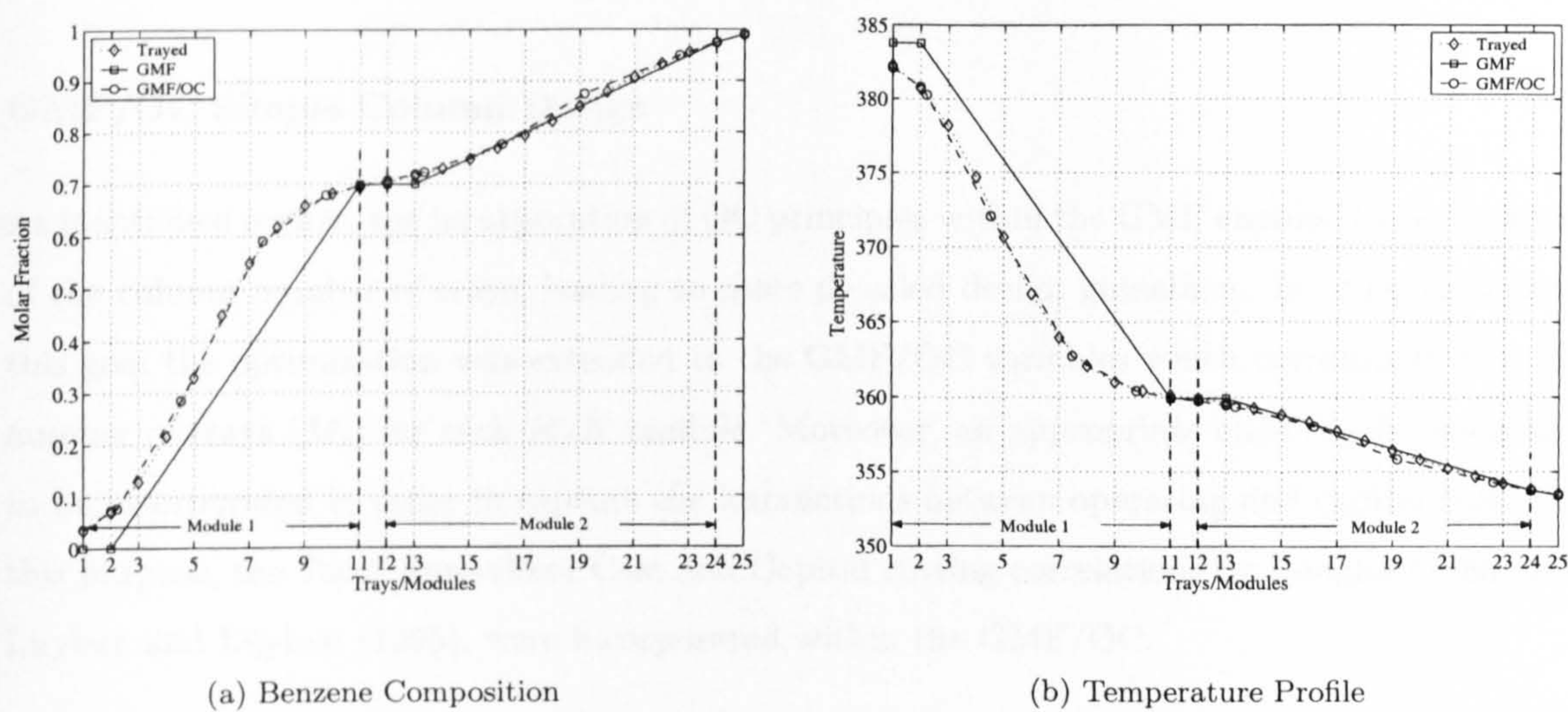


Figure 6.9: GMF/OC Qualitative Validation for Binary Distillation

Table 6.3: GMF/OC Binary Distillation Optimization Statistics

	Trayed	GMF/OC	GMF
Continuous Variables	283	244	134
Continuous Equalities	282	243 †	127

where:

$$C=2, N=25, E^E=2, E^{CE}=E^{HE}=1, P=2, I=1, NC=4$$

$$† E^E(5NC+3NC C+14C+26)+(E^{CE}+E^{HE})(3C+6)+P(2C+4)+I(C+3)+2=243$$

size. The incorporation of trays has been kept in the continuous space, avoiding the introduction of binary variables. The continuous size of the problem is larger than that of the GMF but it is still smaller than that of the Trayed model. A size comparison of the three models is given in Table 6.3, based on the GMF/OC Degree of Freedom analysis of Appendix C.1.

In the pertinent table is shown that the GMF/OC problem size is still smaller than that of the rigorous Trayed model, despite being almost double the GMF problem size. However, the GMF/OC still maintains the GMF advantage of generating a problem whose size is independent of the number of trays, as it still depends solely on the number of column sections (M/H modules) and interior collocation points. For instance, if the number of trays doubles ($N=50$) the number of equations for the trayed model will be 557, whereas the GMF/OC will still have the same size as given in Table 6.3.

GMF/OC Simple Column Design

As mentioned earlier, the incorporation of OC principles within the GMF enabled the estimation of the column number of trays, leading to more detailed design guidelines. In order to achieve this goal the optimization was extended to the GMF/OC variables which corresponded to the number of trays (M_e) for each M/H module. Moreover, an appropriate objective function had to be incorporated in order to capture the interactions between operating and capital cost. For this purpose, the Total Annualized Cost and Capital costing correlations by Douglas (1988) and Luyben and Luyben (1995), were incorporated within the GMF/OC:

$$TAC = C^{op} + CCF C^{cap} \quad (6.84)$$

$$C^{op} = \sum_{e \in E^H} C^{st} Q_e^H y_e^H + \sum_{e \in E^C} C^{cw} Q_e^C y_e^C \quad (6.85)$$

$$C^{cap} = \sum_{e \in E} C_e^{col} y_e + \sum_{e \in E^H} C_e^H y_e^H + \sum_{e \in E^C} C_e^C y_e^C \quad (6.86)$$

In the above expressions CCF is the Capital Charge Factor which, in this work, was taken equal to $(1/3)$. The model for the Capital Costing of each M/H module (column section) (C_e^{col}) is given below:

$$C_e^{col} = \frac{M\&S}{280} [101.9 D_e^{1.066} H_e^{0.802} (2.18 + Fc) + 4.7 D_e^{1.55} H_e^{ts} Fc] \quad (6.87)$$

$$D_e = 0.1838 (f_{ea,ea}^{HV})^{0.5}, \quad (ft) \quad (6.88)$$

$$H_e = (2 + 0.2)(M_e + 2), \quad (ft) \quad (6.89)$$

$$H_e^{ts} = 2(M_e + 2), \quad (ft) \quad (6.90)$$

In the above expressions the Marshall and Swift index (M&S) was taken equal to 1108.1 and the Correction Factor (Fc) equal to 1. Equation (6.88) which was taken from Luyben and Luyben (1995), uses a correlation calculating the M/H module diameter with respect to the column boil-up (*note*: the boil-up must be given in $lbmol/hr$, for which the correlation is defined). The boil-up in GMF terms, is the vapour interconnection, $f_{ea,ea}^{HV}$, between the (column) Heater and its associated Lower M/H module. For simplicity reasons, the diameter was assumed uniform throughout the column and was equal to that of the lower M/H module (representing the stripper section). Equation (6.89) gives the height of each M/H module and it is based on 2 ft spacing per tray and 20% more for base level (Luyben and Luyben, 1995). $M_e + 2$ is the overall number of trays per M/H module (M_e trays in the main M/H block and 2 trays corresponding to the two Auxiliary blocks, which are essentially modelled as trays). H_e^{ts} is the height of the tray stacks in each M/H module (equal to tray spacing multiplied by the number of trays). Furthermore, the capital costing model for the heat units is specified below:

$$C_e^H = \frac{M\&S}{280} 101.3 (2.29 + Fc) (A_e^H)^{0.65} \quad (6.91)$$

$$A_e^H = \frac{Q_e^H}{11250}, \quad (ft^2) \quad (6.92)$$

$$C_e^C = \frac{M\&S}{280} 101.3 (2.29 + Fc) (A_e^C)^{0.65} \quad (6.93)$$

$$A_e^C = \frac{Q_e^C}{150 LMTD_e^C}, \quad (ft^2) \quad (6.94)$$

$$LMTD_e^C = \frac{2}{3} (\Delta T1_e^C)^{0.5} (\Delta T2_e^C)^{0.5} + \left(\frac{\Delta T1_e^C + \Delta T2_e^C}{6} \right) \quad (6.95)$$

$$\Delta T1_e^C = T_e^{CI} - T_w \quad (6.96)$$

$$\Delta T2_e^C = T_e^{CO} - T_w \quad (6.97)$$

According to Douglas (1988), for the Heater module area the following simplification was used: $U^H LMTD^H \simeq 11250 \text{ Btu/hrft}^2$. An analytic relation of the logarithmic mean average temperature was not employed, since after its implementation it was found that it did not make significant difference in the results, while adding complexity in the calculations. *Note:* In equations (6.92) and (6.93) the heat duties must be given in Btu/hr for use in the above relations. In equation (6.93) the overall heat transfer coefficient was taken equal to $150 \text{ Btu/hrft}^2 F$ (Luyben and Luyben, 1995) and the Cooler module's logarithmic mean average temperature ($LMTD_e^C$) was analytically calculated using the Paterson approximation (Paterson, 1984) (*note:* in equations (6.96) and (6.97) the temperature units must be given in F).

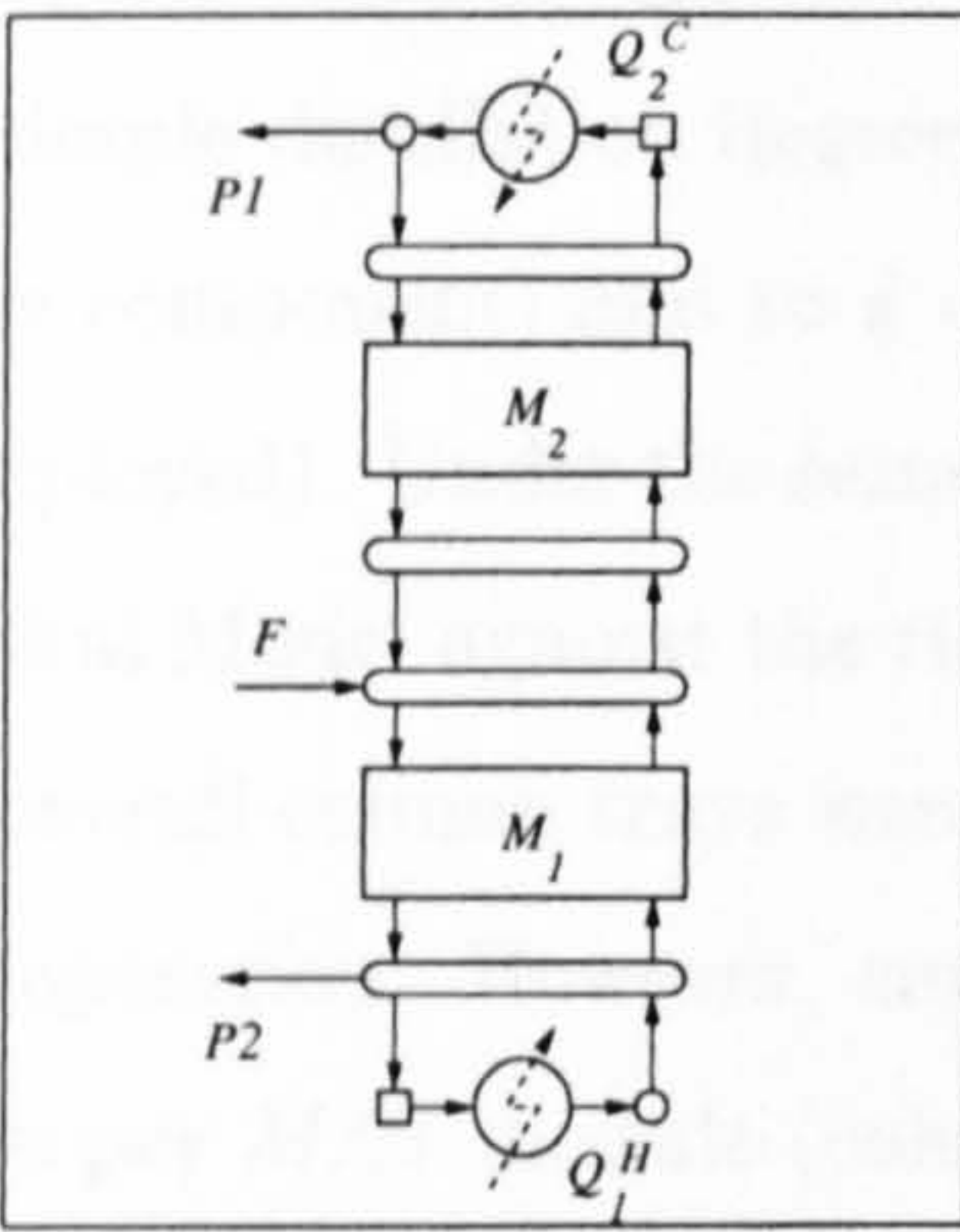
Having provided an analytic relation of the Total Annualized Cost objective function to be minimized, the Benzene - Toluene case study was re-revisited with the new objectives given in Table 6.4. The number of degrees of freedom was increased to 4 due to the addition of the variables corresponding to the trays per each main M/H module (M_e).

Table 6.4: Binary Column Design Objectives

Objective Function	$\min TAC$
Benzene at distillate ($P1$)	$x_{P1,Benzene}^P \geq 0.99$
Toluene at bottoms ($P2$)	$x_{P2,Toluene}^P \geq 0.99$

The results from the generated NLP problem, solved in GAMS with CONOPT2 as the nonlinear solver are given in Table 6.5. The Total Annualized Cost was found equal to $881,200 \text{ \$}/\text{yr}$, from which 79% were attributed to the operating cost ($693,900 \text{ \$}/\text{yr}$) and 21% to the annualized capital cost ($187,300 \text{ \$}/\text{yr}$). A note must be made regarding the non-integer tray numbers per M/H module (column section). A rounding to the nearest highest integer was possible, but it was not considered necessary as the contribution to actual TAC would have been minimal. The above results were in accord with common distillation column heuristics (Douglas, 1988), which estimate the contribution of annualized capital cost to around 20-30% of the TAC. Therefore, the GMF/OC design model was found able to *effectively* capture interactions of operating *and* capital cost for the design of distillation columns.

Table 6.5: GMF/OC Column Optimal Design and Operating Conditions

		F (mol/s)	x_{Benz}	x_{Tol}
	$P1$	70.4	0.99	0.01
	$P2$	29.6	0.01	0.99
		Heat Duties (kW)		
	Q_1^H	4252.1		
	Q_2^C	4208.5		
		Estimated Trays		
	M_1	12.2		
	M_2	13.4		

6.5.2 GMF/OCFE Formulation and Results

The binary distillation case study was examined using the GMF/OCFE Physical Model, enhancing the GMF with principles from the Orthogonal Collocation on Finite Elements method. For the implementation of this model the number of Finite Elements and Collocation Points per M/H module was set equal to 2 (Figure 6.10). This discretization scheme was found sufficient for obtaining the desired accuracy in the distillation separation examined.

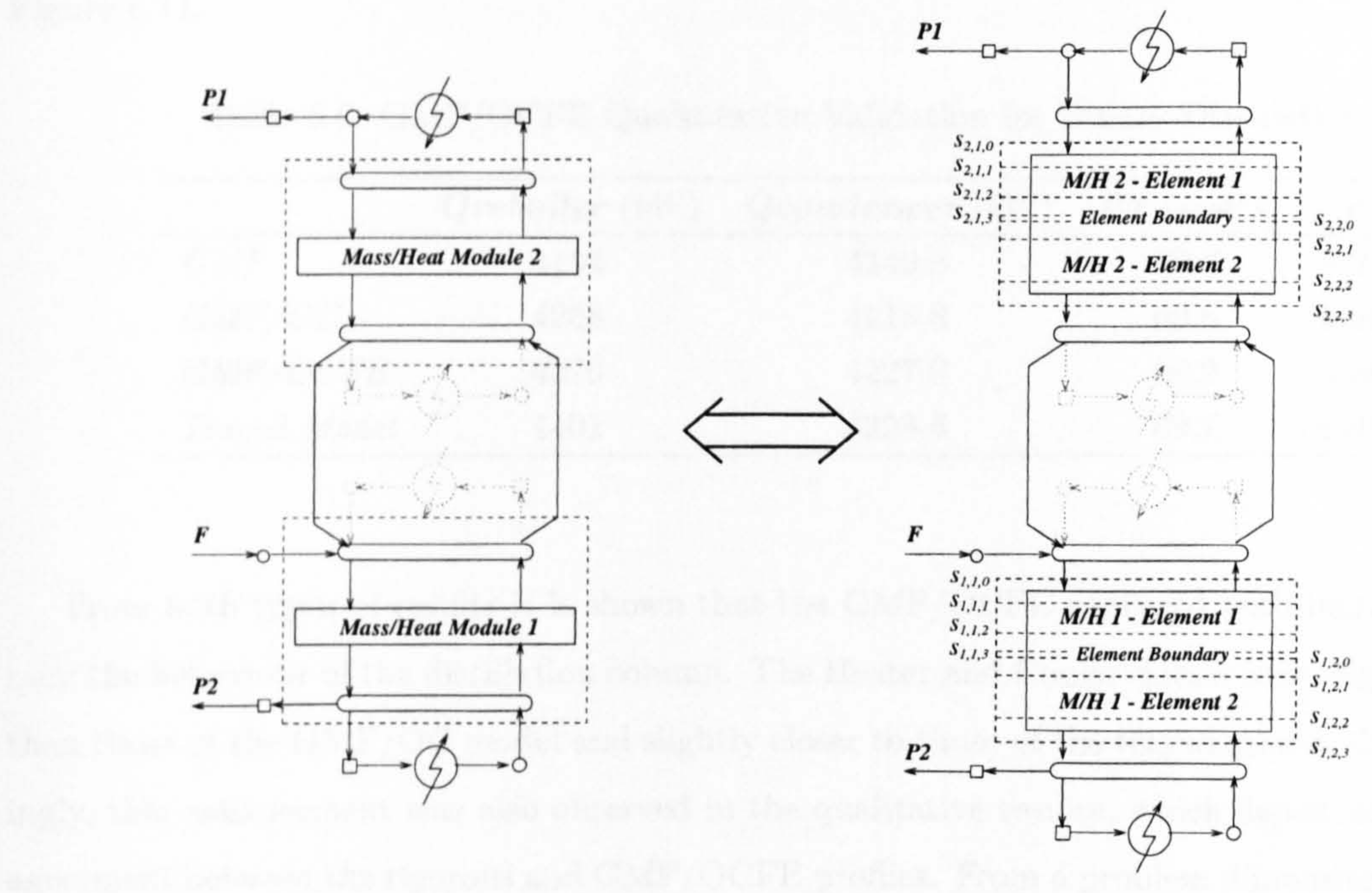


Figure 6.10: GMF and GMF/OCFE Representations of a Simple Column

Having discretized each main M/H module into Finite Elements the number of degrees of freedom for the simple column design NLP problem increased to 6. These corresponded to the 2 operation-related simple distillation degrees of freedom (for instance, reflux ratio and distillate composition for one component) and to 4 design-related degrees (tray numbers of each of the 4 Finite Elements employed). Under the same reasoning as in Section 6.5.1, in order to validate the GMF/OCFE Physical Model against the rigorous model of Viswanathan and Grossmann (1990) and the GMF the overall column trays were fixed, thus fixing the column design and optimizing solely the column operation. However, since the available design information referred only to the number of trays per M/H module (column section) and not to the Elements' boundaries, it was not possible to assign *a priori* the number of trays per Finite Element and thus eliminate all the 4 design-related degrees of freedom.

However, this was overcome by specifying the sum of the number of trays of the two Elements of each M/H module to be equal to the number of trays of the corresponding column section upon which the model of Viswanathan and Grossmann (1993) was based (9 and the 11 in the 1st and 2nd M/H modules, respectively). These two equality constraints eliminated 2 degrees of freedom from the system. The optimization problem objectives were the same as those of Table 2.4.1. The *quantitative* and *qualitative* optimization results are given in Table 6.6 and in Figure 6.11.

Table 6.6: GMF/OCFE Quantitative Validation for Binary Distillation

	$Q_{reboiler}$ (kW)	$Q_{condenser}$ (kW)	$P1$ (mol/s)	r
<i>GMF</i>	4194	4149.5	70.7	0.91
<i>GMF/OC</i>	4258	4216.8	69.6	0.96
<i>GMF/OCFE</i>	4270	4227.9	69.9	0.96
<i>Trayed Model</i>	4401	4398.6	69.7	0.97

From both types of results it is shown that the GMF/OCFE captured with increased accuracy the behaviour of the distillation column. The Heater and Cooler duties were slightly higher than those of the GMF/OC model and slightly closer to those of the trayed model. Correspondingly, this enhancement was also observed in the qualitative results, which depict an enhanced agreement between the rigorous and GMF/OCFE profiles. From a problem dimensionality point of view, an enumeration of the GMF/OCFE model equations and variables is given in Appendix

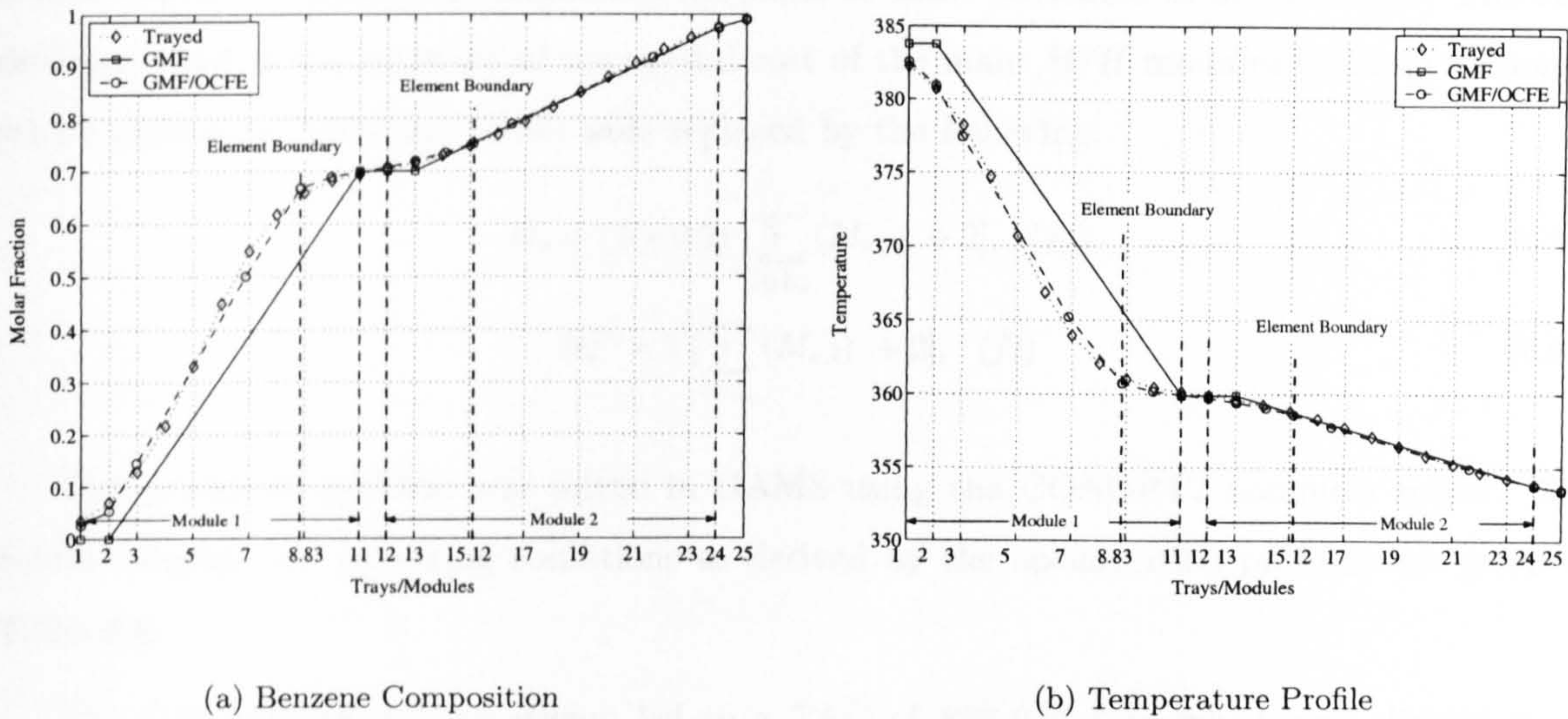


Figure 6.11: GMF/OCFE Qualitative Validation for Binary Distillation

C.2. Based on that, a problem size comparison of the models employed is given in Table 6.7. The information on this table demonstrates that the GMF/OCFE generated the largest problem size of all the GMF-related methods. Nevertheless, its size was still smaller than that of the rigorous model and still independent of the number of trays in a column.

Table 6.7: GMF/OCFE Binary Distillation Optimization Statistics

	Trayed	GMF/OCFE	GMF/OC	GMF
Continuous Variables	283	266	244	134
Continuous Equalities	282	263 ‡	243	127

where:

$$C=2, N=25, E^E=2, E^{CE}=E^{HE}=1, P=2, I=1, L=2, NC=2$$
$$\ddagger E^E[(5NC+3NC \ C+2C+6)L+12C+20]+(E^{CE}+E^{HE})(3C+6)+P(2C+4)+I(C+3)+2=263$$

GMF/OCFE Simple Column Design

The GMF/OCFE Physical Model was also applied, similarly to the GMF/OC model, for the examination of the binary column design problem. In this problem the number of trays was also optimized along with the operating cost for the minimization of the Total Annualized Cost (TAC). The problem objectives were the same as those of Table 6.4. The functions for the

estimation of the latter were essentially the same as those presented in Section 6.5.1. The only difference lied in the estimate of the capital cost of the main M/H modules (column sections), where equations (6.89) and (6.90) were replaced by the following:

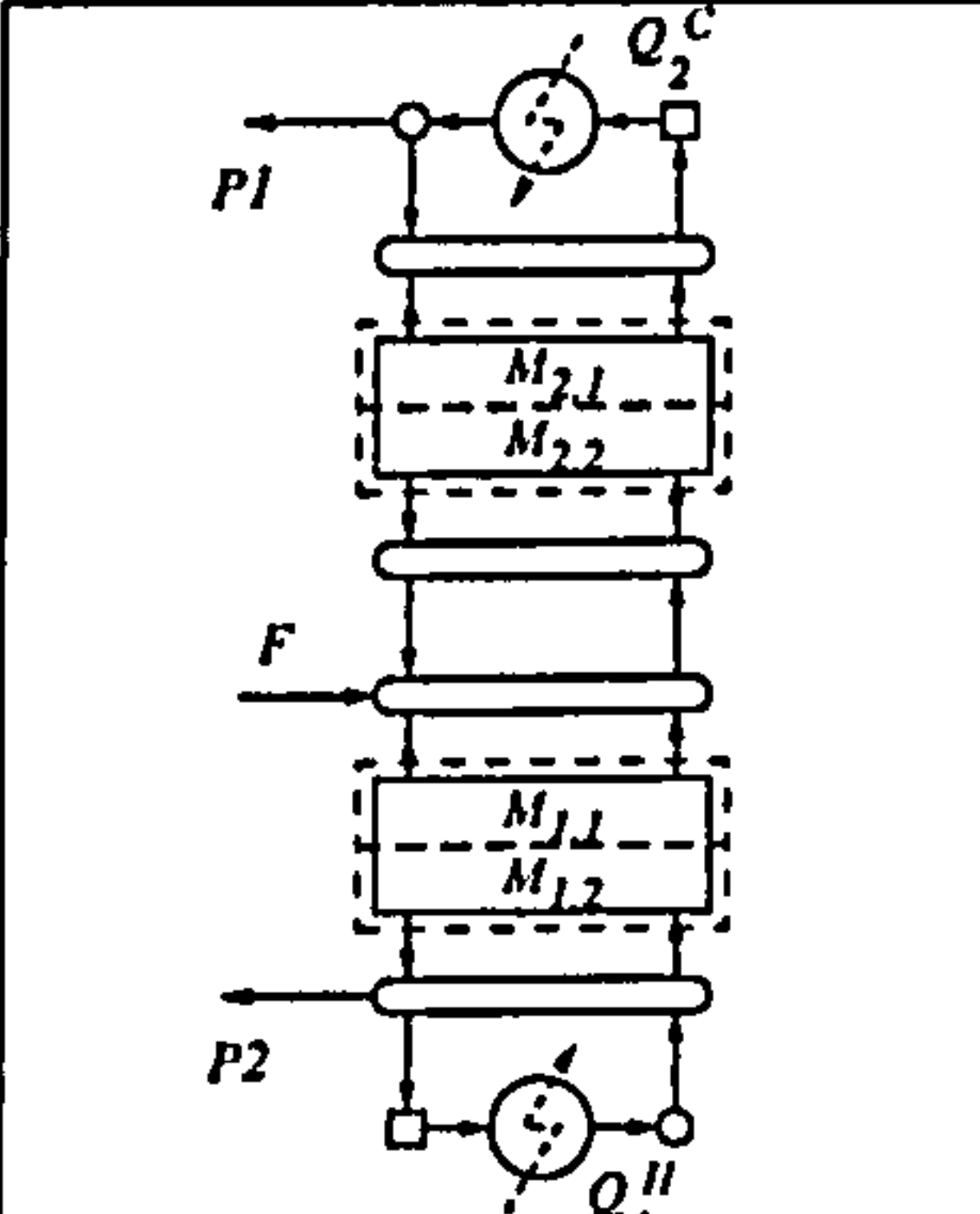
$$H_e = (2 + 0.2) \left[\sum_{l \in L_e} (M_{e,l}) + 2 \right], \quad (ft) \quad (6.98)$$

$$H_e^{ts} = 2 \left[\sum_{l \in L_e} (M_{e,l}) + 2 \right], \quad (ft) \quad (6.99)$$

The generated problem was solved in GAMS using the CONOPT2 nonlinear solver. The column design and operating conditions as derived by the optimization problem are given in Table 6.8.

The GMF/OCFE column design led to a TAC of 872,030 \$/yr which was slightly more improved from the solution obtained through the GMF/OC (881,200 \$/yr). Examining closer the contribution to this TAC, it was found that the GMF/OCFE found a slightly better solution than the GMF/OC both with respect to the operating cost (690,350 \$/yr versus the 693,900 \$/yr of the GMF/OC) and with respect to the annualized capital cost (181,680 \$/yr versus 187,300 \$/yr). Similarly to the GMF/OC results, the annualized capital cost participation in the TAC was found here equal to 20.8% which indicated the good balance of capital and operating cost in the column design procedure through the GMF/OCFE.

Table 6.8: GMF/OCFE Column Optimal Design and Operating Conditions

		F (mol/s)	x_{Benz}	x_{Tol}
	P1	70.4	0.99	0.01
	P2	29.6	0.01	0.99
		Heat Duties (kW)		
	Q_1^H	4230.3		
	Q_2^C	4186.7		
		Estimated Trays		
	M/H 1	$M_{1,1} = 2.11, \quad M_{1,2} = 8.36$		
	M/H 2	$M_{2,1} = 11.22, \quad M_{2,2} = 2.09$		

6.6 Conclusions

In the current Chapter the GMF Physical Model was enhanced through the incorporation of components belonging to formal techniques for distillation column order reduction (namely, to the Orthogonal Collocation (OC) and Orthogonal Collocation on Finite Element (OCFE) techniques). New GMF/OC and GMF/OCFE Physical Models were proposed, utilizing the modular formalism of the aforementioned techniques. These models consisted of newly introduced *substituting* and *supplementary* constraints, replacing or being added to the existing constraints of the ‘*conventional*’ GMF model. These constraints were introduced in such a way allowing the modeler the freedom to use each GMF-based model (GMF, GMF/OC and GMF/OCFE) according to the problem solved and the representational detail desired.

The new physical models were then applied to the representation of a binary simple distillation separation and were validated over a rigorous distillation model. The results demonstrated a remarkable enhancement of the GMF physical representation, which produced predictions very close to those of the rigorous model while still maintaining the GMF advantages, especially that of the generated problem size. The latter, despite being larger than that of the ‘*conventional*’ GMF, remained smaller than that of the rigorous model and independent of the number of trays in the represented column. From a functionality point of view, the discretization of the main *M/H* modules had also the effect of allowing the GMF to be used for simulation analysis thus providing additional versatility to the GMF which can now be implemented in computational environments other than GAMS, making use of their additional features and advantages.

Furthermore, a distillation column design methodology was introduced, which allowed the GMF to be used for the derivation of detailed design information such as number of trays and column diameters, while avoiding the introduction of additional binary variables. Overall, the use of discretization techniques in the GMF, can be viewed as the incorporation of elements of a simulation tool within the GMF conceptual design tool, while keeping intact the latter’s representational advantages and compactness.

Chapter 7

Enhanced GMF for the Synthesis of Distillation Column Sequences

In Chapters 3, 4 and 5, GMF methods were proposed for the systematic generation and evaluation of Simple, Heat Integrated and Complex distillation column sequences, aiming at finding the most energy efficient column sequence. Alternative GMF Structural Models were proposed for the generation of these column sequences (Sections 3.2, 4.3 and 5.2), which were coupled to the ‘*conventional*’ GMF Physical Model (Section 2.3.3). The latter evaluated the generated structural alternatives based on an aggregated distillation column model providing an efficient representation of the underlying physical phenomena and a valid lower bound on the sequences’ energy consumption. In Chapter 6, the GMF Physical Model was coupled to the Orthogonal Collocation (OC) and Orthogonal Collocation on Finite Element (OCFE) techniques for distillation column order reduction, generating two new physical models, namely the GMF/OC and GMF/OCFE. As shown in that chapter the physical representation abilities of the GMF were enhanced remarkably, attaining the accuracy and detail levels of rigorous models, providing intra-module information and detailed column design (number of trays, column diameters), while maintaining the GMF advantages and its continuous and combinatorial compactness. The obtained results have provided the motivation of coupling these new GMF Physical Models to the GMF Structural Models, mentioned above, for the distillation column sequencing problems examined.

In this Chapter, the ternary case studies examined in previous chapters will be addressed

through the GMF/OC and GMF/OCFE formal synthesis methods for the generation of *cost efficient* simple, heat integrated and complex column sequences, with respect to their operating and capital cost and providing detailed guidelines on the design of the optimal column sequences.

7.1 Enhanced GMF for the Simple Distillation Column Sequencing

The simple column sequencing problem was examined by coupling the GMF Structural Model to the GMF/OC and GMF/OCFE Physical Models. For illustration purposes the Ternary Sequencing problem of Section 3.3 was revisited, initially, through the GMF/OC and then through the GMF/OCFE complete synthesis models. These models extended the synthesis target to finding the most economical column sequence, that is, the optimal sequence with respect to both energy consumption and capital expenditure. Through this enhancement, the GMF provided complete design guidelines that did not only provide the best column sequence but also the number of trays of each column.

7.1.1 GMF/OC Simple Column Sequencing Formulation and Results

The problem statement was taken from Section 3.3.1 and the necessary data for the Stage 3 construction of the Structural Model (Structural Sets) was the same as in Section 3.3.2. For the construction of the GMF/OC Physical Model each M/H module of the set E was discretized using 6 collocation points (2 exterior and 4 interior). This discretization scheme was found adequate for the accurate representation of the underlying physical phenomena. For the mixed integer constraints $\mathcal{F}^{max}$ was set to 1800 kmol/hr and the problem objectives included the minimization of the sequences' TAC subject to product specifications (Table 7.1).

Table 7.1: Ternary Simple Column Sequencing Objectives

Objective Function	$\min TAC$
Benzene at Product $P1$	$x_{P1,Benzene}^P \geq 0.95$
Toluene at Product S	$x_{S,Toluene}^P \geq 0.95$
o-Xylene at Product ($P2$)	$x_{P2,o-Xylene}^P \geq 0.95$

The TAC model was the same as in Section 6.5.1, with the only difference associated to the definition of the diameter of each column, D_e . Therefore equation (6.88) was replaced by equations defining uniform diameters for M/H modules belonging to the same column:

$$D_e = 0.1838(f_{1,1}^{HV})^{0.5}, \quad e = 1, 2 \quad (7.1)$$

$$D_e = 0.1838(f_{3,3}^{HV})^{0.5}, \quad e = 3, 4 \quad (7.2)$$

$$D_e = 0.1838(f_{5,5}^{HV})^{0.5}, \quad e = 5, 6 \quad (7.3)$$

The synthesis problem was implemented in GAMS using the APROS methodology for the GBD MINLP algorithm. The optimal solution was found, as in Section 3.3.3, in 2 GBD iterations and corresponded to the Direct Sequence. In the GBD algorithm the Direct Sequence was the initial structure to be evaluated. The 1st Master generated the Indirect Sequence and the 2nd Master the 3-Column Sequence, which was not evaluated, since the algorithm convergence criterion was met (upper-lower bound crossing). The optimal design and operating conditions for the examined sequencing problem are given in Table 7.2. The TAC of the sequence was found equal to 2,912,500 \$/yr which consisted of an Operating Cost of 2,431,900 \$/yr (83% contribution to the TAC) and of an Annualized Capital Cost of 480,600 \$/yr (17% contribution to the TAC).

From a comparison of the results obtained with the GMF/OC to those of the GMF it is apparent of the former enhanced model can now provide detailed design guidelines, which do not only include energy consumption information but are extended to the actual sequence design (number of trays, diameter, etc). Comparing the solutions obtained between the GMF and

Table 7.2: GMF/OC Simple Column Sequencing Optimal Design and Operation

		F (kmol/hr)	x_{Benz}	x_{Tol}	x_o-Xyl
	P1	210.5	0.95	0.05	0
	S	388.9	0	0.95	0.05
	P2	400.6	0	0.05	0.95
		Column 1		Column 2	
	Trays	$M_1=25.8$		$M_3=11.3$	
		$M_2=5.6$		$M_4=8.2$	
	D_e (ft)	7.12		7.67	
	Q_e^H (kW)	6860.3		8090.4	
	Q_e^C (kW)	6562.2		7934.4	

GMF/OC models it is noted that the former, indeed, provided a lower bound on the operating cost (equal to $2,369,000$ \$/yr) versus the $2,431,900$ \$/yr of the GMF/OC. This difference of 2.6% , which is due to the trading off between operating and capital cost in the GMF/OC model also demonstrated the validity of the original GMF Physical Model, which captured the physical behaviour and the energy efficiency of the represented sequences, while using only an aggregated model.

7.1.2 GMF/OCFE Simple Column Sequencing Formulation and Results

The GMF/OCFE Synthesis Model was then employed for the Ternary Sequencing problem in the same way as the GMF/OC model. The GMF Structural Model with the necessary Structural Sets were taken from Sections 3.2 and 3.3.2, respectively, while the Physical Model was taken from Section 6.4. The discretization scheme employed 2 Finite Elements of 4 Collocation Points each (2 interior and 2 exterior) for the main M/H modules. Given the same case study problem statement as in the previous Section, the task was to find the optimal sequence, subject to the objectives of Table 7.1. The TAC model was taken from Section 6.5.2 and the diameter equations were adjusted for the sequencing case using equations (7.1) to (7.3).

The MINLP problem was implemented in GAMS and solved using the GBD algorithm and the APROS methodology. As in Section 7.1.1, the Direct Sequence was found as the solution (optimal sequence) after 2 GBD iterations, in exactly the same way as in the GMF/OC case. The results of the synthesis problem are given in Table 7.3.

Table 7.3: GMF/OCFE Simple Column Sequencing Optimal Design and Operation

The figure shows a process flow diagram of a distillation system with two columns. The left column has a condenser at the top with cooling water flow Q_2^C and a reboiler at the bottom with heating steam flow Q_1^H . The right column has a condenser at the top with cooling water flow Q_4^C and a reboiler at the bottom with heating steam flow Q_3^H . Feed F enters the left column. Side stream S is drawn from the left column and enters the right column. Product $P1$ exits the top of the left column, and product $P2$ exits the bottom of the right column. The table provides data for the streams and columns.

	F (kmol/hr)	x_{Benz}	x_{Tol}	$x_o - x_{yl}$
$P1$	210.5	0.95	0.05	0
S	388.9	0	0.95	0.05
$P2$	400.6	0	0.05	0.95

	Column 1	Column 2
Trays	$M_{1,1}=19.5, M_{1,2}=2.4$ $M_{2,1}=3.2, M_{2,2}=3.9$	$M_{3,1}=3.4, M_{3,2}=7.3$ $M_{4,1}=5, M_{4,2}=3.1$
D_e (ft)	7.02	7.67
Q_e^H (kW)	6655.0	8107.6
Q_e^C (kW)	6356.9	7951.6

The TAC of the Direct Sequence was found equal to 2,868,700 \$/yr (Operating Cost 2,401,200 \$/yr and Annualized Capital Cost 467,500 \$/yr). The GMF/OCFE, from a TAC aspect, managed to further improve the solution of the GMF/OC (additional savings of 43,800 \$/yr). By comparing the two designs, it is found that the main contribution to this improvement can be traced in the operation of the first column of the sequence, where the GMF/OCFE model found an improved optimal point with further reductions in this column's operating cost.

7.2 Enhanced GMF for the *HI* Simple Distillation Column Sequencing

The previous sections have demonstrated that the enhanced GMF Physical Model with OC and OCFE principles has achieved in finding the most economically efficient ternary simple column sequence, while providing detailed guidelines regarding the sequence's design and optimal operation. The task at this point is to achieve even higher TAC savings through Heat Integration and to incorporate the enhanced GMF models in order to capture the potential interactions of the represented sequences' operating and capital expenditures. For this purpose the Ternary Sequencing problem, including *HI* possibilities, was revisited in the following sections, initially through the GMF/OC and then through the GMF/OCFE Synthesis Models.

7.2.1 GMF/OC *HI* Column Sequencing Formulation and Results

The GMF/OC synthesis model for the synthesis of ternary Heat Integrated (*HI*) simple column sequences employed the GMF Structural Model of Section 4.3 (with the Structural Sets for the ternary separation from Section 4.4.2) and the GMF/OC Physical Model of Section 6.3. For the latter, in the same fashion as throughout this work, each *M/H* module was discretized into 4 interior collocation points. Since in the *HI* case the column pressure is considered an additional degree of freedom, the pressure that participated in the OC constraints was set equal to that of each *M/H* module. A pressure drop profile was not employed for simplicity reasons, however, without affecting the validity of the results. In the mixed integer physical-structural constraints $\mathcal{F}^{max}$ was set to 1800 kmol/hr. The problem statement was taken from Table 3.3 and the synthesis objectives included the minimization of TAC, subject to the product purity specifications of Table 7.1. For the *HI* case the TAC model of the GMF/OC simple column

sequencing method was arranged appropriately in order to incorporate the capital cost of *HI* blocks, as shown below:

$$C^{cap} = \sum_{e \in E} C_e^{col} y_e + \sum_{e \in E^H} C_e^H y_e^H + \sum_{e \in E^C} C_e^C y_e^C + \sum_{e, ea \in E^X} C_{e,ea}^{HI} y_{e,ea}^{HI} \quad (7.4)$$

$$D_e = 0.1838(f_{1,1}^{HV} + \sum_{ea \in E_1^{XCE}} f_{1,ea}^{XV})^{0.5}, \quad e = 1, 2 \quad (7.5)$$

$$D_e = 0.1838(f_{3,3}^{HV} + \sum_{ea \in E_3^{XCE}} f_{3,ea}^{XV})^{0.5}, \quad e = 3, 4 \quad (7.6)$$

$$D_e = 0.1838(f_{5,5}^{HV} + \sum_{ea \in E_5^{XCE}} f_{5,ea}^{XV})^{0.5}, \quad e = 5, 6 \quad (7.7)$$

$$C_{e,ea}^{HI} = \frac{M\&S}{280} 101.3(2.29 + Fc)(A_{e,ea}^{HI})^{0.65} \quad (7.8)$$

$$A_{e,ea}^{HI} = \frac{Q_{e,ea}^{HI}}{150 LMTD_{e,ea}^{HI}}, \quad (ft^2) \quad (7.9)$$

$$LMTD_{e,ea}^{HI} = \frac{2}{3}(\Delta T_{e,ea}^{HI1})^{0.5}(\Delta T_{e,ea}^{HI2})^{0.5} + \left(\frac{\Delta T_{e,ea}^{HI1} + \Delta T_{e,ea}^{HI2}}{6}\right) \quad (7.10)$$

$$\Delta T_{e,ea}^{HI1} = T_{e,ea}^{XHI} - T_{e,ea}^{XCO} \quad (7.11)$$

$$\Delta T_{e,ea}^{HI2} = T_{e,ea}^{XHO} - T_{e,ea}^{XCI} \quad (7.12)$$

The capital costing of the *HI* blocks was calculated analytically through the Logarithmic Mean Temperature Difference calculation and equations (7.5) to (7.7) provided the diameter - boil-up correlations, adjusted for the incorporation of potential contributions to the columns' boil-up from Heaters and/or *HI* blocks.

The GMF/OC Synthesis Model for ternary *HI* simple column sequencing was implemented in GAMS and solved using the GBD/APROS methodology. The optimal solution was obtained in 5 GBD iterations and corresponded to a Heat Integrated variant of the Direct Sequence. The optimal configuration, with its design and operating parameters are shown in Table 7.4. The TAC at the optimal solution was found equal to 2,008,400 \$/yr, consisting of an Operating Cost of 1,455,500 \$/yr (72% of the TAC) and of an Annualized Capital Cost of 552,900 \$/yr (28% of the TAC). From a comparison with the *non-HI* optimal sequence and design, the Heat Integration provided annual savings of 31% (2,912,500 \$/yr versus 2,008,400 \$/yr). From a closer investigation it was found that this improvement was due to a substantial decrease of the Operating Cost, which has been reduced to 40% (from 2,431,900 \$/yr to 1,455,500 \$/yr) due to the *HI* of the two columns. This has been achieved by increasing the pressure in the first

Table 7.4: GMF/OC *HI* Simple Column Sequencing Optimal Design and Operation

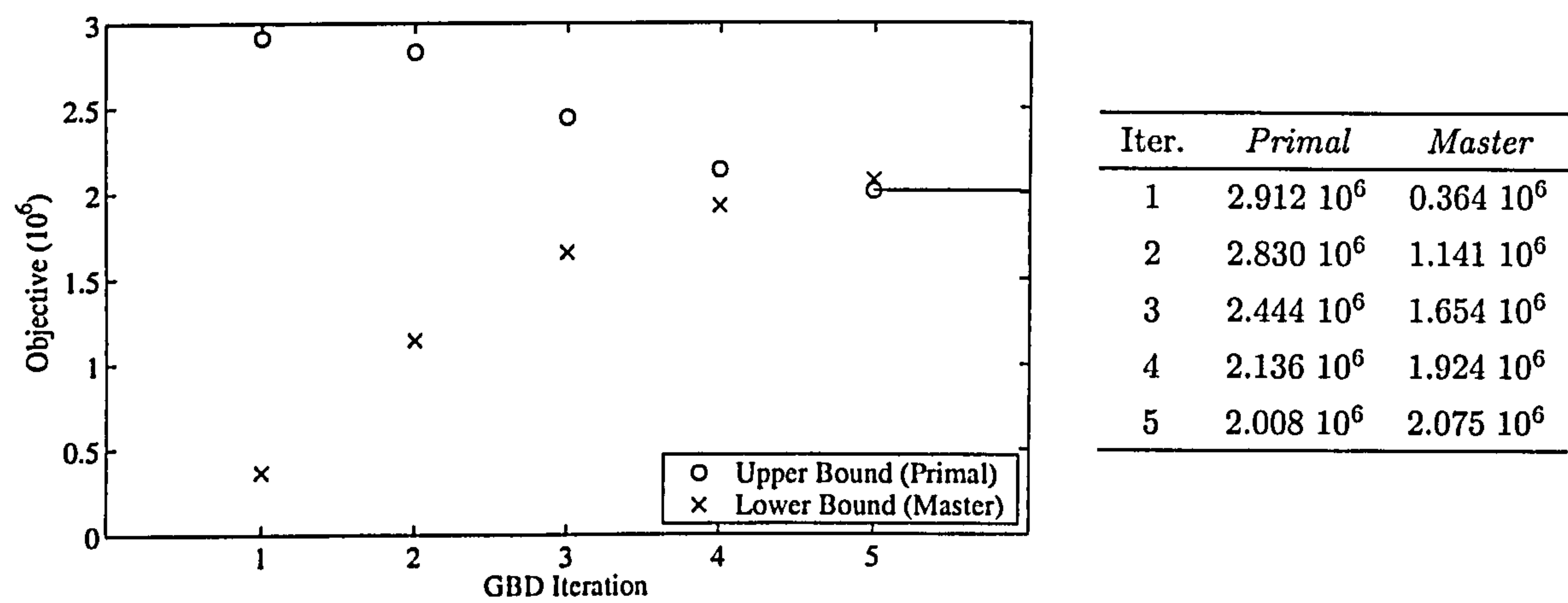
		F (kmol/hr)	x_{Benz}	x_{Tol}	x_o-x_{yl}
	$P1$	190.6	0.95	0.05	0
	S	388.9	0.049	0.95	0.001
	$P2$	420.5	0	0.05	0.95
		<i>Column 1</i>		<i>Column 2</i>	
	<i>Trays</i>	$M_1=17.4$ $M_2=6.9$		$M_3=5.3$ $M_4=10$	
	D_e (ft)	7.91		7.71	
	Q_e^H (kW)	8488.4		-	
	Q_e^C (kW)	-		11082.6	
	P_e (atm)	6.12		1	

column of the sequence so that its condenser could be Heat Integrated with the reboiler of the second column.

From a comparison with the optimal solution provided by the ‘conventional’ GMF (Section 4.4.3) for the same problem, it was found that both synthesis frameworks have resulted in the same optimal sequence, with the same Heat Integration scheme. The GMF, as expected, provided a lower bound of the Operating Cost, namely 1,392,000 \$/yr versus 1,455,500 \$/yr of the GMF/OC. The reason that both frameworks have resulted in the same structure and in comparable operating costs (even when GMF/OC takes into account capex interactions) is that the main driving force in the examined optimization problem is the operating cost, which makes, *by far*, the dominant contribution into the examined distillation system’s expenditure.

From a computational point of view, the optimal structure was found in 5 GBD iterations. The convergence history is given in Table 7.5. Starting from the *non-HI* optimal sequence (Direct Sequence), the 2nd and 3rd GBD iterations corresponded to *HI* variants of the Indirect Sequence. The final two iterations (4th and 5th) corresponded to *HI* variants of the Direct Sequence. Convergence was achieved in the 5th iteration when the lower bound of the 5th Master subproblem crossed the current best upper bound.

Table 7.5: GMF/OC *HI* Column Sequencing GBD Convergence History



7.2.2 GMF/OCFE *HI* Column Sequencing Formulation and Results

The GMF/OCFE Synthesis Model was also applied to the same ternary *HI* column sequencing problem. The GMF structural model of Section 4.3 was coupled to the GMF/OCFE Physical Model, with the additions shown in the previous section for the incorporation of *HI* blocks' capex. The problem statement and objectives were those of the GMF/OC case.

As in GMF/OC, the optimal solution was found after 5 GBD iterations and corresponded to the same Heat Integrated structure as in the GMF/OC model. The optimal design and operating conditions are given in Table 7.6. The TAC of the Heat Integrated sequence was

Table 7.6: GMF/OCFE *HI* Simple Column Sequencing Optimal Design and Operation

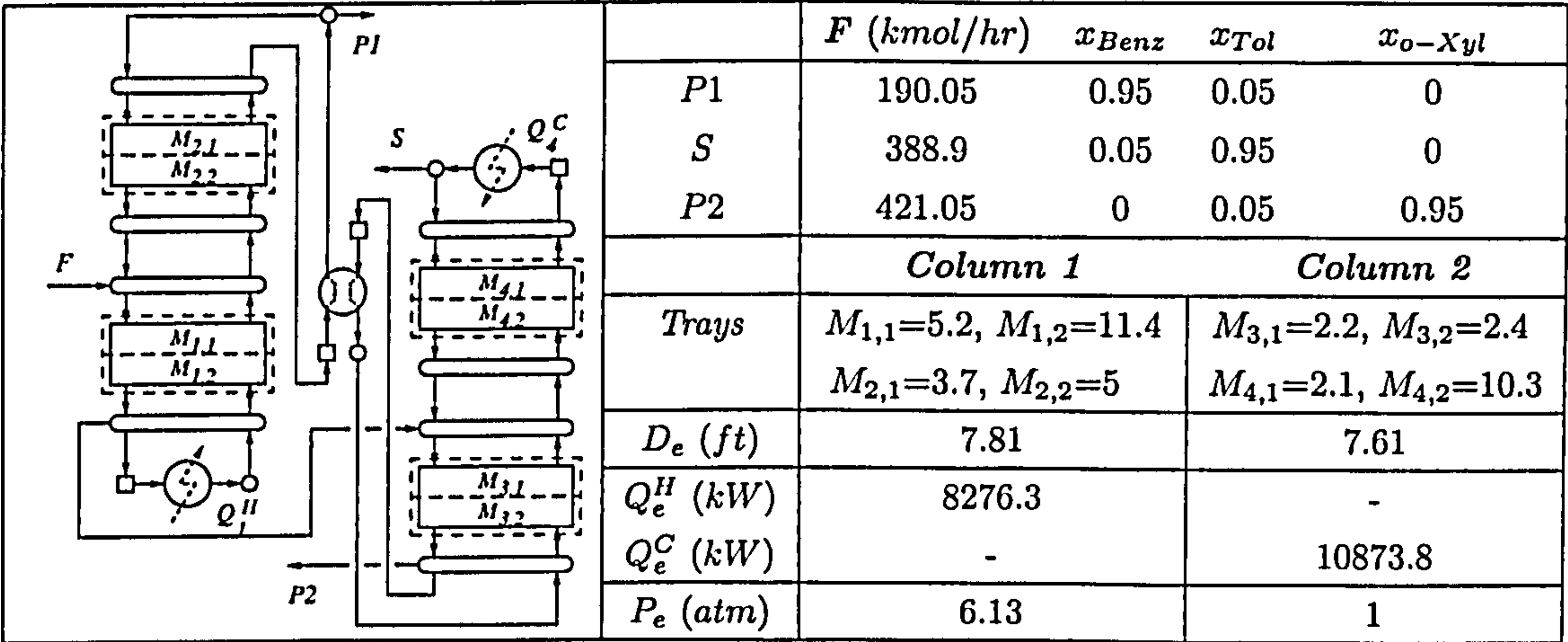
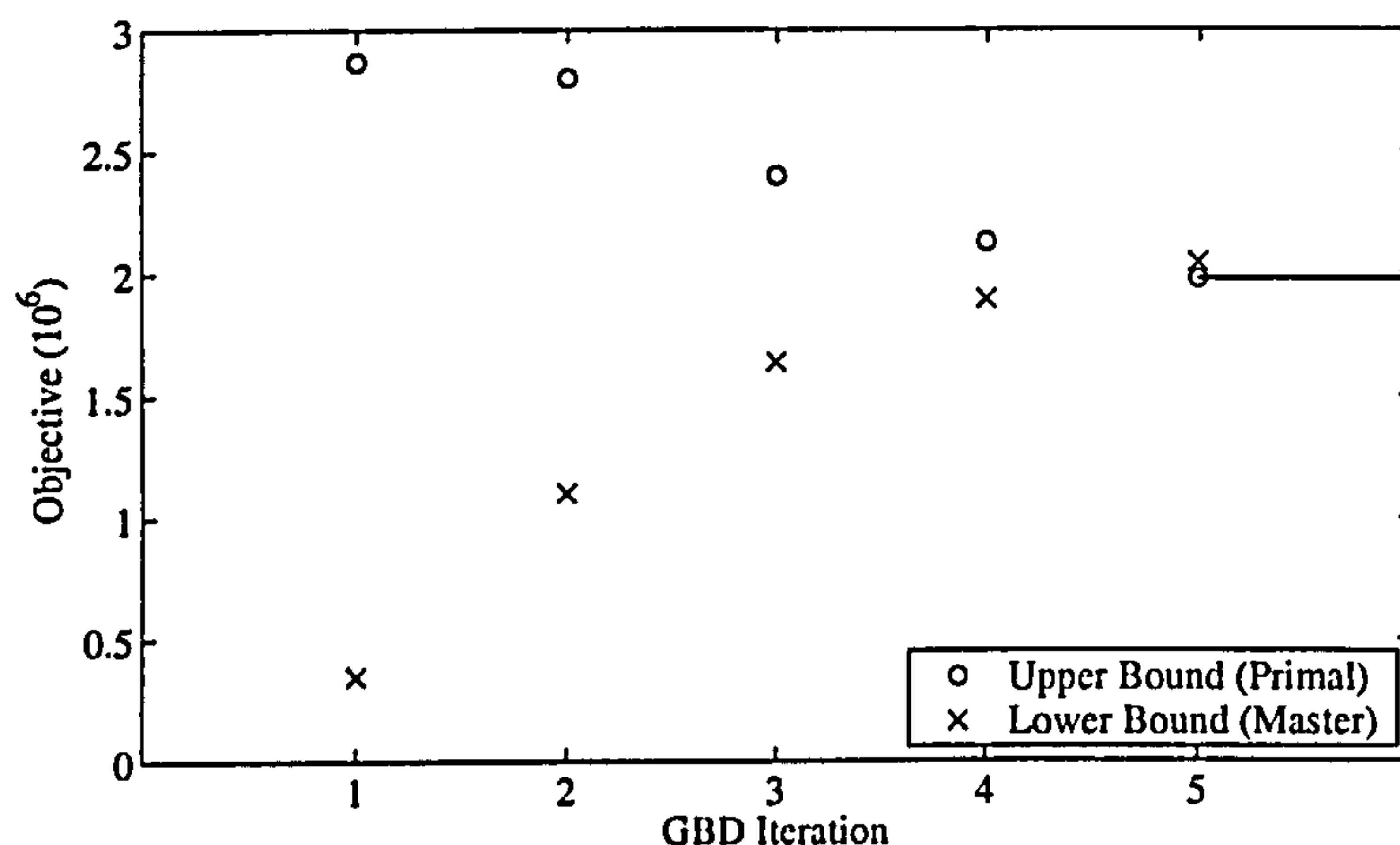


Table 7.7: GMF/OCFE *HI* Column Sequencing GBD Convergence History

Iter.	<i>Primal</i>	<i>Master</i>
1	2.868 10 ⁶	0.349 10 ⁶
2	2.801 10 ⁶	1.102 10 ⁶
3	2.398 10 ⁶	1.638 10 ⁶
4	2.126 10 ⁶	1.892 10 ⁶
5	1.974 10 ⁶	2.040 10 ⁶

found to be 1,974,400 \$/yr (operating cost of 1,420,900 \$/yr and annualized capital cost of 553,500 \$/yr). This solution demonstrated improved savings when compared to that of the GMF/OC (whose TAC was found equal to 2,008,410 \$/yr), which was mainly due to a decrease in the operating cost. This decrease has led to a slight increase of the number of trays (capital cost) of the sequence. The above results demonstrated the ability of the GMF/OCFE to provide more economically improved designs than the GMF/OC.

From a computational point of view, it was found that in every GBD iteration the structures generated and evaluated were the same for the GMF/OC and GMF/OCFE, which is something which was expected since the two frameworks are based on the same principles and their solutions are quite close. The solution evolution for the GMF/OCFE ternary *HI* simple column sequencing problem along with the Upper and Lower Bounds are given in Table 7.7.

7.3 Enhanced GMF for the Complex Distillation Column Sequencing

In the previous section, it was shown that the proposed GMF/OC and GMF/OCFE synthesis models achieved substantial TAC savings in the simple column sequences represented, by incorporating formal *HI* possibilities. In this section, these models will be arranged in order to address the column sequencing problem for cost efficiency by employing Thermal Coupling

techniques, for the synthesis of Complex and Simple column sequences for ternary separations. Moreover, the discretization enhancements in the GMF will be used for the *explicit* representation of complex arrangements such as the Dividing Wall Column (DWC), exploring the potential for further cost savings. To illustrate the potential of the proposed synthesis methods, the Benzene, Toluene, o-Xylene case study examined in the previous sections was revisited, employing simple and complex column structural possibilities. For this purpose, both GMF/OC and GMF/OCFE Physical Models were coupled to the complex column sequencing GMF Structural Model of Section 5.2 defined over the Structural Sets of Table 5.2.

7.3.1 GMF/OC Complex Column Sequencing Formulation and Results

The GMF/OC Physical Model was formulated using the 4 interior collocation point discretization scheme. For the mixed integer constraints $\mathcal{F}^{max}$ was set equal to 1800 kmol/hr . The Total Annualized Cost Model was the same as the one defined in the simple column sequencing problem. The only particularities were found in the M/H module diameter (D_e) and height (H_e) of *complex* columns, whose definition was more involved. For the complex columns of Figure B.1, the new diameter and height definitions are given below for each M/H module (*note*: if the diameter or height is not defined for a column, then equations (7.1) to (7.3) and (6.89), respectively for the diameter and height should be used - in the simple column alternatives, these hold by default):

Prefractionator (Figure B.1.d) and SL Column (Figure B.1.i)

$$D_e = 0.1838(f_{3,3}^{HV})^{0.5}, \quad e = 3, 4, 5, 6 \quad (7.13)$$

$$H_e = 2(M_e + 2), \quad e = 4, 5 \quad (7.14)$$

Petlyuk (Figure B.1.e) and RV Column (Figure B.1.h)

$$D_e = 0.1838(f_{3,1}^{VV})^{0.5}, \quad e = 1, 2 \quad (7.15)$$

$$D_e = 0.1838(f_{3,3}^{HV})^{0.5}, \quad e = 3, 4, 5, 6 \quad (7.16)$$

$$H_e = 2(M_e + 2), \quad e = 4, 5 \quad (7.17)$$

Side Stripper (Figure B.1.f - initial structure in Figure 5.6.a)

$$D_e = 0.1838(f_{1,1}^{HV})^{0.5}, \quad e = 1, 2, 6 \quad (7.18)$$

$$D_e = 0.1838(f_{5,5}^{HV})^{0.5}, \quad e = 5 \quad (7.19)$$

$$H_e = 2(M_e + 2), \quad e = 2 \quad (7.20)$$

$$H_e = (2 + 0.4)(M_e + 2), \quad e = 5 \quad (7.21)$$

Side Rectifier (Figure B.1.g - initial structure in Figure 5.6.b)

$$D_e = 0.1838(f_{3,3}^{HV})^{0.5}, \quad e = 1, 2, 3 \quad (7.22)$$

$$D_e = 0.1838(f_{3,4}^{VV})^{0.5}, \quad e = 4 \quad (7.23)$$

$$H_e = 2(M_e + 2), \quad e = 1 \quad (7.24)$$

$$H_e = (2 + 0.4)(M_e + 2), \quad e = 4 \quad (7.25)$$

In the Prefractionator, Petlyuk, RV and SL Columns, for the main column (M/H modules 3-6) the diameter is related to the column boil-up ($f_{3,3}^{HV}$) and the height of M/H modules 3 and 4 is equal to that of the internals, since these are intermediate sections in the aforementioned columns. In the Petlyuk and RV columns the diameter of the prefractionation column (M/H modules 1-2) is related to the vapour interconnection ($f_{3,1}^{VV}$). In order to define correctly diameters and module heights of the Side Stripper and Side Rectifier sequences their original designs have to be taken into account (Figure 5.6). For the former, M/H modules 1, 2 and 6 belong to the same column whose diameter is related to the column boil-up ($f_{1,1}^{HV}$) and M/H module 2 is an intermediate section. However, M/H module 5 is a side column with additional height due to existing top and bottom sections, with its diameter defined in equation 7.3. Similar considerations are made for the Side Rectifier Sequence where the M/H modules 1, 2 and 3 belong to the same column, with M/H module 2 an intermediate section and M/H module 4 a separate side column. In the GAMS implementation, the aforementioned correlations were incorporated using Dollar Operators, \$, in conjunction with the parameterized binary variables of the corresponding structures, after each structure has been generated.

The resulting MINLP problem was solved in GAMS using the GBD/APROS methodology. The solution of the MINLP problem corresponded to the Petlyuk Sequence. The Total Annualized Cost of the Petlyuk Column was found equal to 2,095,900 \$/yr, which corresponded to operating cost of 1,681,500 \$/yr and to annualized capital cost of 414,400 \$/yr. The optimal design with the optimized operating conditions are given in Table 7.8.

Having obtained these results, some very interesting conclusions can be made regarding the ternary distillation problem examined. Namely, if the Petlyuk sequence is compared to the optimal simple column sequence (the direct sequence), it can be found that the former provides savings of 816,600 \$/yr, corresponding to an improvement of 28% in the separation

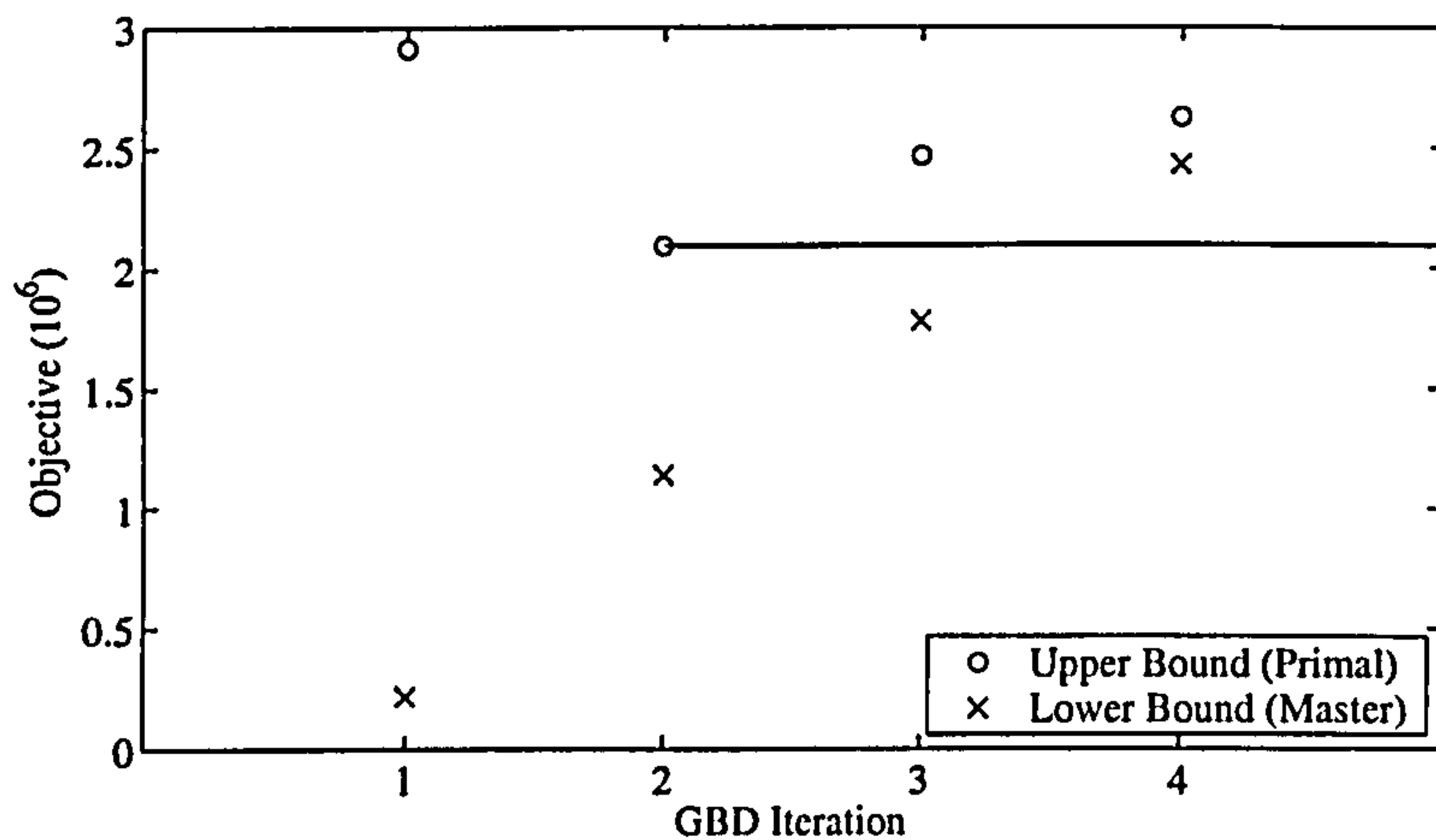
Table 7.8: GMF/OC Complex Column Sequencing Optimal Design and Operation

	$F(\text{kmol/hr})$	x_{benz}	x_{tol}	$x_{\text{o-xyl}}$
$P1$	207.5	0.95	0.05	0
S	388.9	0.007	0.95	0.043
$P2$	403.6	0	0.05	0.95
$f_{6,2}^{LL}$	234.2	0.237	0.74	0.023
$f_{2,6}^{VV}$	627.7	0.402	0.571	0.027
$f_{3,1}^{VV}$	618.0	0.008	0.733	0.259
$f_{1,3}^{LL}$	1224.5	0.007	0.546	0.448
<i>Prefrac.</i>		<i>Main</i>		
<i>Trays</i>		$M_6=4.3$		
		$M_2=6.8$		
		$M_1=6.2$		
		$M_5=5.8$		
		$M_4=8.5$		
		$M_3=6.4$		
D_e	6.78	8.67		
Q_e^H	-	10359.5		
Q_e^C	-	9906.1		

economics. This is due to large savings both in the operating cost (30%) and in the capital cost (13%). However, by comparing the Petlyuk column to the best Heat Integrated simple column sequence (*HI* Direct Sequence), it is found that, for the examined problem, Heat Integration leads to a slightly better economic performance than that of Full Thermal Coupling. The total annual expenditure of the *HI* sequence is 87,500 \$/yr less than that of the Petlyuk column, corresponding to a difference of 4%. From the corresponding results the *HI* sequence produced more operating cost savings, whereas the complex column more capital expenditure savings. The close performance of these alternatives can demonstrate the importance of synthesis tools, like the GMF, which can generate all these alternatives in a unified way and can then evaluate them in order to provide the most cost efficient design.

From a computational point of view, convergence was achieved in 4 GBD iterations, from which the optimal solution corresponded to the solution of the 2nd Primal subproblem as it can be seen in Table 7.9. The initial structure to be evaluated (1st Primal) was the best simple column solution (Direct Sequence). The second sequence generated and evaluated corresponded to the Petlyuk column, whereas the 3rd and 4th iterations generated the suboptimal Side Stripper

Table 7.9: GMF/OC Complex Column Sequencing GBD Convergence History



Iter.	<i>Primal</i>	<i>Master</i>
1	2.912 10 ⁶	0.219 10 ⁶
2	2.096 10 ⁶	1.140 10 ⁶
3	2.467 10 ⁶	1.783 10 ⁶
4	2.680 10 ⁶	2.463 10 ⁶

and Side Rectifier Sequences. It must be, however, noted that the GMF in Section 5.3.4 found the Petlyuk column as the optimal sequence, in the same number of iterations and in the same sequence generation per GBD iteration. From a comparison with the computational performance of the simple column and Heat Integrated simple column sequencing synthesis problems, the fastest solution (with respect to GBD iterations) was that of the simple column sequencing problem (2 iterations), which is, of course, due to the small number of alternatives. The slowest solution was that of the *HI* simple column sequencing problem (5 iterations).

GMF/OC Dividing Wall Considerations

As indicated in Section 5.1 the Dividing Wall Column (DWC) is essentially a side stream column, that has a vertical wall splitting its middle section in two separate compartments (as shown in Figure 5.1.f). Under the assumption of no heat transfer through the vertical wall, the DWC is considered thermally equivalent to the Petlyuk column, therefore encompassing the same thermal coupling effects and generating equivalent energy savings. However, it also provides capital cost savings by including the main and the prefractionation columns of the Petlyuk arrangement in the same shell. However, as pointed out in Section 5.2.1, since the Dividing Wall Column could not be explicitly represented in the GMF by a combination of *M/H* modules, it was *implicitly* considered for its energy efficiency, using its thermally equivalent Petlyuk column.

However, due to the enhancement of the GMF with OC principles, thus allowing for efficient estimates of Capital Expenditure, the DWC can now be represented and evaluated *explicitly*

through the GMF/OC with respect to its Total Annualized Cost. This was achieved in a two step optimization problem. The first step is the solution of the complex column sequencing problem as described earlier in this section. If this has the Petlyuk Column as its optimal solution, then a second step is introduced which involves the optimization of the DWC. If the solution of the first step is not the Petlyuk Column then the DWC is not evaluated. This utilizes the fact that in the examined distillation separation the operating cost is the main economic driving force and if the Petlyuk column is suboptimal, with respect to the latter, then the capital cost savings of its thermally equivalent DWC cannot compensate for the suboptimal energy savings. An alternative way of including the DWC in the structural model is by incorporating an additional binary variable designating if the prefractionating column is fitted within the main column shell, as specified in Dunnebir and Pantelides (1999).

In order to model the DWC starting from the Petlyuk design, the following conditions are imposed: (i) The number of trays in the prefractionation column (M/H modules 1 and 2) must be equal to those in the intermediate sections of the main column (M/H modules 4 and 5), (ii) the diameter of these 4 M/H modules should be approximately the half of that in M/H modules 3 and 6 so that the column has a uniform diameter and (iii) the height (H_e) of M/H modules 1, 2, 4 and 5 is calculated using the intermediate section definition (equation (7.17)) whereas for the remaining M/H modules equation (6.89) holds. These conditions are given below:

$$M_1 + M_2 - M_4 - M_5 = 0 \quad (7.26)$$

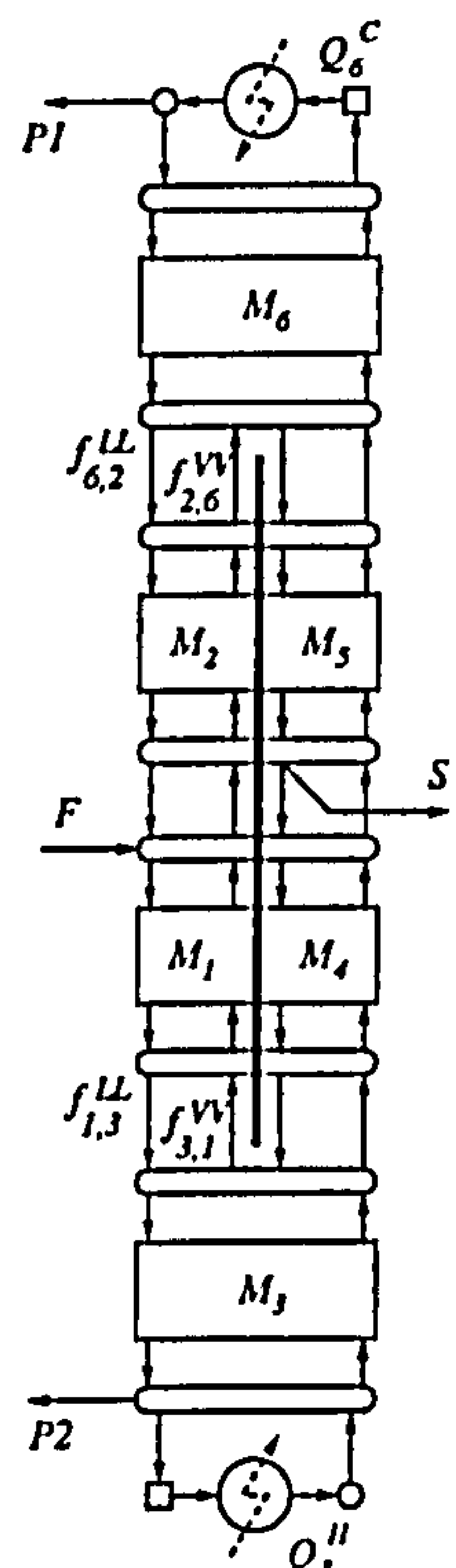
$$D_1 = D_2 = D_4 = D_5 = D_3/2 \quad (7.27)$$

$$H_e = 2(M_e + 2), \quad e = 1, 2, 4, 5 \quad (7.28)$$

$$H_e = (2 + 0.2)(M_e + 2), \quad e = 3, 6 \quad (7.29)$$

Having incorporated the above structural particularities in the GMF/OC Physical Model of the DWC, the synthesis problem was implemented in GAMS minimizing the column's TAC. The GMF/OC DWC structural representation along with the optimization results are given in Table 7.10. The TAC of the DWC was found equal to 2,010,000 \$/yr, which corresponded to an operating cost of 1,673,800 \$/yr and to an annualized capital cost of 336,200 \$/yr. This column provided annual savings of \$85,900 in comparison to the Petlyuk column and is slightly less economical than the best HI simple sequence. From these results, it is shown that the DWC has indeed almost the same energy consumption as the Petlyuk column, which validated

Table 7.10: GMF/OC Dividing Wall Column Optimal Design and Operation



	$F(kmol/hr)$	x_{benz}	x_{tol}	x_{o-xyt}
$P1$	208.7	0.95	0.05	0
S	388.9	0.004	0.95	0.046
$P2$	402.4	0	0.05	0.95
$f_{6,2}^{LL}$	264.6	0.24	0.737	0.023
$f_{2,6}^{VV}$	685.6	0.383	0.592	0.025
$f_{3,1}^{VV}$	673.7	0.003	0.735	0.262
$f_{1,3}^{LL}$	1252.7	0.002	0.547	0.451
Column Design				
Trays	$M_6=4.3$ $M_2=9.6, M_5=8.2$ $M_1=7.2, M_4=8.6$ $M_3=6.4$			
D_e	$D_{3,6}=8.6, D_{1,2,4,5}=4.3$			
Q_e^H	10312.5			
Q_e^C	9858.8			

the thermal equivalence assumption. Therefore, the main advantage of the DWC, which makes it the most economical complex column for the examined separation problem, is related to its capital cost savings by achieving this separation from one column.

7.3.2 GMF/OCFE Complex Column Sequencing Formulation and Results

In order to construct the GMF/OCFE synthesis model for the ternary complex column sequencing problem of Benzene, Toluene and o-Xylene, the corresponding GMF Structural Model was coupled to the GMF/OCFE Physical Model, using the 2 Finite Element - 2 Interior Collocation point discretization scheme for each M/H module. $\mathcal{F}^{max}$ was set equal to 1800 kmol/hr , for the mixed integer constraints. The GMF/OCFE model also incorporated the additions made in the GMF/OC model for addressing the particularities in the M/H module diameter and height definition of complex columns (*note*: in these additional equations the M/H module heights had to be modified according to the OCFE principles, by replacing each M_e term with $\sum_{l \in L_e} M_{e,l}$).

The GMF/OCFE complex column sequencing problem was implemented in GAMS and

solved using the GBD/APROS methodology. As in the GMF/OC, the optimal sequence was found to be the Petlyuk column, with a Total Annualized Cost of 2,075,100 \$/yr (operating cost of 1,657,200 \$/yr and Annualized Capital Cost of 417,900 \$/yr). The design and operation optimization results are shown in Table 7.11.

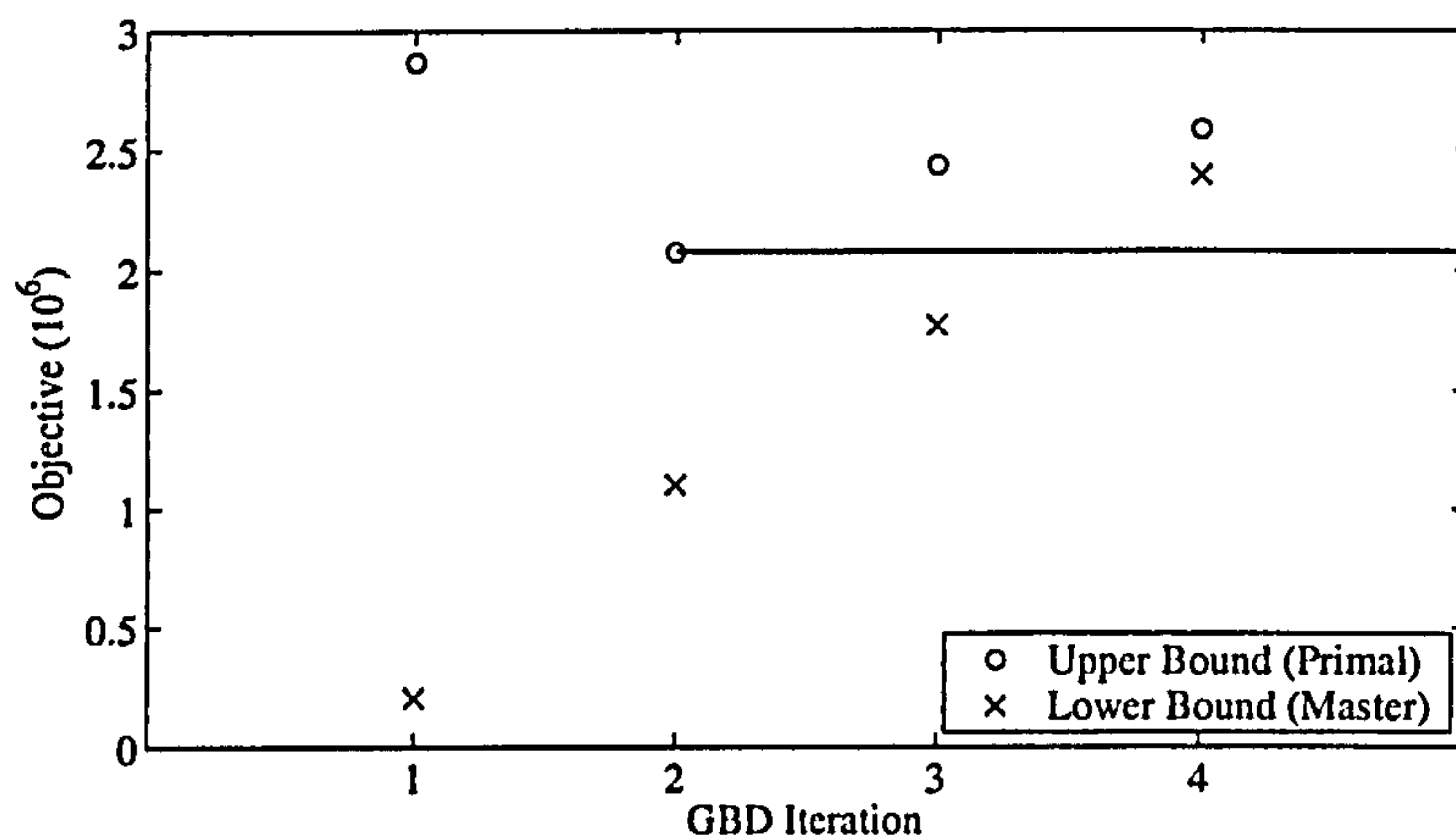
As encountered throughout this work, the GMF/OCFE optimal design and operation of the Petlyuk column was found to be slightly improved over that of the GMF/OC (whose TAC was equal to 2,095,900 \$/yr). Moreover, by a comparison of all the simple, *HI* and complex column optimal solutions obtained through the GMF/OCFE, the Petlyuk column was found 28% more economical than the best simple column sequence (savings of 793,600 \$/yr) and slightly less economical than the best Heat Integrated simple column sequence (4% difference in the TAC, corresponding to 100,700 \$/yr). This remark was in agreement with the results obtained also through the GMF/OC.

The details of the MINLP/GBD iterations from the problem solution using the GMF/OCFE are given in Table 7.12. The computational performance of the GMF/OCFE for the complex column sequencing is the same as that of the GMF/OC. Convergence was obtained in 4 GBD

Table 7.11: GMF/OCFE Complex Column Sequencing Optimal Design and Operation

	$F(kmol/hr)$	x_{benz}	x_{tol}	x_{o-xyI}		
$P1$	207.5	0.95	0.05	0		
S	388.9	0.007	0.95	0.043		
$P2$	403.6	0	0.05	0.95		
$f_{6,2}^{LL}$	220.4	0.25	0.731	0.019		
$f_{2,6}^{VV}$	592.4	0.425	0.552	0.023		
$f_{3,1}^{VV}$	585.3	0.009	0.755	0.237		
$f_{1,3}^{LL}$	1213.3	0.007	0.557	0.436		
	<i>Prefrac.</i>		<i>Main</i>			
<i>Trays</i>	$M_{6,1}=2.1, M_{6,2}=2.1$					
	$M_{2,1}=4.7, M_{2,2}=2.5$					
	$M_{5,1}=2.9, M_{5,2}=2.6$					
	$M_{1,1}=5.1, M_{1,2}=2.3$					
	$M_{4,1}=5.7, M_{4,2}=2.3$					
	$M_{3,1}=4.6, M_{3,2}=3.8$					
D_e	6.602	8.612				
Q_e^H	-	10211.2				
Q_e^C	-	9757.8				

Table 7.12: GMF/OCFE Complex Column Sequencing GBD Convergence History



Iter.	<i>Primal</i>	<i>Master</i>
1	2.868 10 ⁶	0.205 10 ⁶
2	2.075 10 ⁶	1.102 10 ⁶
3	2.434 10 ⁶	1.769 10 ⁶
4	2.637 10 ⁶	2.423 10 ⁶

iterations starting from the Simple Sequence (best simple column). The best upper bound to the solution was found in the second Primal subproblem which corresponded to the Petlyuk column (optimal sequence). The last 2 GBD iterations generated the suboptimal Side Stripper and Side Rectifier Sequences.

GMF/OCFE Dividing Wall Considerations

In order to evaluate the DWC using the GMF/OCFE model, the same 2-step optimization problem was employed. Since the first step, that is, the solution of the MINLP complex column sequencing problem, generated as the optimal sequence the Petlyuk column (thermally equivalent of the DWC), the second step optimized the DWC with respect to its TAC and subject to the product stream specifications. The GMF/OCFE Physical Model incorporated the additional structural conditions of Section 7.3.1, imposing the prefractionating column to be located within the main column shell. From these conditions, equation (7.27) remained unchanged, however, equations (7.26), (7.28) and (7.29), were replaced by the following:

$$\sum_{l \in L_1} M_{1,l} + \sum_{l \in L_2} M_{2,l} - \sum_{l \in L_4} M_{4,l} - \sum_{l \in L_5} M_{5,l} = 0 \quad (7.30)$$

$$H_e = 2 \left[\sum_{l \in L_e} M_e + 2 \right], \quad e = 1, 2, 4, 5 \quad (7.31)$$

$$H_e = (2 + 0.2) \left[\sum_{l \in L_e} M_e + 2 \right], \quad e = 3, 6 \quad (7.32)$$

The generated NLP problem was solved in GAMS for the minimization of the system's TAC. The results of the optimization with respect to the column design and operating conditions are given in Table 7.13. The TAC of the DWC was found equal to 1,983,600 \$/yr (operating cost 1,643,400 \$/yr and annualized capex 340,200 \$/yr). That means that the GMF/OCFE model also found the DWC as the most economical complex column, with annual savings of 91,500 \$/yr in comparison to the Petlyuk column. The main contribution to this improvement was related to the capital expenditure of the DWC, whilst the operating cost of the two columns was found equivalent. However, from a comparison to the best Heat Integrated simple column, the latter still remained the most economical sequence, even by a small margin, which was the result obtained also through the GMF/OC. Finally, from a comparison between the DWC results obtained through the GMF/OC and GMF/OCFE, the latter like elsewhere in this work has resulted in a slightly more improved column design and operation from an economical point of view.

Table 7.13: GMF/OCFE Dividing Wall Column Optimal Design and Operation

	$F(\text{kmol/hr})$	x_{benz}	x_{tol}	$x_{\text{o-xyl}}$
$P1$	208.9	0.95	0.05	0
S	388.9	0.004	0.95	0.046
$P2$	402.2	0	0.05	0.95
$f_{6,2}^{LL}$	245.3	0.253	0.726	0.021
$f_{2,6}^{VV}$	643.8	0.405	0.572	0.023
$f_{3,1}^{VV}$	635.1	0.004	0.757	0.239
$f_{1,3}^{LL}$	1236.6	0.003	0.559	0.438
Column Design				
Trays	$M_{6,1}=2.1, M_{6,2}=2.1$ $M_{2,1}=5.4, M_{2,2}=3.4, M_{5,1}=4.3, M_{5,2}=3.4$ $M_{1,1}=4.3, M_{1,2}=3.3, M_{4,1}=5.4, M_{4,2}=3.3$ $M_{3,1}=4.6, M_{3,2}=3.8$			
D_e	$D_{3,6}=8.6, D_{1,2,4,5}=4.3$			
Q_e^H	10126.5			
Q_e^C	9672.8			

7.4 Conclusions

In the previous chapters of this work, GMF Structural Models have been developed for the synthesis of distillation column sequences involving simple, heat integrated and complex columns. The task in this chapter was the enhancement of the GMF synthesis model for the above problems by incorporating in the GMF Physical Model principles from the Orthogonal Collocation and Orthogonal Collocation on Finite Elements methods for order reduction of distillation models. The enhancements were directed towards obtaining more accurate representations of the underlying physical phenomena and more detailed sequencing designs, with information about the modules' dimensions (trays, diameters) capturing the interactions between operating and capital cost, while maintaining the GMF's combinatorial and continuous compactness.

The two synthesis frameworks, namely the GMF/OC and the GMF/OCFE were applied to the ternary sequencing problems, allowing for formal Total Annualized Cost optimizations using detailed costing models thus determining both column design and operation. Moreover, both of the proposed synthesis methods were found capable of *explicitly* representing and capturing the economic advantages of particular designs, such as the Dividing Wall Column, which was evaluated only *implicitly* through the 'conventional' GMF. Moreover, from a distillation separation point of view, both models demonstrated the overwhelming economic benefits by employing Heat Integration and Thermal Coupling techniques in distillation sequence design instead of the traditional simple columns.

The above enhancements were achieved while keeping the problem size small and independent of the number of trays in each column and without the introduction of additional binary variables. The GMF/OCFE despite adding a slight representational complexity and increase of the problem size, has been proven of obtaining slightly better designs from an economic point of view, which is inherently related to the increase of the method's accuracy through the incorporation of Finite Elements. Finally, from the examined sequencing problems, both discretization methods were found highly compatible with the GMF Physical and Structural Models, both from a distillation representation and computational point of view.

Chapter 8

Conclusions and Suggestions for Future Directions

8.1 Conclusions

In Chapter 1, the target for this thesis was set as the synthesis of energy efficient simple, heat integrated and complex distillation column sequences, through the systematic generation and evaluation of the alternatives designs, in a compact and unified way. This problem of significant economic and scientific interest required the tackling of underlying structural and physical complicating issues. These were inherently related to the increasing 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 prompted many major research groups both in academia and industry to propose methods for the distillation column sequencing problem, addressing it in its entirety or certain components of it.

In this work the synthesis of distillation column sequences for energy efficiency was addressed through the Generalized Modular Framework (GMF), which is a superstructure optimization method for process synthesis at the conceptual level. Like most superstructure methods the GMF consists of a Structural and a Physical Model, which are, respectively, responsible for the generation of the process alternatives and for their physical representation and evaluation with respect to the design targets. The GMF Structural Model employs multipurpose Mass/Heat (M/H) and Pure Heat (He) modules as building blocks. In the distillation sequencing prob-

lem the embedded connectivities of the latter allowed for the structural representation of the alternative column sequences. The GMF Physical Model which is based on aggregated models captured the underlying physical phenomena and the energy consumption of the represented systems. This was achieved while avoiding potentially limiting simplifying assumptions and while generating considerably compact problems, thus reducing the computational effort required for their solution. In order to tackle the column sequencing problem efficiently the problem was *systematically* decomposed and examined into its constituent components, namely the evaluation of the GMF distillation column physical representation and then the synthesis of sequences of simple, heat integrated and complex columns.

GMF Distillation Column Physical Representation

In Chapter 2 focus was laid on the physical representation of non-azeotropic distillation columns through the GMF. Based on previous experience using the GMF, its physical model was modified through the introduction of Auxiliary blocks replacing the mixers and splitters at the two ends of each M/H module. This allowed for a more accurate representation of the physical phenomena in distillation systems. The physical models and the interconnections of the GMF Building Blocks were then systematically defined and organized in order to provide the basis for the representation of single and sequences of distillation columns. The validation of the GMF distillation physical representation was carried out over the examination of a binary distillation separation and a comparison to a rigorous tray-by-tray model. The GMF achieved capturing the general mass and heat exchange trends in the column and its energy consumption, for which it provided a valid lower bound. The validity of the results was based on the fact that the GMF is based on a physical model which avoids common simplifying and potentially limiting assumptions such as sharp splits, isothermal operation, equimolar flowrates, *etc.*. At the same time, through a systematic degree of freedom analysis, it was found that these results were obtained, while generating a physical problem of significantly smaller size when compared to that of the rigorous model, with immediate effects on the computational effort.

GMF Simple Distillation Column Sequencing

The work on the GMF representation of a single distillation column focused on addressing the physical complexity of the examined distillation systems. The structural complexities were ev-

ident only when the synthesis of simple column sequences was examined in Chapter 3. The number of structural alternatives increased with the number of components to be separated. Beyond the identification of the structural alternatives, the GMF building blocks had to be interconnected in appropriate ways so that these alternatives were structurally represented through the GMF. For that purpose, a systematic method was proposed for the construction of the GMF Structural Model for the automatic arrangement of the GMF Building Blocks for the generation of all the alternative sequences. This model was then coupled to the GMF Physical Model as developed in Chapter 2 and to a formal solution algorithm for the generated MINLP problem. The method was employed for the first two members of the multicomponent distillation column sequencing problem. From the derived results the GMF obtained the optimal column sequences, which provided large energy savings when compared to the other (suboptimal) alternatives. Moreover, the results which were in agreement with those reported in the literature, were derived from the GMF aggregated models generating compact MINLP problems. The efficiency of the method was particularly enhanced through the use of the decomposition MINLP solution procedure, through which the most energy efficient sequence was found without the evaluation of *all* the alternative sequences, as would have occurred through enumeration techniques.

GMF Heat Integrated Distillation Column Sequencing

In Chapter 4 the energy savings achieved through the selection of the most energy efficient distillation column sequence were enhanced considerably through the formal incorporation of heat integration techniques. A method was proposed which was based on the use of a newly introduced Heat Integration (*HI*) block in the GMF, which allowed for the systematic incorporation of heat integration possibilities structurally and physically. The GMF Synthesis Model for the simple column sequencing problem was modified accordingly for the incorporation of the *HI* block and its accompanying structural and physical models. Particular attention was laid on the GMF *HI* Physical Model, so that the effects of pressure were *explicitly* taken into consideration. The method was used for the ternary and quaternary *HI* sequencing problems. The GMF generated the optimal *HI* sequences obtaining energy savings of 40% when compared to the non-heat integrated optimal column sequences. The GMF also captured accurately the effects of the columns' pressure, so that feasible heat integration schemes could be realized.

GMF Complex Distillation Column Sequencing

In Chapter 5 the simple column sequencing problem for energy efficiency was extended to include complex column sequences, that is, columns which are partially or fully thermally coupled. For this purpose, a new synthesis method was proposed where the complex structural possibilities could be efficiently captured. The method was applied to the ternary complex sequencing problem, based on the development of a new GMF Structural Model incorporating all the simple and complex column sequences in a unified way. Furthermore a systematic initialization and bounding procedure was applied for the solution of the generated physical NLP problems, in order to tackle the increased complexity of the physical representation of complex columns with their multiple interconnections for their thermal coupling. From the examined case study the GMF captured the energy efficiency of the thermally coupled columns and especially that of the Petlyuk column. The latter was found to provide energy savings around 30% when compared to the best simple column sequence. Moreover, the GMF despite using only aggregated models provided useful insights on the operation and thermodynamic efficiency of this column, which were validated *quantitatively* and *qualitatively* for their accuracy through a comparison to a rigorous tray-by-tray model.

GMF Structural Modelling

It must be mentioned that all the proposed GMF synthesis models for the sequencing problems examined were based on alternative GMF Structural Models which were constructed in a systematic 3-stage procedure. Appropriate GMF Structural Sets were introduced arranging the GMF Building Blocks according to their topology in the problem superstructures. In the 1st stage the Interconnection Principles between the GMF Building Blocks were posed as propositional logic expressions, where the binary variables were replaced by their corresponding Boolean (logical) variables. The propositional expressions according to their function in the GMF Structural Model were categorized into Superstructure Basis, Intra-Column and Inter-Column. The Superstructure Basis expressions provided information on the maximum or minimum number of building blocks and fixed structural components that participated in all the structural alternatives. The Intra and Inter-Column expressions were responsible for providing the necessary rules, interconnecting the GMF Building Blocks for the representation of single columns and their sequences, respectively. In the 2nd stage the propositional expressions were

transformed into their conjunctive normal form and then into their corresponding (pure integer) GMF Structural Constraints, while replacing the Boolean variables with their corresponding binary variables. From the generic models of stage 2 the structural models for the particular problems examined (ternary or quaternary) were generated through the appropriate assignment of the GMF Structural Sets, which constituted the 3rd stage of the procedure. These constraints were incorporated in the generated MINLP problems. It must be noted that the GMF Structural Models generated in this systematic procedure were always accurate and tight, which was proved particularly beneficial for the accurate generation of all the feasible (physically meaningful) structural alternatives and the solution of the synthesis problems. This was particularly important for the GMF which is based on building blocks of high levels of structural abstraction (where distillation columns are not represented *a priori*). Moreover, the tightness of the generated problems enhanced considerably the computational efficiency of the proposed methods since the solution of each structural problem in the decomposition MINLP algorithm required only minimum computational effort for its solution.

GMF Physical Representation Enhancement

The GMF Physical Model employed in the above sequencing synthesis methods was based on aggregated models which captured the general trends of the underlying physical phenomena and generated valid lower bounds on the energy consumption of the represented systems. Information was utilized only at the boundaries of the building blocks and the capital costing could potentially be estimated through approximate models. In order to enhance the representation of the physical phenomena taking place within the GMF Building Blocks and to obtain detailed design results (column trays and diameters) along with the sequencing results, in Chapter 6 the GMF Physical Model was coupled to formal discretization techniques for distillation order reduction. Alternative GMF Orthogonal Collocation (GMF/OC) and GMF Orthogonal Collocation on Finite Elements (GMF/OCFE) Physical Models were therefore proposed. Each main *M/H* module was discretized into collocation points (and Finite Elements) and the enthalpies and component flowrates were approximated by appropriate Lagrange polynomials. The locations of the collocation points over a *M/H* module were explicit functions of the number of trays in the column section to be included in the optimization problem. The distillation MESH equations were only imposed on the interior collocation points, thus maintaining the compactness of the

GMF. Moreover, the estimation of the tray numbers did not introduce new binary variables, thus not increasing the combinatorial size of the generated problem. This also had the advantageous effect of allowing the solution of formal design problems for distillation, by taking into consideration the interactions between operating and capital expenditure simultaneously, during the solution of the continuous optimization subproblems. The proposed GMF/OC and GMF/OCFE models were validated for a binary distillation separation through a comparison to a rigorous tray-by-tray model. The GMF results were virtually identical to those of the rigorous model, demonstrating a significant enhancement in the physical representation of the GMF, while still generating compact optimization problems and maintaining the representational advantages of the GMF.

GMF Distillation Column Sequencing For Cost Efficiency

In Chapter 7 the proposed GMF/OC and GMF/OCFE Physical Models were coupled to the GMF sequencing structural models as proposed in the previous chapters, allowing the derivation of not only the optimal column sequences and their energy consumption but also their detailed designs with respect to the number of trays and the column diameters. That allowed for the use of accurate costing models to be employed, increasing the accuracy of the obtained results. Therefore, the Synthesis Target was extended to the synthesis of simple, heat integrated and complex column sequences for overall *cost efficiency*. Moreover, from a representation perspective, specific designs such as the Dividing Wall Column, which could only be *implicitly* examined through the ‘*conventional*’ GMF, were now able to be evaluated *explicitly*. The results obtained for the sequencing problems demonstrated the efficiency and accuracy of the proposed methods, providing *actual* energy consumptions (not lower bounds) and detailed sequencing designs. The GMF/OC obtained cost efficient column sequences trading-off operating and capital cost and generating detailed column designs. Furthermore, the GMF/OCFE provided even better solutions from an economic point of view, but at an increase of the generated problem size and complexity, due to the introduction of the Finite Elements in each main M/H module. However, despite its increase, the size of both the GMF/OC and GMF/OCFE was still smaller than that of the rigorous models and independent of the increase in the number of trays, thus maintaining the compactness advantage of the ‘*conventional*’ GMF. Finally, it is particularly interesting to note that the obtained optimal sequences for all the examined synthesis problems were identical

to those of the ‘conventional’ GMF. This is the direct result of the latter’s accurate capture of the systems’ energy consumption, which provides the main contribution to the Total Annual Cost of distillation columns and thus constitutes the main driving force in the optimization synthesis problems.

GMF Enhancement - Computational Implementation

From a computational implementation point of view, the GMF/OC and GMF/OCFE were found highly compatible with the ‘conventional’ GMF (Structural and Physical Models). That was made possible due to the modular formalism of the GMF and of the collocation techniques, which treat the distillation columns in a section-wise manner. The GMF/OC and GMF/OCFE were implemented using blocks of *common* and *substituting* and *supplementary* constraints. The last two constraint blocks replace and are added to the ‘conventional’ GMF constraints for the generation of the GMF/OC and GMF/OCFE models. This implementation provided a certain ‘separability’ effect, so that the user could select, at will, the model to utilize according to the synthesis targets and the representation detail desired. The ‘conventional’ GMF could be used for conceptual design studies, selecting accurately the most energy efficient column sequence, while generating the most compact problem size. The GMF/collocation models can be used for detailed design studies for total cost efficiency targets, at a relative increase of the problem size.

Furthermore, from a computational functionality perspective, the GMF/collocation methods allowed the GMF to be used for simulation analysis. This provided additional versatility and efficiency to the GMF, being readily implementable in modelling environments, such as gPROMS (Process Systems Enterprise Ltd., 1998), thus allowing the use of the latter’s embedded features and advantages, such as physical property packages, more rigorous solvers, *etc.*. As an illustration, this was found considerably useful during a synthesis study of the reactive absorption of NO_x gases (OPT ABSO European Project, 2003). The latter is a system used for the production of nitric acid and the removal of NO_x from flue gases of combustion plants. A GMF/OC reactive absorption model was developed and implemented in gPROMS for the validation of the physical representation of a two-section absorption column system with a side stream feed, taken from Emig and Wohlfahrt (1979). The model included additional constraints defining a reaction system of reversible and irreversible reactions in both the gas and liquid phases, correlations for the column hydraulics and equations for removal of heat due to reaction

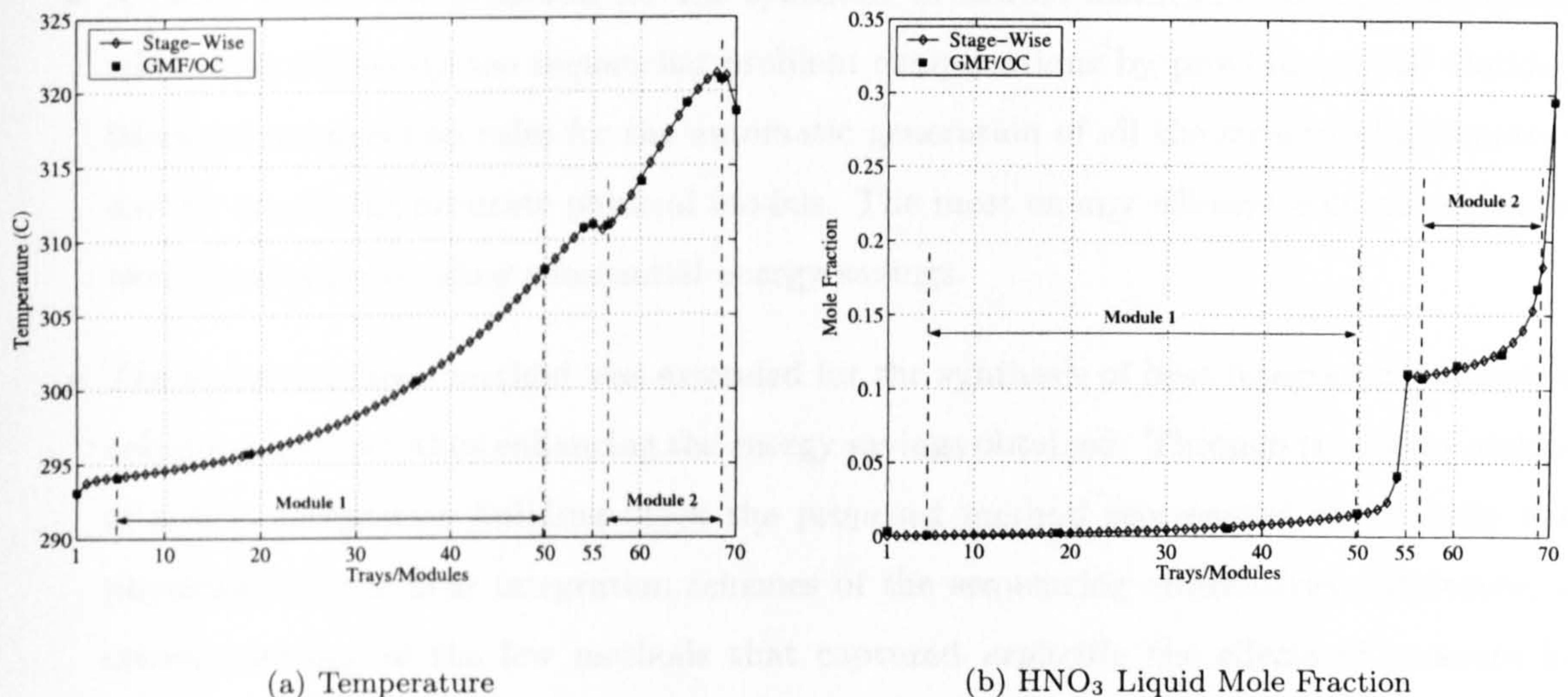


Figure 8.1: Comparison of GMF/OC to Stage-Wise Model - NO_x Absorption

from the column. Using gPROMS allowed the determination of the physical property variables via the physical property package MultiFlash, using the Soave-Redlich-Kwong model for the fluid enthalpies and densities and the NRTL model for the liquid phase activities.

The simulation problem was solved using the non-linear equation solver NLSOL and compared to a rigorous tray-by-tray model for the system. Key internal profiles from the simulation results are given in Figure 8.1. These results illustrate the accuracy and versatility of the GMF/OC which approximated closely the rigorous model for this complex system. It must be stressed that the solution of the generated problem was facilitated considerably by the use of the MultiFlash package, which is readily available in gPROMS and not in GAMS.

8.1.1 Key Contributions From This Work

The key contributions from this work can be *summarized* in the following points:

- The GMF Physical Model was modified systematically through the introduction of Auxiliary Blocks, enhancing the physical representation of systems where mass and heat exchange take place simultaneously. Moreover, the GMF Building Blocks and their underlying physical models and interconnections were systematically organized providing accurate physical representations of distillation columns and a basis for distillation column sequencing problems.

- A GMF model was proposed for the synthesis of simple distillation column sequences, addressing efficiently the sequencing problem complications by providing GMF Building Block interconnection rules for the automatic generation of all the structural alternatives and by employing accurate physical models. The most energy efficient column sequences were obtained, providing substantial energy savings.
- The above synthesis method was extended for the synthesis of heat integrated distillation column sequences, thus enhancing the energy savings obtained. Through the incorporation of a heat integration building block the proposed method represented structurally and physically all the heat integration schemes of the sequencing alternatives. Moreover, it constituted one of the few methods that captured *explicitly* the effects of pressure by including it in the optimization problems as an additional degree of freedom.
- A GMF model was proposed for the synthesis of complex distillation column sequences, based on a structural model that captured the complex structural possibilities. The GMF Physical Model, despite its aggregation, provided useful insights on the thermodynamic efficiency of the Thermally Coupled Columns and the subsequent energy savings they generated. The method constitutes one of the few MINLP methods addressing efficiently the structural and physical aspects of the complex column sequencing problem.
- The developed GMF Structural Models for the above sequencing problems were generated in a systematic 3-stage procedure and were proven accurate and efficient for the problems examined. Moreover, these structural models were also implemented as *stand-alone* and easy to use GAMS MILP computer codes, which can be readily coupled to methods for distillation physical representation, whether they use shortcut or rigorous models. This could potentially provide a substantially useful tool to the distillation column sequencing research both in academia and in industry.
- In general, the GMF addressed efficiently the synthesis of *energy efficient* distillation column sequences, which constitutes one of the most challenging problems in chemical engineering. This was achieved by coupling a formal MINLP solution algorithm to alternative structural models and to aggregated physical models, which generated compact optimization problems while avoiding common distillation simplifying and potentially limiting assumptions. Due to its representational validity and its compactness, the GMF can

be viewed as a '*best of both worlds*' approach for conceptual design, between rigorous and simplified models, balancing model accuracy and computational efficiency.

- The GMF Physical Model was further enhanced through the incorporation of formal collocation techniques, discretizing the GMF Building Blocks and allowing the derivation of valuable intra-module information. This led to a GMF physical representation of distillation columns which *virtually* attained that of rigorous models. In general this can be viewed as the incorporation of components of a simulation tool into the GMF conceptual design method. Moreover, this was achieved while maintaining the representational advantages of the GMF, that is, avoiding simplifying assumptions and generating compact optimization problems.
- The proposed GMF/Collocation methods extended the Synthesis Target into the synthesis of *cost efficient* distillation column sequences. Based on the developed GMF sequencing Structural Models and on formal MINLP solution algorithms, the GMF/Collocation synthesis methods, obtained the most cost efficient simple, heat integrated and complex column sequences. Moreover, the proposed GMF/Collocation methods allowed the *explicit* representation and evaluation of complex columns such as the Dividing Wall Column, which could only be implicitly represented through the '*conventional*' GMF. Using explicit functions of column trays and diameters without the use of additional binary variables, accurate costing models were employed, capturing *simultaneously* the interactions between operating and capital cost in the distillation sequencing design.
- In general, through the GMF it was the *first time* that the collocation models for distillation were employed in a formal distillation column sequencing synthesis method. The proposed methods and the derived results demonstrated the validity, efficacy and adequacy of the collocation models for the synthesis problems examined.
- The incorporation of collocation method principles in the GMF allowed the latter to be used in simulation analysis and its implementation in modelling packages, such as gPROMS, allowing the use of the latter's embedded features and advantages, such as the use of thermodynamic property packages. This enhanced the efficacy and flexibility of the GMF, making it capable of tackling even highly complex synthesis problems.

8.2 Suggestions for Future Directions

Potential areas for further investigation, along the lines set in this thesis, can focus on:

8.2.1 GMF Representations

GMF Satellite Column Superstructure

For the examination of the ternary complex distillation sequencing problem, the construction of the GMF Structural Model was based on the Sequential Column Superstructure of Sargent and Gaminibandara (1976). However, as shown in Agrawal (1996), when higher than ternary separations are examined, this superstructure incorporates only a subset of the structural alternatives. On the contrary, the satellite column superstructure of Agrawal (1996) is a more complete superstructure incorporating more Fully Thermally Coupled distillation columns. Nevertheless, the work on this type of superstructures has been conceptual and, apart from an effort in Caballero and Grossmann (2001), has never been implemented in a formal synthesis method. Based on the systematic 3-stage procedure employed throughout this work, a GMF Structural Model can be generated translating mathematically the satellite column guidelines proposed in Agrawal (2003), for the generation of *all* the Fully Thermally Coupled columns. Using the guidelines of the aforementioned publication the derived structural models could be extended to the generation of *all* the structural alternatives, including non-(Fully) Thermally Coupled columns, in a unified way. The derived models could then be used as stand-alone MILP problems implemented in GAMS for the generation of *all* the structural alternatives or could be coupled to the GMF, GMF/OC or GMF/OCFE models for the complete complex column sequencing problem for energy or cost efficiency, generating potentially highly economic designs.

GMF Heat Integrated Complex Distillation Columns

In the reported literature and in this work the Heat Integrated and Complex column sequences for energy and total cost efficiency were examined separately. Both types of column sequences generated high energy savings. It is an open question whether the combination of heat integration and thermal coupling techniques can be combined for the increase of the obtained energy savings. From a structural and physical point of view, the GMF can provide the framework in order to examine the effects of heat integrating the various sections of thermally coupled

columns. The underlying issue is whether the two techniques are contradictory to each other, that is, if the enforcement of heat integration and thus the pressure shifting of some column sections can have a negative effect on the thermal coupling of the columns. However, if this cannot be derived theoretically, then a simple motivating example (using, for instance a partially thermally coupled sequence, like the side stripper or the side rectifier) can be used for examining the energy savings of the method. If the latter is proven valid by generating substantial energy savings, then it could be readily extended to a formal synthesis method.

GMF Reactive Complex Distillation Columns

In this work, the GMF has been implemented for the investigation of energy efficiency possibilities through the use of complex arrangements in distillation, such as the Petlyuk Column. The GMF has also been used for the representation of reactive distillation columns (Ismail *et al.*, 2001). However, these column arrangements have been studied separately. It is possible that energy favourable structures could be generated by a potential combination of thermal coupling and reactive distillation. These possibilities could be investigated through a potential GMF representation of a (fully) thermally coupled reactive distillation column. Furthermore, for reactive distillation systems (for instance, the metathesis of 2-Pentene into 2-Butene and 3-Hexene (Al-Arfaj and Luyben, 2002)), a reactive Petlyuk column with a recycle side stream could be proven particularly beneficial to the system economics. The prefractionating column could operate as a reactive/separating section operating at temperature levels more suitable for reaction and the main column of the Petlyuk arrangement could operate as a pure separating column at temperatures more adequate for separation. Since the main column can produce 3 product streams of high purity, it could potentially separate the reaction products (2-Butene and 3-Hexene) at the distillate and bottoms, respectively, and recover the unreacted components (2-Butene) from the side stream to be recycled back to the reactive/separating prefractionating column, potentially improving reaction yields and the overall TAC of the system. This example serves as a simple motivation and more reactive distillation systems and other complex columns could be integrated within this methodology. However, complicating issues might arise, like the appearance of reactive azeotropes, that would need to be taken into consideration.

Unified Framework For Process Synthesis

It was mentioned that based on the fact that most process flowsheets are based on reactive and separating parts, the GMF can be used in order to generate flowsheets in a unified way, using its *M/H* modules in a reactive and/or separating mode. In the current work, by incorporating Collocation techniques in the GMF, a substantial representation enhancement of the separating *M/H* modules was achieved. However, these Collocation techniques (using adequate polynomials) can be also used for the representation of reactive systems. An interesting and highly *ambitious* target would be to define GMF/Collocation modules for separation and for reaction and to combine them appropriately as building blocks for process flowsheets, without pre-postulating units. Based on appropriate structural models and on the enhanced and unified representational abilities of the GMF/Collocation building blocks, novel flowsheets or units could potentially be generated, enhancing considerably the economics of current processes.

8.2.2 GMF for the Control and Dynamic Behaviour of Distillation Systems

Multi-objective Optimization For Controllability Of Distillation Columns

The distillation column sequencing methods proposed in this work concentrated on the determination of the optimal process configuration with respect to economic criteria, such as the minimization of Total Annualized or Operating cost. However, issues like controllability were beyond the purpose of this work. Controllability indicates quantitatively how easily the system moves between multiple operating conditions, how severely multiple variables interact and the ability of a particular design to reject disturbances. Since controllability is an integral aspect of any process design study, it is particularly useful to be taken into consideration along with any economic criteria in the design stage. A research direction that could potentially enhance the applicability of the GMF is to extend the framework so that economic and controllability criteria can be considered. As proposed in Luyben and Floudas (1994), controllability can be examined in the distillation systems through the incorporation of open-loop steady-state controllability measures, relating the controlled, manipulated and disturbance variables, which also participate in the design problems. These controllability measures which depend on the process itself do not require the *a-priori* knowledge of a particular control scheme. Common controllability measures can be used as objectives in the optimization problem, such as the minimization of the condition

number of the process transfer function matrix, the minimization of the disturbance condition numbers, *etc.* In order to perform the distillation column sequencing design and controllability studies simultaneously, so that the existing interactions between them are captured efficiently, a multi-objective optimization problem could be formulated. The resulting problem can be solved employing formal multi-objective solution algorithms, like the ϵ -Constraint method.

Distillation Column Dynamic Behaviour And Interactions Of Design And Control

The discretization of the main M/H modules has allowed the incorporation of explicit functions of tray numbers and diameters of distillation column sections in the GMF. This information can then be utilized in functions providing the hold-up of the column trays. The steady-state distillation GMF/Collocation models proposed in this work can be extended to the dynamic behaviour of distillation columns and their sequences. These models can be readily employed for distillation column operation (simulation) and design studies (determination of the column sequences and tray numbers). If alternative control scheme functions are used between state and manipulated variables, to be included as additional constraints in the optimization problem along with potential disturbances, then the interactions of design and control can be simultaneously and efficiently captured. The solution of the optimization problem will generate distillation column designs that provide cost optimality and controllability. The advantages of this method will be inherently related on the compactness and accuracy of the generated problems. Moreover, the estimation of the tray numbers in the continuous problem will lead to an enhancement of the simultaneous capture of the interactions of design and control. The method can be tested, initially, for a single distillation column and can be easily extended to the sequencing problems using the structural models proposed in this thesis. The solution of the sequencing-control problems will be considerably facilitated by the compactness of the GMF/Collocation methods employed. Furthermore, the use of gPROMS for the dynamic optimization problems will be particularly beneficial, replacing the need to solve multi-period optimization problems in GAMS.

8.2.3 Solution Procedures and Logical Modelling

The robustness of the solution procedure for the physical problems (Primal subproblems) could be improved by the incorporation of well established tearing methods, such as the Sum Rates Method (Friday and Smith, 1964). In this method the temperature and pressure profiles are

initially fixed for the simultaneous solution of the mass balances and equilibrium constraints in an inner loop and then, in an outer loop, the temperature and pressure profiles are adjusted by solving the energy balances. This solution procedure could be very useful, since due to the compact size of the aggregated physical models, the solution in the inner loop (mass balances) is quite easy and fast, allowing more effort on the temperature-driven outer loop. Even if this method fails to converge, it should provide very good initial guesses, facilitating the derivation and improving the robustness of the nonlinear solutions.

As mentioned in this work, one of the most promising techniques in superstructure optimization is the Generalized Disjunctive Programming, (GDP). The work of Yeomans and Grossmann (2000*b*) has generated efficient distillation design methods. These modelling enhancements could be potentially implemented in the GMF Physical Models, increasing their efficiency and robustness. This could ultimately lead to a further enhancement of the GMF's structural and physical advantages.

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Appendix A

The Generalized Modular Framework

A.1 GMF Representation of Units

Using the GMF building blocks (Section 2.1.1) and appropriate interconnection principles, structural alternatives can result as combinations of *He* and *M/H* modules. The following process units have been represented by a single, or a combination, of the framework's building blocks (Papalexandri and Pistikopoulos, 1996).

Condenser/Reboiler/Heat Exchanger

A condenser, a reboiler or a heat exchanger can be represented in this framework through a *He* module where the two heat exchanging streams do not come into mass active contact. In the case of a condenser, the hot process stream is in the vapour phase, which changes phase while exchanging heat with a cold utility or a cold process stream. For a reboiler, the cold process stream is in the liquid phase, which changes phase while exchanging heat with a hot utility or a hot process stream. In a heat exchanger a hot process stream or utility exchanges heat with a cold process stream or utility, with or without phase changes.

A partial reboiler or condenser may be similarly defined, by relaxing the Phase Defining Constraints (presented in Appendix A.2) so that two phase streams are taken into consideration (a flash operation could then be used for the phase separation and the further stream processing within the framework).

Distillation Columns

A distillation column (equilibrium or not) which separates, for example, a binary mixture AB (assuming A more volatile than B) into two products A(B) and (A)B (with higher concentration of A and B, respectively), involves mass and heat transfer between the liquid and vapour mixtures $L_{A(B)}-V_{A(B)}$ and $V_{(A)B}-L_{(A)B}$ due to volatility differences. Therefore, a binary distillation column can be represented with at least two *M/H* modules (representing a rectifier and a stripper) and two *He* modules (representing a condenser and a reboiler).

In the lower module, representing the stripper, the liquid stream is enriched in the heavier component, B, which is transferred from the vapour stream $V_{(A)B}$ (rich in B, as its concentration in B decreases) to the liquid stream $L_{(A)B}$ (lean in B, as its concentration in B increases). At the same time A is transferred from the liquid (rich in A) to the vapour (lean in A) stream. In the Upper *M/H* module which represents the rectifier, A is transferred from the liquid stream (rich in A) to the vapour stream (lean in A), therefore enriching the vapour stream in A (the most volatile component) in the higher part of the column. Additionally, appropriate liquid and vapour interconnecting streams are necessary between the *M/H* and *He* modules.

Homogeneous Reaction

A reactor can be represented as a *M/H* module between the reagent mixture and the reaction product mixture. In the case of a reaction ($A + B \rightarrow C$), the liquid - liquid match occurs between: $L_{AB(C)} - L_{(AB)C}$. In this case only one inlet and outlet streams are allowed in the module. But the framework can include possibilities of recycle using bypass streams from the splitter of the *M/H* module outlet (product mixture stream). The possibility of a jacketed reactor can also be represented by interlinking the *M/H* module with a *He* module. In this case the product mixture stream (from the *M/H* module) exchanges heat with a cold utility. A CSTR is represented by the homogeneous liquid - liquid *M/H* module, assuming that the two streams in the match are well mixed. In the same way, a PFR can be realized as a battery of *M/H* modules.

Absorption/ Extraction

A single *M/H* module can represent an absorber or an extractor where a set of components is transferred between a process stream and a mass separating agent (not between the same

process streams as in distillation). The M/H module could correspond to trayed or to packed absorption/extractive columns.

Two Phase Reaction

The difference between the homogeneous reactor and the two phase reactor is that in the latter, streams of different phases are involved, where all the components of the reacting system can be found. Here, the lean side is the stream in which the concentration of the component of interest increases. The mass transfer term consists of two parts, one for the chemical equilibrium (reaction) and one for the phase equilibrium. The streams, as before are immiscible and recycle (bypass) streams can only be directed from the exchanger outlet stream splitters to the same stream inlet module mixers.

Reactive Distillation

As mentioned above, liquid - vapour matches with reaction can be represented in the GMF as a cluster of trays of reactive distillation. A reactive distillation column can be represented through the GMF with the minimum requirements of three liquid - vapour M/H modules (1 reactive/separating and 2 pure separating). In the reactive/separating M/H module, mass transfer is due to consumption/generation (reaction) and to volatility differences. In the case of the reaction of the type $(A + B \rightarrow C)$ all possible stream combinations are being considered in the superstructure: $L_{AB(CD)}$, $V_{AB(CD)}$, $L_{(ABC)D}$, $V_{(ABC)D}$, $L_{(AB)C(D)}$, $V_{(AB)C(D)}$, etc. Depending on the synthesis objectives different structures can evolve out of the superstructure, in which the reaction could take place in the liquid phase with the simultaneous transfer of some components from the vapour phase to the liquid and vice versa due to volatility differences in order to aid the chemical reaction. In similar fashion, reactive absorption or extraction can be accordingly represented.

The above show the versatility of the proposed framework, as process units can be identified from a process flowsheet of M/H and He modules, without the need to postulate these units during the synthesis task, since the superstructure only considers as building blocks modules, which are physically modelled including only fundamental mass and heat exchange principles.

A.2 Phase Defining Constraints

The streams that participate in the superstructure have postulated phases, depending on their composition, temperature and pressure. The Phase Defining Constraints are continuous inequality constraints applied in order to define the phase of each stream (liquid or vapour). The importance of having well defined liquid and vapour streams lies in the fact that the interconnections between the various blocks are such that allow mixing of streams of the same phase. Moreover, the Phase Defining Constraints, along with the Driving Force Constraints are needed for the thermodynamic consistency of the model, upon which the whole framework is based, since in the GMF no phase equilibrium constraints are applied directly between streams of different phases leaving the same M/H module.

For liquid phase streams at a given composition and pressure, the Phase Defining Constraints impose that the stream should be subcooled or, at the limit, saturated:

$$\sum_j^C (K_j x_j)^L \leq 1 \quad (\text{A.1})$$

$$K_j - \frac{\gamma_j P_{sat_j}}{\phi_j P} = 0 \quad (\text{A.2})$$

$$\sum_j^C x_j = 1 \quad (\text{A.3})$$

$$P_{sat_j} - P_{sat_j}(T) = 0 \quad (\text{A.4})$$

$$\gamma_j - \gamma_j(x_j, T, P) = 0 \quad (\text{A.5})$$

$$\phi_j - \phi_j(y_j^*, T, P) = 0 \quad (\text{A.6})$$

where, L , x_j , T , P , K_j , P_{sat_j} , γ_j , ϕ_j , y_j^* are the examined liquid stream and its liquid molar fraction, temperature, pressure, phase equilibrium constant, vapour pressure, liquid activity coefficient, fugacity coefficient and incipient vapour molar fraction, respectively.

Accordingly, for vapour streams at a given composition and pressure, the Phase Defining Constraints impose that the stream should be superheated or, at the limit, saturated:

$$\sum_j^C \left(\frac{y_j}{K_j}\right)^V \leq 1 \quad (\text{A.7})$$

$$K_j - \frac{\gamma_j P_{sat_j}}{\phi_j P} = 0 \quad (\text{A.8})$$

$$\sum_j^c y_j = 1 \quad (\text{A.9})$$

$$P_{sat,j} - P_{sat,j}(T) = 0 \quad (\text{A.10})$$

$$\gamma_j - \gamma_j(x_j^*, T, P) = 0 \quad (\text{A.11})$$

$$\phi_j - \phi_j(y_j, T, P) = 0 \quad (\text{A.12})$$

where, V , y_j , T , P , K_j , $P_{sat,j}$, γ_j , ϕ_j , x_j^* are the examined vapour stream and its vapour molar fraction, temperature, pressure, phase equilibrium constant, vapour pressure, liquid activity coefficient, fugacity coefficient and incipient liquid molar fraction, respectively.

In the above constraints any method for calculating the thermophysical properties can be incorporated. Therefore, the framework can be applied beyond cases where ideality is assumed. If however ideality can be assumed, then the following simplifications can be made:

- For ideality in the vapour phase (common assumption when pressures are lower than 10 atm), the fugacity coefficient can be assumed equal to unity: $\phi_j = 1$.
- For ideality in the liquid phase (when known ideal liquid mixtures are used and the pressures are low), the liquid activity coefficient is also assumed equal to unity: $\gamma_j = 1$.

Both the expressions for the liquid and the vapour phase defining constraints have an upper bound of unity. A lower bound is imposed on these constraints, with the nominal value of 0.8 (Ismail, 1998). This bound is not necessary and it is used in order to prohibit the system from high levels of superheating and supercooling.

A.3 Driving Force Constraints

The Driving Force Constraints were developed based on the analogies between mass and heat transfer. In the case of pure heat exchange, heat is transferred from a hot to a cold stream due to a temperature gradient. The pure heat transfer constraints are constructed according to the type of contact (countercurrent, concurrent, etc). For instance, in the case of the countercurrent *He* modules of the GMF, assuming a minimum temperature approach of ΔT_{min} , the Driving Force Constraints, applied at both sides of the module, are:

$$T_{hot}^{in} - T_{cold}^{out} \geq \Delta T_{min} \quad (\text{A.13})$$

$$T_{hot}^{out} - T_{cold}^{in} \geq \Delta T_{min} \quad (A.14)$$

However, in the case of mass transfer between two streams, the phenomena are multidimensional due to the number of components that simultaneously exchange mass and on the type of mass exchange mechanisms taking place. Usually, mass exchange occurs due to a concentration gradient between different immiscible phases, or between reactive streams (between reagent and product streams) or in combinations of the two. In these cases, the limiting condition for mass exchange is the physical equilibrium, the chemical equilibrium or a combination of the two, respectively. This limiting condition is a function of stream composition, temperature and pressure and it constitutes the basis of the Driving Force Constraints. Since temperature changes are allowed in the *M/H* modules, the latter can represent cases of either sequential or simultaneous mass and heat exchange. Therefore, the framework's *M/H* modules can be used for the representation of both energy and mass separating agent processes.

According to Papalexandri and Pistikopoulos (1996), mass and heat transfer occurs between streams of different phase and between reagent/product streams when reactions are possible. In Ismail (1998), these cases were extended to the combination of the two, covering simultaneous hybrid reactive/separating systems. The Driving Force Constraints were developed in order to ensure mass transfer feasibility between a rich and a lean stream, same as the heat Driving Force Constraints between a hot and a cold stream and to define the distribution of the components, in conjunction with the conservation laws. A rich stream, in a component of interest, j , is a stream with decreasing j concentration and a lean stream is the one with increasing j concentration (El-Halwalgi and Manousiouthakis, 1989). It is possible that the same stream could have the opposite identity for another component in a multicomponent mass transfer process. For instance, in the stripper of an ideal binary distillation column, the light component is transferred from the liquid to the vapour phase (hence, the liquid is the rich stream and the vapour is the lean stream). At the same time, the heavy component is transferred from the vapour to the liquid phase, hence, for that component the vapour is the rich stream and the liquid is the lean stream. Therefore, Driving Force Constraints have to be imposed for all transferred components, defining their distribution.

The condition for mass transfer between a rich and a lean stream is shown below. Let's assume two streams, Y and X with y_j and x_j concentrations in j , respectively. If the Y stream is the rich stream in j then, the following mass transfer condition should hold:

$$y_j \geq x_j \quad (\text{A.15})$$

on the contrary, if the X stream is the rich stream in j , then:

$$x_j \geq y_j \quad (\text{A.16})$$

To be more precise, mass transfer feasibility is ensured when the concentration of the transferred component in the rich stream is higher than its concentration that would have been in equilibrium with that of the lean stream. For instance, when physical equilibrium takes place between the above X and Y streams, the equilibrium relation and the mass transfer feasibility condition (assuming that Y is the rich stream in j), are:

$$(y_j)^{eq} = f_j^{eq}(x_j) \quad (\text{A.17})$$

$$y_j \geq (y_j)^{eq} \Rightarrow y_j \geq f_j^{eq}(x_j) \quad (\text{A.18})$$

In the above binary distillation example, these mean that for a rich stream in component j , the operating line should always be above the equilibrium line in a x - y diagram (the opposite should hold for the lean stream).

Similarly to the heat Driving Force Constraints, the Driving Force Constraints for mass and heat exchange are dependent on the type of contact. The Driving Force Constraints should be written for both sides of a M/H module, ensuring mass transfer feasibility inside the module. However, this holds when the equilibrium lines are convex for the rich and concave for the lean streams (as defined for each component). When this is not the case, driving force constraints should be taken in discrete points inside the M/H module.

Driving Force Constraint Property

An interesting point is that the Driving Force Constraints of the GMF do not require an *a-priori* knowledge of the mass transfer direction for each component in the various M/H modules. The framework determines the mass transfer direction for each component according to the phenomena taking place. The condition that always holds is that, *for each component, the product of the distance from the equilibrium and the change of the component's amount after passing through a M/H module, will always be greater or equal to zero, regardless of the mass transfer direction.* This property is demonstrated in the following example.

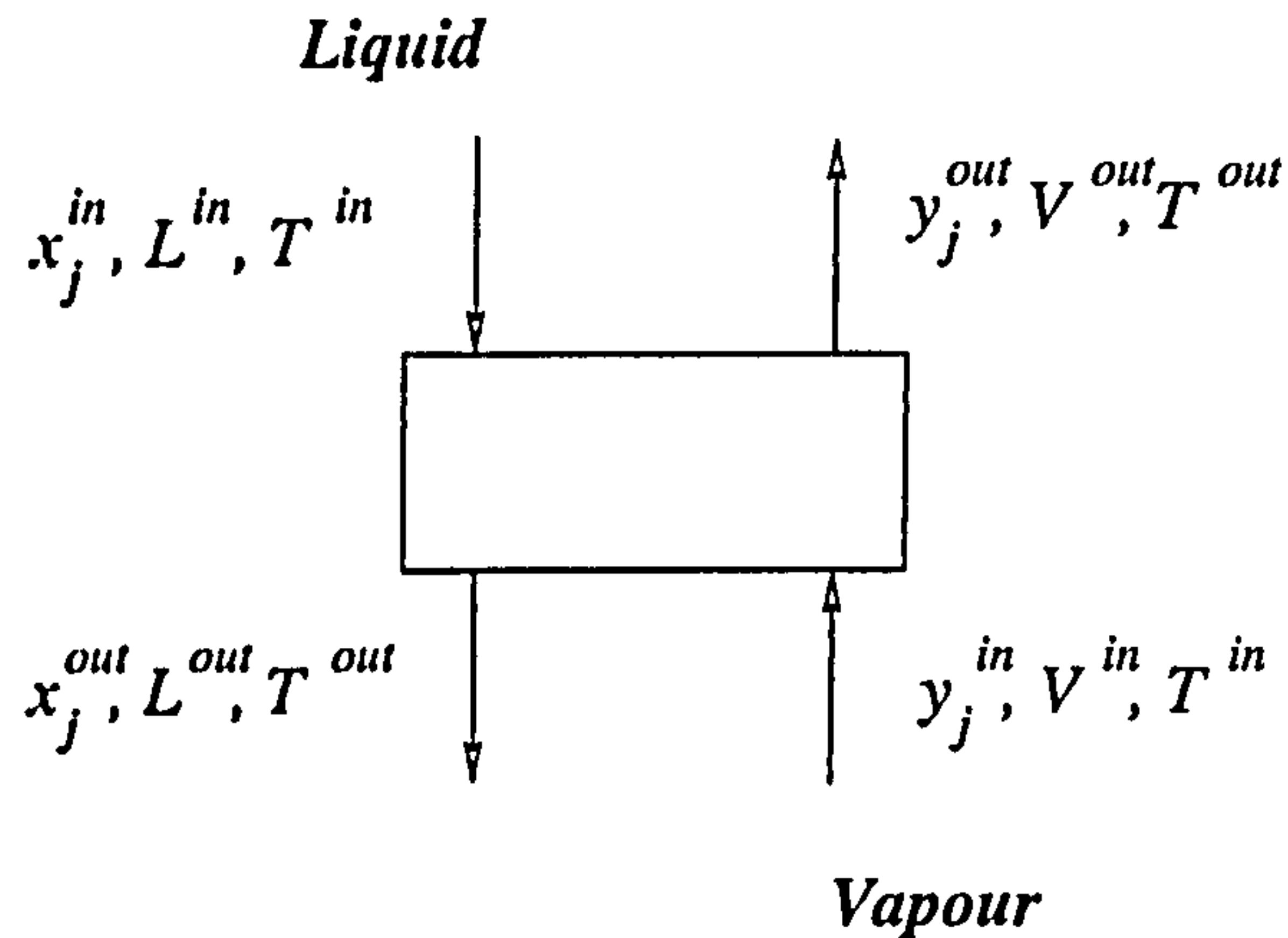


Figure A.1: Mass/Heat module

Lets assume the countercurrent M/H module of Figure A.1 between two streams (for instance a liquid and a vapour stream) with a physical equilibrium condition, as in equation (A.17).

Case 1

If component j is transferred from the vapour (rich) to the liquid (lean) stream, then the amount of this component in the effluent vapour stream should decrease, defining the quantity $g1_j$, as:

$$g1_j = V^{in} y_j^{in} - V^{out} y_j^{out} \geq 0 \quad (\text{A.19})$$

The feasibility condition is based on the limiting countercurrent equilibrium condition, defining the distance from equilibrium ($g2_j$ and $g3_j$) at the two sides of the module, as:

$$g2_j = y_j^{in} - (y_j^{in})^{eq} \geq 0 \Rightarrow y_j^{in} - f_j^{eq}(x_j^{out}) \geq 0 \quad (\text{A.20})$$

$$g3_j = y_j^{out} - (y_j^{out})^{eq} \geq 0 \Rightarrow y_j^{out} - f_j^{eq}(x_j^{in}) \geq 0 \quad (\text{A.21})$$

The Driving Force Constraints are defined as:

$$(g1_j \ g2_j) \geq 0 \quad (\text{A.22})$$

$$(g1_j \ g3_j) \geq 0 \quad (\text{A.23})$$

Case 2

If however, j is actually transferred from the liquid to the vapour streams, then:

$$g1_j = V^{in} y_j^{in} - V^{out} y_j^{out} \leq 0 \quad (\text{A.24})$$

$$g2_j = y_j^{in} - (y_j^{in})^{eq} \leq 0 \Rightarrow y_j^{in} - f_j^{eq}(x_j^{out}) \leq 0 \quad (\text{A.25})$$

$$g3_j = y_j^{out} - (y_j^{out})^{eq} \leq 0 \Rightarrow y_j^{out} - f_j^{eq}(x_j^{in}) \leq 0 \quad (\text{A.26})$$

The Driving Force Constraints in this case will also be:

$$(g1_j \ g2_j) \geq 0 \quad (A.27)$$

$$(g1_j \ g3_j) \geq 0 \quad (A.28)$$

As it can be seen, the Driving Force Constraints (equations (A.22) and (A.23)) hold for any direction of mass transfer for each component. The actual mass transfer direction for each component does not need to be postulated and it is determined by these general Driving Force Constraints in conjunction with the other constraints of the GMF physical model.

A.4 GMF GBD MINLP Formulation

We consider the solution of a problem of the form:

$$\begin{aligned}
 & \min_{\underline{x}, y_e} f(\underline{x}, y_e) \\
 & \text{s.t.} \quad h_e(\underline{x}) = 0, \quad e \in E^E \\
 \text{(P)} \quad & g_e(\underline{x}) \leq 0, \quad e \in E^E \\
 & g_e^I(\underline{x}, y_e) \leq 0, \quad e \in E
 \end{aligned}$$

where,

$\underline{x}$: continuous variables

y_e : binary variables

E : all building blocks

E^E : existing building blocks, where $E^E \subseteq E$

Note: For simplicity, the pure integer constraints are not included in the above problem definition. Also, the characterization of binary variables into primary and secondary is also not used here.

A.4.1 GMF Formulation (P1)

GBD P1 Primal

$$\begin{aligned}
 & \min_{\underline{x}} f(\underline{x}, y_e^k) \\
 & \text{s.t.} \quad h_e(\underline{x}) = 0, \quad e \in E^{Ek} \\
 & g_e(\underline{x}) \leq 0, \quad e \in E^{Ek} \\
 & g_e^I(\underline{x}, y_e^k) \leq 0, \quad e \in E
 \end{aligned}$$

where,

y_e^k : binary variables at iteration k (fixed)

E^{Ek} : existing building blocks at iteration k ($y_e^k = 1$), where $E^{Ek} \subseteq E$

GBD P1 Master

$$\min_{y_e} f(\underline{x}^k, y_e) + \sum_{e \in E^E} [\mu_e^{Ik} \cdot g_e^I(\underline{x}^k, y_e)]$$

where,

$\underline{x}^k$: continuous variables at iteration k (fixed)

A.4.2 Shadow Constraint Formulation (P2)

GBD P2 Primal

$$\begin{aligned} \min_{\underline{x}} \quad & f(\underline{x}, y_e^k) \\ \text{s.t.} \quad & h_e(\underline{x}) \cdot y_e^k = 0, \quad e \in E \\ & g_e(\underline{x}) \cdot y_e^k \leq 0, \quad e \in E \\ & g_e^I(\underline{x}, y_e^k) \leq 0, \quad e \in E \end{aligned}$$

The difference between $P1$ and $P2$ Primal Subproblems is that the latter includes *all* the problem constraints at iteration k (constraints of existing and non-existing (shadow) building blocks). The shadow constraints, which are set to zero along with their variables (since they correspond to non-existing building blocks), are the following:

$$\begin{aligned} h_e(\underline{x}) \cdot y_e^k &= 0, \quad e \in E, e \notin E^{Ek} \\ g_e(\underline{x}) \cdot y_e^k &\leq 0, \quad e \in E, e \notin E^{Ek} \end{aligned}$$

GBD P2 Master

$$\min_{y_e} \quad f(\underline{x}^k, y_e) + \sum_{e \in E} [\lambda_e^k \cdot h_e(\underline{x}^k) \cdot y_e + \mu_e^k \cdot g_e(\underline{x}^k) \cdot y_e + \mu_e^{Ik} \cdot g_e^I(\underline{x}^k, y_e)]$$

However, at the solution of the Primal Subproblem, the KKT complementarity conditions impose:

$$\begin{aligned} \lambda_e^k \cdot h_e(\underline{x}^k) &= 0, \quad e \in E \\ \mu_e^k \cdot g_e(\underline{x}^k) &= 0, \quad e \in E \end{aligned}$$

These conditions hold whether the above constraints are shadow or not. Then, the GBD $P2$ Master objective function becomes:

$$\min_{y_e} \quad f(\underline{x}^k, y_e) + \sum_{e \in E} [\mu_e^{Ik} \cdot g_e^I(\underline{x}^k, y_e)]$$

As can be seen, the $P1$ and $P2$ problem formulations generate the same GBD Master Subproblems.

A.5 Simple Distillation Column Statistics - Trayed Model

Model Equations

<i>Feeds Splitter</i>	(I)
<i>Feed Bubble Point</i>	(I)
<i>Total Mass Balances</i>	(N)
<i>Component Mass Balances</i>	(N C)
<i>Energy Balances</i>	(N)
<i>Phase Equilibrium</i>	(N C)
<i>Summation Corrections</i>	(N)
<i>Reflux Ratio Definition</i>	(1)
<i>Product P2 Definition</i>	(1)
<i>Zeroing of V_N</i>	(1)
<i>Liquid and Vapour Enthalpy Definitions</i>	2(N)
<i>Equilibrium Constant Definitions</i>	(N C)
<i>Uniform Column Pressure Spec</i>	(1)
<i>Distillate Purity Spec</i>	(1)

Overall:

$$N (3C+5)+2I+5$$

Model Variables

<i>Feed Interconnection</i>	(I)
<i>Feed Temperature</i>	(I)
<i>Liquid and Vapour Flowrates</i>	2(N)
<i>Distillate Flowrate</i>	(1)
<i>Bottoms Flowrate</i>	(1)
<i>Liquid and Vapour Molar Fractions</i>	2(N C)
<i>Reboiler Duty</i>	(1)
<i>Condenser Duty</i>	(1)
<i>Reflux Ratio</i>	(1)
<i>Column Pressure</i>	(1)
<i>Liquid and Vapour Enthalpies</i>	2(N)
<i>Equilibrium Constant</i>	(N C)

Overall

$$N (3C+5)+2I+6$$

The above statistics are based on the tray-by-tray rigorous distillation column model of Viswanathan and Grossmann (1993). For the examined optimization problem of Section 2.4.3 (where $N=25$ and $C=2$) the number of equations and variables is 282 and 283, respectively. The remaining degree of freedom is the reflux ratio, which will be optimized in the optimization problem posed.

A.6 Simple Distillation Column Statistics - GMF Model

According to the GMF Physical Model of Section 2.3.3 and to the problem specific specifications of the binary distillation separation case study of Section 2.4.3, the system equality constraints and variables are given below, on a GMF building block basis. For simplicity C , I , E^E , E^{CE} and E^{HE} represent here the corresponding sets' cardinalities.

Model Equations

<i>Feed Splitters</i>	$2(I)$
<i>Upper Auxiliary Block</i>	$(4E^E + 2E^E C)$
<i>M/H Main Block</i>	$(3E^E + E^E C)$
<i>Lower Auxiliary Block</i>	$(4E^E + 2E^E C)$
<i>Cooler Module</i>	$(4E^{CE} + E^{CE} C)$
<i>Heater Module</i>	$(4E^{HE} + E^{HE} C)$
<i>Product Mixers</i>	$(3P + P C)$
<i>Enthalpy Definitions</i>	$(I + 6E^E + 2E^{HE} + 2E^{CE} + P)$
<i>Equil. Const. Definitions</i>	$(I + 6E^E + 2E^{HE} + 2E^{CE} + P) C$
<i>Module Pressure Spec</i>	(E^E)
<i>Reflux Ratio Definition</i>	(1)
<i>Distillate Purity Spec</i>	(1)
Total	$E^E (11C + 18) + (E^{CE} + E^{HE})(3C + 6) + P(2C + 4) + I(C + 3) + 2$
 <i>Model Variables</i>	
<i>Flowrates (†)</i>	$(4E^E + E^{CE} + E^{HE} + P)$
<i>Molar Fractions (‡)</i>	$(6E^E + E^{CE} + E^{HE} + P)C$
<i>Temperatures (§)</i>	$(I + 6E^E + 2E^{CE} + 2E^{HE} + P)$
<i>Heater Duty (Q_e^H)</i>	(E^{HE})
<i>Cooler Duty (Q_e^C)</i>	(E^{CE})
<i>Enthalpies (§)</i>	$(I + 6E^E + 2E^{CE} + 2E^{HE} + P)$
<i>Equilibrium Constants (¶)</i>	$(I + 6E^E + 2E^{CE} + 2E^{HE} + P)C$
<i>M/H module Pressure (P_e)</i>	(E^E)
<i>Reflux Ratio (r)</i>	(1)
Total	$E^E (12C + 17) + (E^{CE} + E^{HE})(3C + 6) + P(2C + 3) + I(C + 2) + 1$

where:

$$\dagger (f_e^{LI}, f_e^{LO}, f_e^{VI}, f_e^{VO}, f_e^C, f_e^H, f_p^P)$$

$$\ddagger (x_{e,c}^{LI}, x_{e,c}^{LO}, x_{e,c}^{VI}, x_{e,c}^{VO}, x_{e,c}^{LA}, x_{e,c}^{VA}, x_{e,c}^C, x_{e,c}^H, x_{p,c}^P)$$

$$\S (T_i^F, T_e^{LI}, T_e^{LO}, T_e^{VI}, T_e^{VO}, T_e^{LA}, T_e^{VA}, T_e^{CI}, T_e^{CO}, T_e^{HI}, T_e^{HO}, T_p^P)$$

$$\S (H_i^F, H_e^{LI}, H_e^{LO}, H_e^{VI}, H_e^{VO}, H_e^{LA}, H_e^{VA}, H_e^{CI}, H_e^{CO}, H_e^{HI}, H_e^{HO}, H_p^P)$$

$$\P (K_{i,c}^F, K_{e,c}^{LI}, K_{e,c}^{LO}, K_{e,c}^{VI}, K_{e,c}^{VO}, K_{e,c}^{LA}, K_{e,c}^{VA}, K_{e,c}^{CI}, K_{e,c}^{CO}, K_{e,c}^{HI}, K_{e,c}^{HO}, K_{p,c}^P)$$

The above sets of variables are not complete unless the system includes the *case specific* stream Interconnections. These are represented in the Structural Model through the secondary binary variables and in the Physical Model through the corresponding flowrates. The Mixed Integer constraints included in the model of Section 2.3.3, become continuous inequality constraints in the Primal subproblem (through the parameterization of the binary variables to the values they obtained by the solution of the Master subproblem). These inequality constraints either impose flowrate bounds for existing interconnections, or zero the flowrates of non-chosen (non-existing) interconnections. In the simple distillation column, the existing interconnections are known *a-priori* and they are given in detail in the GMF Structural Sets of Table 2.3. The remaining interconnections are treated as non-existing.

For the examined problem where $C=2$, $E^E=2$, $E^{CE}=E^{HE}=1$, $P=2$ and $I=1$, the *non-zero* continuous interconnection flowrates are given below:

$$f_{1,1}^{FL}, f_{2,1}^{LL}, f_{1,2}^{VV}, f_{2,2}^{VC}, f_{2,2}^{CL}, f_{1,1}^{LH}, f_{1,1}^{HV}, f_{2,P1}^{CP}, f_{1,P2}^{LP}$$

The above 9 flowrates are added to the other 125 system variables (calculated above for the specified number of building blocks, feeds, products and components specified in the examined case study), thus generating 134 variables overall. The number of equality constraints is 127.

Appendix B

GMF Representation of Ternary Complex Column Sequences

B.1 Rearranged GMF Ternary Complex Column Sequences

As specified in Section 5.2.1, the 10 GMF structural alternatives for the Ternary Complex Column Sequencing problem (Figures 5.5 and 5.6), were rearranged for the facilitation of the construction of the GMF superstructure. This rearrangement affected, essentially, only the Side Petlyuk Column, which was eliminated from the set of alternative structures, and the Side Stripper and Side Rectifier Sequences, which were appropriately restructured. The final GMF representation of the 9 Ternary Complex Column alternatives is shown in Figure B.1.

B.2 STN Representation of GMF Complex Column Sequences

The alternatives of Figure B.1 can be represented in a State Task Network (STN) formalism, as shown in Figure B.2. Each M/H module can perform one or more separation tasks and the States are the products of the separation tasks. The arrows represent the separation tasks carried out by the corresponding M/H module (the number above each line corresponds to the number of the M/H module, as shown in each one of the alternative sequences). Since the GMF allows the free distribution of components (no simplifying assumptions of sharp splits need to be made), all the components, for this case, A, B and C, can be present at each state. Components

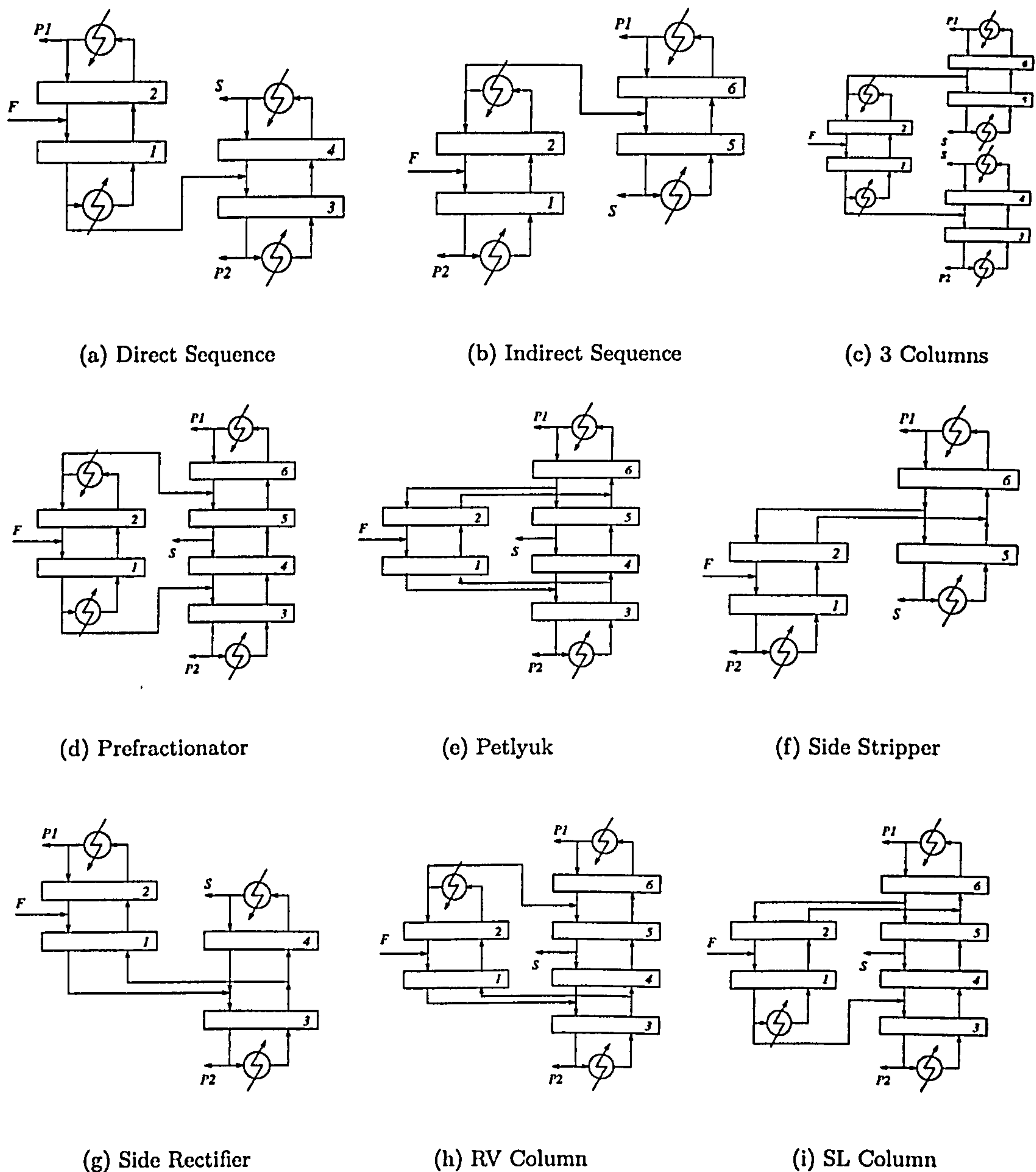


Figure B.1: Rearranged GMF Complex Distillation Column Alternatives

in parenthesis indicate participation of these components only in small amounts. For instance, the state (AB)C, indicates a stream with high concentration in C and small concentration of A and B. The tasks that take place in each M/H module can be found in Table B.1. The '/' indicates the split that takes place. For instance, 'AB/C' stands for the general separation of component C from A and B. As shown in Table B.1, M/H modules 1 and 2 perform multiple tasks (*one-to-many*), whereas the other 4 M/H modules perform the same tasks.

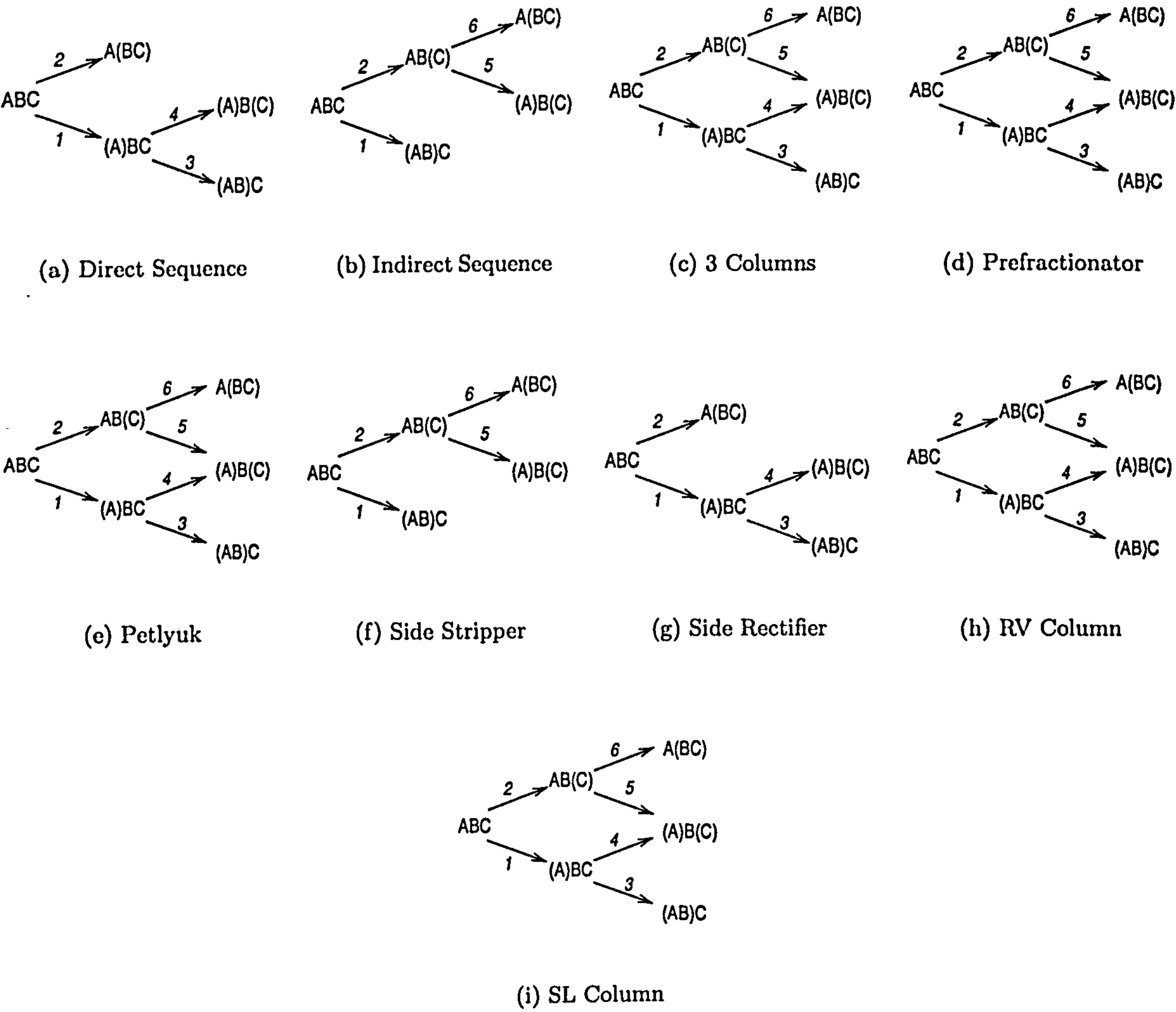


Figure B.2: STN Representations of the GMF Ternary Complex Distillation

Table B.1: GMF *M/H* Modules and Tasks in Ternary Complex Column Sequencing

<i>M/H</i>	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
1	A/BC	AB/C	A/BC	A/BC	A/BC	AB/C	A/BC	A/BC	A/BC
2	A/BC	AB/C	AB/C	AB/C	AB/C	AB/C	A/BC	AB/C	AB/C
3	AB/C	-	AB/C	AB/C	AB/C	-	AB/C	AB/C	AB/C
4	B/AC	-	B/AC	B/AC	B/AC	-	B/AC	B/AC	B/AC
5	-	B/AC	B/AC	B/AC	B/AC	B/AC	-	B/AC	B/AC
6	-	A/BC	A/BC	A/BC	A/BC	A/BC	-	A/BC	A/BC

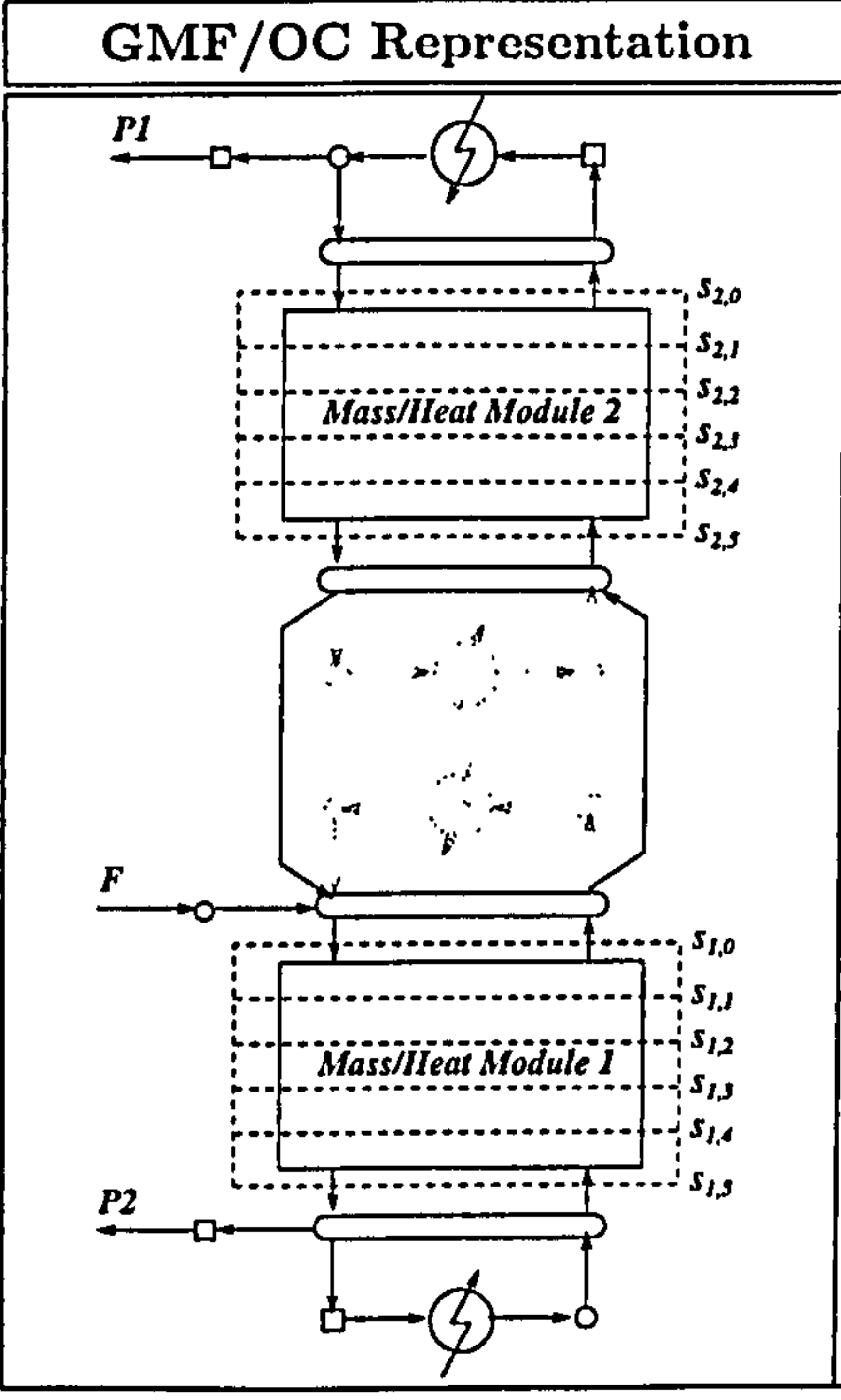
Appendix C

Enhanced GMF Physical Model

C.1 GMF/OC Distillation Column Degrees Of Freedom

The GMF/OC representation of a simple distillation column along with the Structural Sets and assigned binary variables are shown in Table C.1. The GMF/OC equality constraints are

Table C.1: GMF/OC Structural Data for a Simple Distillation Column

GMF/OC Representation	Structural Sets	Binary Variables
	$E^E = \{1,2\}$ $E^{HE} = \{1\}$ $E^{CE} = \{2\}$ $I = \{F\}$ $C = \{Benz., Tolu.\}$ $P = \{P1, P2\}$ $E_F^{FL} = \{1\}$ $E_2^{LLo} = \{1\}, E_1^{LLi} = \{2\}$ $E_1^{VVo} = \{2\}, E_2^{VVi} = \{1\}$ $E_2^{CLo} = \{2\}, E_2^{CLi} = \{2\}$ $E_1^{LPo} = \{P2\}, E_{P2}^{LPi} = \{1\}$ $E_2^{CPo} = \{P1\}, E_{P1}^{CPi} = \{2\}$	$y_1 = y_2 = 1$ $y_1^H = 1$ $y_2^C = 1$ $y_{1,1}^{HV} = y_{2,2}^{LH} = 1$ $y_{2,2}^{VC} = y_{2,2}^{CL} = 1$ $y_{F,1}^{FL} = 1$ $y_{2,1}^{LL} = 1$ $y_{1,2}^{VV} = 1$ $y_{2,2}^{CL} = 1$ $y_{1,P2}^{LP} = 1$ $y_{2,P1}^{CP} = 1$

enumerated, based on the GMF model statistics provided in Appendix A.6. The placement of the *substituting* and *supplementary* constraints is marked with a † and a ‡.

Model Equations

Feed Splitters	$2(I)$
Upper Auxiliary Block	$(4E^E + 2E^E C)$
M/H Main Block †	$(3NC + 2NC C + 4C + 8)E^E$
Lower Auxiliary Block	$(4E^E + 2E^E C)$
Cooler Module	$(4E^{CE} + E^{CE} C)$
Heater Module	$(4E^{HE} + E^{HE} C)$
Product Mixers	$(3P + P C)$
Enthalpy Definitions †	$[I + (8 + 2NC)E^E + 2E^{HE} + 2E^{CE} + P]$
Equil. Const. Definitions †	$[I + (6 + NC)E^E + 2E^{HE} + 2E^{CE} + P] C$
Module Pressure Spec	(E^E)
Reflux Ratio Definition	(1)
Distillate Purity Spec	(1)
Trays Per M/H module †	(E^E)
Total:	$E^E (5NC + 3NC C + 14C + 26) + (E^{CE} + E^{HE}) (3C + 6) + P(2C + 4) + I(C + 3) + 2$

Model Variables

Flowrates †	$[(6 + 2NC)E^E + E^{CE} + E^{HE} + P]$
Component Flowrates †	$(2NC E^E + 2E^E) C$
Molar Fractions	$(6E^E + E^{CE} + E^{HE} + P) C$
Temperatures †	$[I + (8 + NC)E^E + 2E^{CE} + 2E^{HE} + P]$
Heater Duty	(E^{HE})
Cooler Duty	(E^{CE})
Enthalpies †	$[I + (8 + 2NC)E^E + 2E^{CE} + 2E^{HE} + P]$
Equilibrium Constants †	$[I + (6 + NC)E^E + 2E^{CE} + 2E^{HE} + P] C$
M/H module Pressure	(E^E)
Reflux Ratio	(1)
Interconnection Flowrates	(9)
M/H Module Trays †	(E^E)
Total:	$E^E (5NC + 3NC C + 14C + 24) + (E^{CE} + E^{HE}) (3C + 6) + P(2C + 3) + I(C + 2) + 10$

† GMF/OC additional variables:

Flowrates (Liquid and Vapour) ($f_{e,j}^L, f_{e,j}^V$): $2(NC + 1)E^E$

Component Flowrates (Liquid and Vapour) ($fc_{e,j,c}^L, fc_{e,j,c}^V$): $2(NC + 1)E^E C$

Temperatures ($T_{e,j}$): $(NC + 2)E^E$

Enthalpies (Liquid and Vapour) ($H_{e,j}^L, H_{e,j}^V$): $2(NC + 1)E^E$

Equilibrium Constants ($K_{e,j,c}$): $NCE^E C$

Trays of M/H modules (M_e): E^E

It must be noted that for presentational simplicity throughout this section nc_e has been assumed the same for all M/H modules and replaced by NC . The equality constraints for the collocation point locations and weighting functions were incorporated in the balances. Moreover, for the optimization problem of Section 6.5.1 (where $C=2$, $E^E=2$, $E^{CE}=E^{HE}=1$, $P=2$, $I=1$ and $NC=4$) the number of trays per M/H module (M_e) was assumed fixed, eliminating (E^E) degrees of freedom. Therefore, the GMF/OC generated 244 variables and 243 equality constraints, thus leaving the reflux as the single degree of freedom to be optimized for the fixed design problem.

C.2 GMF/OCFE Distillation Column Degrees Of Freedom

Below, † and ‡ mark the locations of *substituting* and *supplementary* information, respectively.

Model Equations

Feed Splitters	2(I)
Upper Auxiliary Block	(4E ^E +2E ^E C)
M/H Main Block †	[(3NC+2NC C+2C+4)L+2C+4]E ^E
Lower Auxiliary Block	(4E ^E +2E ^E C)
Cooler Module	(4E ^{CE} +E ^{CE} C)
Heater Module	(4E ^{HE} +E ^{HE} C)
Product Mixers	(3P+P C)
Enthalpy Definitions †	[I+(6+2L NC+2L)E ^E +2E ^{HE} +2E ^{CE} +P]
Equil. Const. Definitions †	[I+(6+L NC)E ^E +2E ^{HE} +2E ^{CE} +P] C
Module Pressure Spec	(E ^E)
Reflux Ratio Definition	(1)
Distillate Purity Spec	(1)
Summation of Trays Per M/H module †	(E ^E)

Sum:
E^E [(5NC+3NC C+2C+6)L+12C+20]+(E^{CE}+E^{HE})(3C+6)+P(2C+4)+I(C+3)+2

Model Variables

Flowrates ‡	[(4+2L NC+2L)E ^E +E ^{CE} +E ^{HE} +P]
Component Flowrates ‡	(2E ^E NC L+2E ^E L)C
Molar Fractions	(6E ^E +E ^{CE} +E ^{HE} +P)C
Temperatures ‡	[I+(6+L NC+2L)E ^E +2E ^{CE} +2E ^{HE} +P]
Heater Duty	(E ^{HE})
Cooler Duty	(E ^{CE})
Enthalpies ‡	[I+(6+2L NC+2L)E ^E +2E ^{CE} +2E ^{HE} +P]
Equilibrium Constants ‡	[I+(6+L NC)E ^E +2E ^{CE} +2E ^{HE} +P]C
M/H module Pressure	(E ^E)
Reflux Ratio	(1)
Interconnection Flowrates	(9)
M/H Module Trays	(E ^E L)

Sum:
E^E [(5NC+3NC C+2C+7)L+12C+17]+(E^{CE}+E^{HE})(3C+6)+P(2C+3)+I(C+2)+10

† GMF/OCFE additional variables:

Flowrates (Liquid and Vapour) ($f_{e,l,j}^L, f_{e,l,j}^V$): $2(NC + 1)E^E L$

Component Flowrates (Liquid and Vapour) ($fc_{e,l,j,c}^L, fc_{e,l,j,c}^V$): $2(NC + 1)E^E L C$

Temperatures ($T_{e,l,j}$): $(NC + 2)E^E L$

Enthalpies (Liquid and Vapour) ($H_{e,l,j}^L, H_{e,l,j}^V$): $2(NC + 1)E^E L$

Equilibrium Constants ($K_{e,l,j,c}$): $NC E^E L C$

Trays of M/H modules ($M_{e,l}$): $E^E L$

The GMF/OCFE equality constraints and variables were enumerated, based on the GMF statistics of Appendix A.6. For presentational simplicity in the above enumeration, L_e is used as its cardinality, $|L_e|$, and it has been assumed the same for all M/H modules (which is in accord with the examined GMF/OCFE case studies) and replaced by L . For the examined problem of Section 6.5.2, where $C=2$, $E^E=2$, $E^{CE}=E^{HE}=1$, $P=2$, $I=1$, $L=2$ and $NC=2$, the GMF/OCFE generated 266 variables. The number of equality constraints was found equal to 263 (incorporating the equations for the collocation point locations and weighting functions in the balances), thus leaving the reflux and the tray number of one finite element per M/H module, as the 3 degrees of freedom for the fixed design optimization problem. The additional 2 degrees of freedom were due to that fact that although the overall number of trays per M/H module was known, the boundaries of the Finite Elements could not be specified *a-priori*.